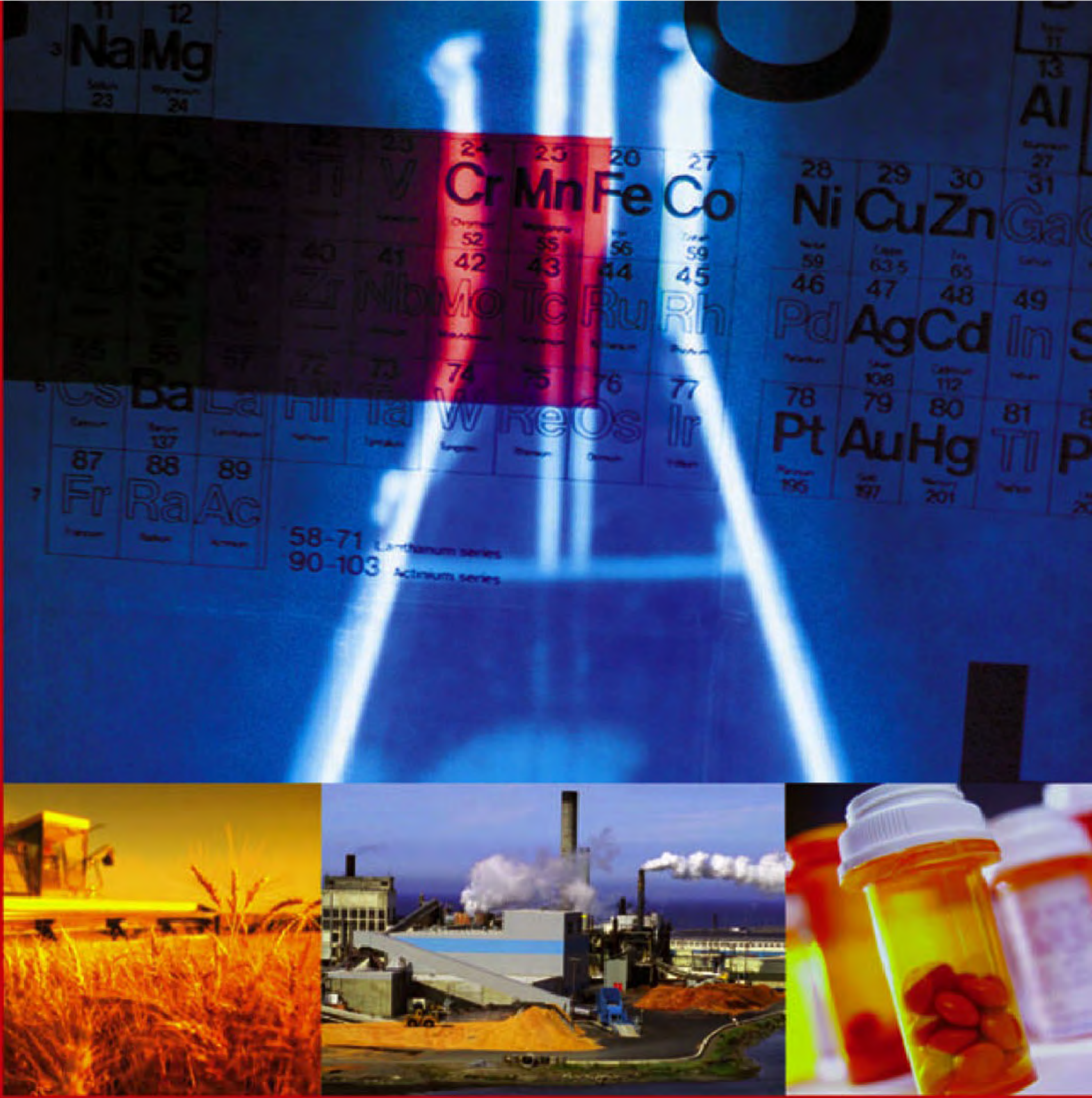

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Chemistry: Foundations and Applications
J. J. Lagowski, Editor in Chief

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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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For Your Reference

TABLE 1. SELECTED METRIC CONVERSIONS

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

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

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

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

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

TABLE 2. ALPHABETIC TABLE OF THE ELEMENTS

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

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

TABLE 3. COMMON ABBREVIATIONS, SYMBOLS, AND ACRONYMS

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

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

Ci	Curies
cm	centimeter
CT	computed tomography
d	d-orbital
D	dipole moment
DC	direct current
deg	degree
dr	diastereomer ratio
e	elementary charge
E	electric field strength; energy
$\mathrm{E_a}$	activation energy
$\mathrm{E_g}$	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
$\mathrm{K_a}$	acidity constant for the dissociation of weak acid (the weaker the acid, the lower the $\mathrm{K_a}$ value
$\mathrm{k_B}$	Boltzmann's constant
Kg	kilogram
kHz	kilohertz
kJ	kilojoule
kJ mol	kilojoule mole
km	kilometer
$\mathrm{K_m}$	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
$\mathrm{T_c}$	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
								1 HYDROGEN **H** 1.008												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													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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Poison *See Toxicity; Venom.*

p

Polonium

MELTING POINT: 254°C
BOILING POINT: 962°C
DENSITY: 9.32 g/cm^3
MOST COMMON IONS: Po^{2-}, Po^{2+}, PoO_3^{2-}

84
Po
POLONIUM
209

Polonium is a silver-grey, radioactive **metal**. Discovered by chemist Marie Curie in 1898, polonium was named after her country of origin (Poland). Curie discovered the element while analyzing samples of pitchblende, or uranium ore, from Bohemia. She found that unrefined pitchblende was more radioactive than the uranium extracted from it. Small amounts of polonium and another radioactive element, radium, were later obtained from the refined ore.

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

Polonium is found in the earth's crust at exceedingly low levels; its natural abundance is only 2 x 10^{-10} milligrams per kilogram. Polonium is produced in pitchblende when the bismuth **isotope** ^{210}Bi, which has a half-life of five days, decays into ^{210}Po. Approximately 100 micrograms of polonium are found in 1 ton of uranium ore. Polonium can also be produced by bombarding ^{209}Bi with neutrons to form ^{210}Bi, which in turn decays into ^{210}Po.

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

Polonium has more isotopes than any other element. The most common isotope is ^{210}Po, which has a half-life of 138.4 days. Other isotopes have half-lives ranging from less than 1 second to 102 years (^{209}Po). Polonium burns in air to form polonium (IV) oxide (PoO_2) and reacts with **halogens** to form tetrahalides (e.g., $PoCl_4$, $PoBr_4$, PoI_4). It also dissolves readily in dilute acids.

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

Polonium is a strong emitter of **α-particles**; approximately 1 gram of ^{210}Po emits 140 watts of heat energy. For this reason, it is used as a source of thermoelectric power in satellites. It is also utilized as a source of neutrons (when mixed with beryllium), as an antistatic device in industrial equipment, and in brushes that remove dust from photographic film. SEE ALSO CURIE, MARIE SKLODOWSKA; HALOGENS; RADIOACTIVITY; RADIUM; URANIUM.

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

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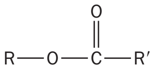
Polyesters

Polyesters are long chain synthetic **polymers** that have ester linkages. Polyester materials are used as fibers, plastics, and films; in composites and elastomers; and as coatings. They are truly versatile materials.

polymer: molecule composed of many similar parts



$R{-}O{-}C({=}O){-}R'$

Ester linkage

In the late 1920s American chemist Wallace Carothers and his research group at DuPont began to investigate the formation of polymers from the reaction of **aliphatic** diacids (having two acid groups) with diols (having two alcohol groups), in search of materials that would give them fibers. At first they were able to form only syrupy mixtures. But the Carothers group did make polyester fibers. They investigated a wide array of dialcohols, diacids, and w-hydroxy acids for use as starting points. Some of the polyesters that they achieved were solids, but they had rather low melting points and thus were not useful as fiber materials. The lack of success was due to the fact that the researchers had used only aliphatic diacids. In order to form long polymer chains, the reactive groups of the reactants must be present in approximately equal amounts. This is easily achieved via the use of amines and the subsequent formation of amine salts. (Diols do not easily form salts.) Carothers's group understood the principle of "driving" an equilibrium reaction and so sought to remove water from their amine salt mixtures, thus forcing the reaction toward **ester** formation. For this they developed a so-called molecular still, which involved heating the mixture and applying a vacuum coupled with a "cold-finger" that allowed evacuated water to condense and be removed from the reaction system. Even with this understanding and lots of hard work, they achieved polymer chains with fewer than 100 repeat units. (See Figure 2.)

aliphatic: having carbon atoms in an open-chain 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; the R(C–O)OR functional group

The DuPont research team turned from the synthesis of polyesters to tackle, more successfully, the synthesis of polyamides. The experience with polyesters was put to use in the making of polyamides.

Initial polyester formation actually occurred much earlier and is attributed to Gay Lussac and Théophile-Jules Pelouze in 1833 and Jöns Jakob

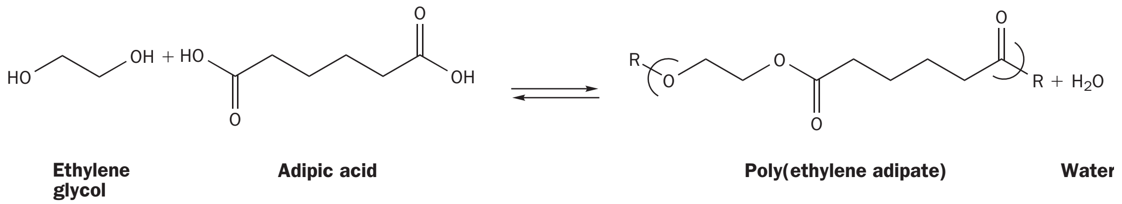


Figure 2. Wallace Carothers attempted to form polymers from the reaction of ethylene glycol (a diol) and apidic acid (an aliphatic diacid).

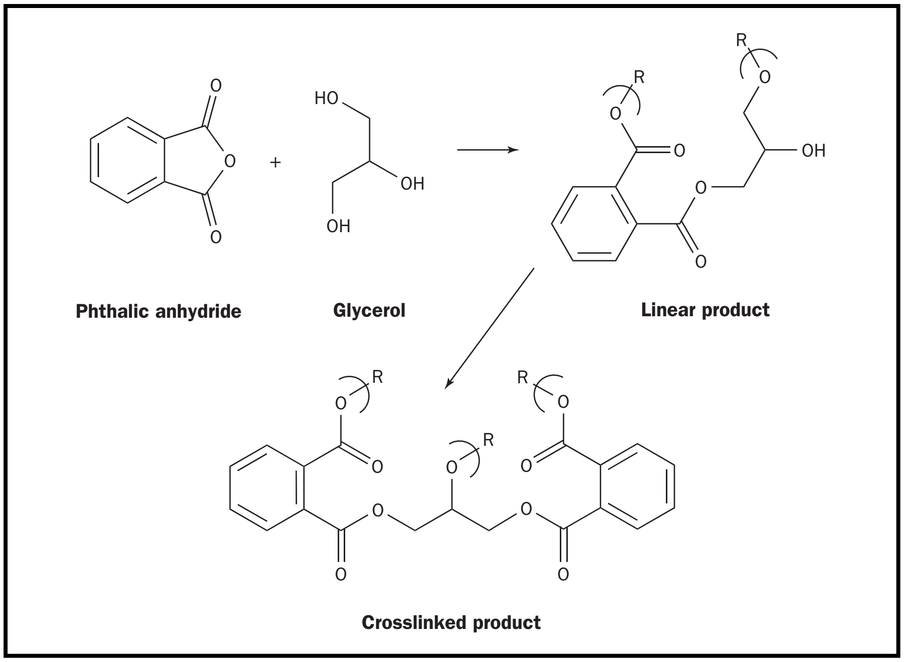


Figure 3. Glyptal polyester formation.

Berzelius in 1847. They did not realize what they had discovered, however, and so moved on to other work.

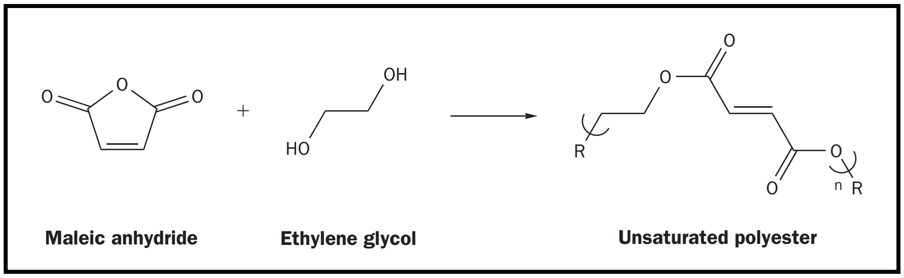
Glyptal polyesters were first produced in 1901 by heating glycerol and phthalic anhydride. (See Figure 3.) Because the secondary hydroxyl is less active than the terminal, primary hydroxyl in glycerol, the initial product formed is a linear polyester. A cross-linked product is produced by further heating through reaction the third alcohol.

Related compounds, alkyds, were synthesized by Kienle in the 1920s from trifunctional alcohols and dicarboxylic acids. Unsaturated oils (alcohols and anhydrides containing double bonds) were also reacted with phthalic anhydride, yielding polyesters that contained a double bond, which could be further reacted to produce cross-linked products. The extent of cross-linking or "drying" depends on the amount of unsaturated oil present.

Today, the term alkyd is often used to describe all polyesters produced from the reaction of a diacid or anhydride and a diol or triol resulting in a product that contains a double bond that can be further reacted, giving a cross-linked product. (See Figure 4.) These polyesters are called unsaturated polyesters. They are mainly used in the production of reinforced plastics (composites) and nonreinforced filled products for the marine, automotive, and other industries.

These glyptal and alkyd polyesters are useful as coating materials but not for fiber or plastic production. The first commercially available polyesters were made by GE in the 1920s. Called Glyptals™, they were used as sealing waxes. Out of the Glyptal™ research came alkyd paints. Although these reactions had low fractional conversions, they formed high molecular weight materials because they had functionalities (i.e., a number of reactive groups on a single reactant) greater than 2, resulting in cross-linking.

Figure 4. Reaction of an anhydride and a diol result in a double bonded product that can be further reacted to produce a cross-linked product called unsaturated polyester.



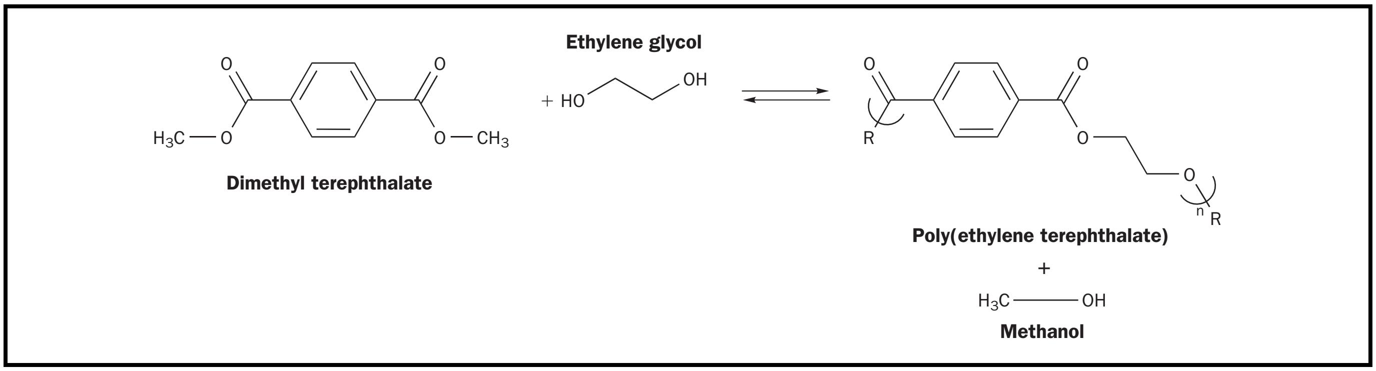
The heat resistance of Carothers's polyesters was not sufficient to withstand the temperature of the hot ironing process. Expanding on the work of Carothers and his coworkers on polyesters, Whinfield and Dickson, in England, overcame the problems of the Carothers group by using aromatic acids, especially terephthalic. This classic reaction, which produces plastics and fibers that are sold under a variety of tradenames, including Dacron, Fortrel, Trevira, and Terylene, and films sold under a variety of trade names that includes Mylar, is shown in Figure 5. All new plants now use pure acid for this reaction.

Methyl alcohol, or methanol, is lower boiling than water (65ºC compared with 100ºC) and is thus more easily removed, allowing the reaction to be forced toward polymer formation more easily. Although this poly(aryl ester), produced by Whinfield and Dickson, poly(ethylene terephthalate) or PET, met the specifications for a useful synthetic fiber, because of inferior molding machines and inadequate plastic technology, it was not possible to use it in injection molds. Until more recently PET was not a widely used plastic or film material.

aromatic: having a double-bonded carbon ring (typified by benzene)

Although aromatic polyesters had been successfully synthesized from the reaction of ethylene glycol with various **aromatic** diacids (almost always terephthalic acid or its ester), commercialization of polyester synthesis awaited an inexpensive source of aromatic diacids. In 1953 an inexpensive process for the separation of the various xylene isomers by crystallization was discovered. The availability of inexpensive xylene isomers enabled the formation of terephthalic acid through the air oxidation of the p-xylene isomer. Du Pont, in 1953, produced polyester fibers from melt spinning, but it was not until the 1970s that these polyester fibers became commercially available.

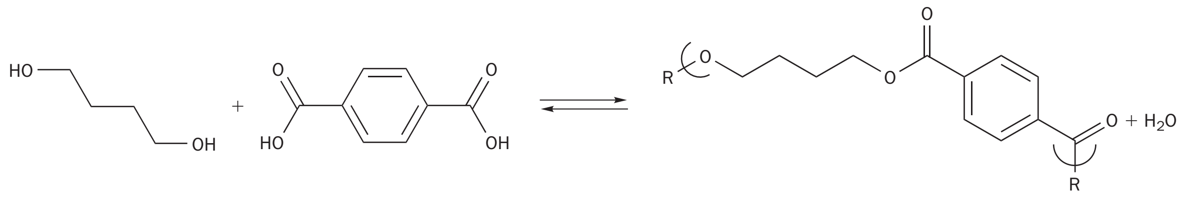
Figure 5. The classic reaction for producing plastics and fibers. New plants use pure acid for this reaction.



John Travolta and Karen Lynn Gorney in the 1970s hit film *Saturday Night Fever.* Polyester was a popular fabric used in clothing in the 1970s.

In 2000 about 3,900 million pounds of polyester fiber were used in the United States, making it the largest single fiber group material. As with nylon, polyester fibers are comparable to and/or surpass common natural fibers such as cotton and wool in heat stability, wash-and-wear properties, and wrinkle resistance. Textiles blended from polyester, cotton, and wool (in varying combinations) can also be made to be "permanent press" and wrinkle resistant. The fibers are typically formed from melt or solvent spinning. Chemical and physical modification can generate fibers of differing fiber appearances from the same basic fiber material. Self-crimping textiles are made by combining materials that have differing shrinkage properties. Different shaped dyes produce materials with varying contours and properties, including hollow fibers.

Along with the famous polyester suits and slacks, polyester fibers are widely used in undergarments, permanent press shirts, tire cord, and felts.



Poly(butylene terephthalate), PBT

Figure 6. Poly(butylene terephthalate), or PBT, has a lower melting point than PET, and it crystallizes more rapidly.

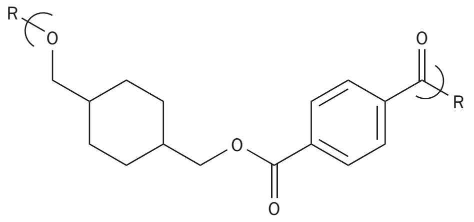
Because the ease of processing and fabricating polyesters is related to the number of methylene groups ($-CH_2-$) in the repeat units, scientists turned to the use of diols with additional methylene units. Whereas PET is difficult to mold because of its high melting point, Tm 240ºC, poly(butylene terephthalate), or PBT, because of its two additional methylene units in the diol-derived portion (see Figure 6), is lower melting with a Tg of about 170ºC. PET also crystallizes relatively slowly, so extra care must be exercised to insure that PET molded products become fully crystallized. Otherwise, the partially crystallized portions will be preferred sites for cracking, crazing, shrinkage, and so on.

By comparison, PBT melts at a lower temperature (as noted above), crystallizes more rapidly, and is often employed as a molding compound. PBT has properties that represent a balance between those of nylons and acetals. It is characterized by low moisture absorption, good fatigue resistance, good solvent resistance, extremely good self-lubrication, and good maintenance of its physical properties even at relatively high use temperatures. Fiber-reinforced PBT molding compound is sold under the tradename Celanex. Another PBT molding compound was first sold under the tradename Valox. Today, there are many PBT molding compounds available.

In 2000 worldwide production of PET was 30 million tons. The manufacture of PET textiles is increasing at 5 percent a year, of PET bottles at 10 percent a year. China produces the most polyesters. PET is now used extensively as bottling material for soft drinks instead of glass because it is shatterproof and lightweight. Carbon dioxide permeability decreases with increasing film thickness and crystallinity. Glass has better CO_2 impermeability than PET in these respects. Therefore, to achieveoptimal crystallinity, partially crystalline PET is employed in the stretch blow molding process, carried out to promote further crystalline formation. It is also used for molded automobile parts. Over 500,000 tons of polyester engineering plastics are produced annually in the United States.

hydrophobic: water repelling

Poly(dihydroxymethylcyclohexyl terephthalate) was introduced by Eastman Kodak as Kodel in 1958. Here, the insertion of the cyclohexyl moiety gives a more **hydrophobic** material (in comparison to PET and PBT) as well as a more moldable product that can very readily be injected-molded. (See Figure 7.) The polymer's sole raw material is dimethyl terephthalate. Reduction of dimethyl terephthalate yields the dialcohol, cyclohexanedimethanol. Kodel, along with its blends and mixtures, is often extruded into film and sheeting for packaging. Kodel-type materials are used to pack-



Poly(dihydroxymethylcyclohexyl terephthalate)

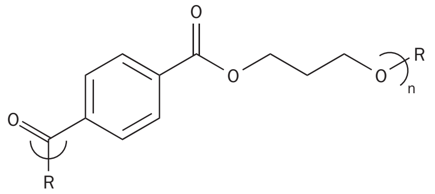
Figure 7. Materials made from Poly(dihydroxy methylcyclohexyl terephthalate) are used in shampoo and detergent bottles.

age hardware and other heavy items; they are also blow-molded to produce packaging for shampoos, liquid detergents, and so on.

Du Pont and Shell have developed a new polyester, poly(trimethylene terephthalate), or PTT, with the trademarks Sorona (Du Pont) and Corterra (Shell). It is structurally similar to poly(ethylene terephthalate), PET, except that 1,3-propanediol (PDO) is used as a reactant in place of ethylene glycol. (See Figure 8.) The extra methylene (CH_2) in PTT allows the fiber to be more easily colored, giving a material that is also softer to the touch and with greater stretch for textile use. Further, PTT offers good wear and stain resistance for carpet use. The ready availability of the monomer PDO is a major consideration, with current efforts underway to create PDO from the fermentation of sugar through the use of biocatalysts for this conversion. Corterra and Lycra blends have already been successfully marketed. Corterra is also targeted for use as a resin and film.

Du Pont first introduced microfibers in 1989. Microfibers have diameters that are less than typical fibers; they are about half the diameter of fine silk fiber, one-quarter the diameter of fine wool, and one hundred times finer than human hair. Denier, the weight in grams of 9,000-meter length of a fiber, is the term used to define the diameter or fineness of a fiber. Microfibers have a denier that is 0.9 denier or less. In comparison, nylon stockings are knit from 10- to 15- denier fiber.

Microfibers allow a fabric to be woven that is lightweight and strong. They can be tightly woven so that wind, rain, and cold do not easily penetrate. Rainwear manufactures use microfibers for this reason. They also have the ability to allow perspiration to pass through them. In addition, microfibers are very flexible because their small fibers can easily slide back and forth on one another. The first fabric made from microfiber was Ultrasuade, in which short polyester microfibers were imbedded into a polyurethane base. Today, microfibers are manufactured primarily from



Poly(trimethylene terephthalate), PTT

Figure 8. The extra methylene in poly(trimethylene terephthalate) (PTT) provides material that is easily colored and soft to the touch.

polyesters, nylon, and acrylic fibers. They are used under various tradenames to make a variety of products, such as clothing, hosiery, bedding, and scarves. SEE ALSO Polymers, Synthetic.

Charles E. Carraher Jr.

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Polymerase Chain Reaction

DNA: deoxyribonucleic acid—the natural polymer that stores genetic information

The polymerase chain reaction (PCR) is used to make millions of copies of a section of deoxyribonucleic acid (**DNA**). Until the 1980s obtaining numerous copies of a section of DNA took one to two weeks and required isolation of the DNA, cloning the DNA into a viral or plasmid vector, growing the cloned DNA using living host cells, usually bacteria, and finally isolating the DNA again. With PCR a scientist can produce thirty million copies of a DNA section in a test tube overnight. In a series of early articles, PCR's inventor, Kary Mullis, described just how valuable he believed this tool would be. He could not have been more correct: PCR is now a mainstay of molecular biology. In 1993 Mullis received the Nobel Prize in chemistry in recognition of his discovery.

How PCR Works

PCR repeats the synthesis of a DNA segment through twenty-five to thirty cycles. The power of the technique resides in its ability to copy the products of each previous cycle along with the original sample. This results in exponential growth in the amount of product, as illustrated in Figure 1. The first stage or round of the process only involves copying the original sample. First, the DNA is separated into its two strands, and each strand acts as an instruction directing a new segment. The two products each contain one original strand and one new one. In the second round of the process, both of the DNA molecules manufactured in stage one are separated and each of the four strands is copied, producing four double-stranded products. The number of DNA segments doubles during each round. Twenty-five rounds can create millions of new segments from each original DNA.

To separate the double-stranded DNA products, the reaction is heated to near boiling, 95°C, for a few minutes. Originally, the catalyst, DNA polymerase, was killed by this treatment and manually replaced after each round. In 1988 Randall Saiki and coworkers dramatically improved the original concept of PCR by using a heat-stable catalyst, taq polymerase, isolated from the bacteria, *Thermis aquaticus*, found in hot springs. This catalyst survives the high temperature step and can start the next round of synthesis when cooled to the start temperature.

The specificity of PCR derives from the primers. Primers are short pieces of single-stranded DNA that are the starting point of the new DNA strands. The primers recognize the target DNA segment in the sample and

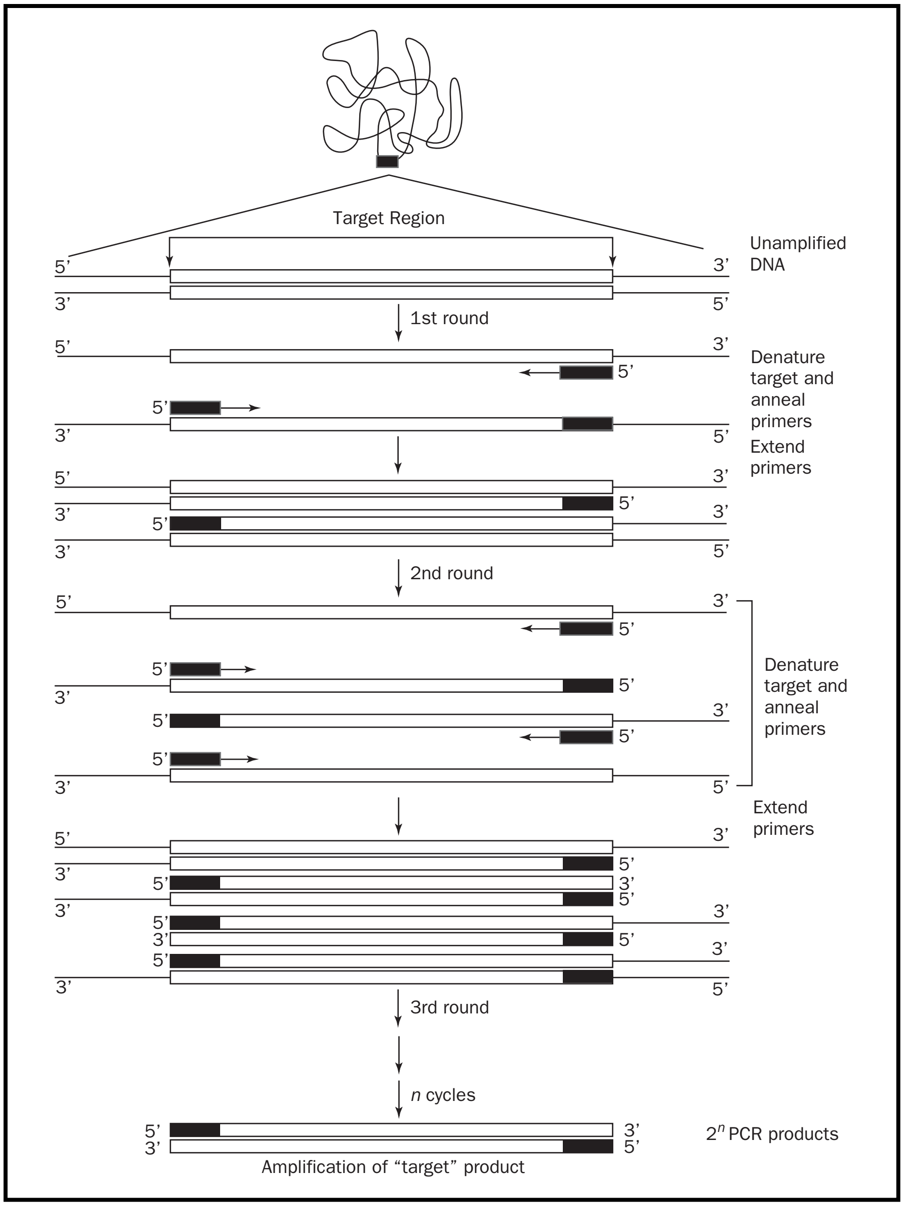

Figure 1. The polymerase chain reaction. PCR is a cycling process; with each stage the amount of target product is doubled.

bind to the target. Taq polymerase uses the primer as the beginning of the new product strand. Taq polymerase cannot synthesize DNA without a primer at the beginning, so the primers and not the catalyst determine what segment of the sample is copied.

Applications of PCR

Originally, PCR was employed to produce usable amounts of small- and medium-sized DNA segments. Many other important techniques quickly developed. PCR is used to identify bacteria and virus infections. It is not only very sensitive but is also selective enough to distinguish closely related strains. For example, this procedure has been adapted to detect genetically modified crops to help ensure they are utilized only in approved ways.

A widely known application of PCR is DNA fingerprinting. Certain regions of the human chromosome have short sections that are repeated up to several hundred times. Different individuals have different numbers of repeats in each section. If several sections are tested, a unique pattern is observed. Initially, these regions were cut out of sample DNA and tested for size. PCR allows the variable regions to be copied millions of times, greatly increasing the sensitivity and speed of the technique. Because of the technique's sensitivity, extreme care must be taken to avoid any contamination of the samples. Forensic scientists continue to make even greater use of this method.

One of the latest applications of PCR is the DNA microarray or gene chip. It allows medical personnel to test a cancer cell before and after chemotherapy with different drugs. If two patterns look the same, the two drugs administered are likely working on the same pathway and may not be as useful as treatment with two drugs that work by different pathways. SEE ALSO DEOXYRIBONUCLEIC ACID (DNA); FORENSIC CHEMISTRY.

David Speckhard

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Polymers, Natural

The word "polymer" means "many parts" (from the Greek *poly*, meaning "many," and *meros*, meaning "parts"). Polymers are giant molecules with molar masses ranging from thousands to millions. Approximately 80 percent of the organic chemical industry is devoted to the production of synthetic polymers, such as plastics, textiles fibers, and synthetic rubbers. A polymer is synthesized by chemically joining together many small molecules into one giant molecule. The small molecules used to synthesize polymers are called monomers. Synthetic polymers can be classified as addition polymers, formed from monomer units directly joined together, or condensation polymers, formed from monomer units combining such that a small molecule, usually water, is produced during each reaction.

Polymers are widely found in nature. The human body contains many natural polymers, such as proteins and nucleic acids. Cellulose, another natural polymer, is the main structural component of plants. Most natural polymers are condensation polymers, and in their formation from monomers water is a by-product.

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

Starch is a condensation polymer made up of hundreds of **glucose** monomers, which split out water molecules as they chemically combine. Starch is a member of the basic food group carbohydrates and is found in cereal grains and potatoes. It is also referred to as a polysaccharide, because it is a polymer of the monosaccharide glucose. Starch molecules include two types of glucose polymers, amylose and amylopectin, the latter being the major starch component in most plants, making up about three-fourths of the total starch in wheat flour. Amylose is a straight chain polymer with an average of about 200 glucose units per molecule.

A typical amylopectin molecule has about 1,000 glucose molecules arranged into branched chains with a branch occurring every 24 to 30 glucose units. Complete hydrolysis of amylopectin yields glucose; partial hydrolysis produces mixtures called dextrins, which are used as food additives and in mucilage, paste, and finishes for paper and fabrics.

Glycogen is an energy reserve in animals, just as starch is in plants. Glycogen is similar in structure to amylopectin, but in a glycogen molecule a branch is found every 12 glucose units. Glycogen is stored in the liver and skeletal muscle tissues.

Cellulose is the most abundant organic compound on Earth, and its purest natural form is cotton. The woody parts of trees, the paper we make from them, and the supporting material in plants and leaves are also mainly cellulose. Like amylose, it is a polymer made from glucose monomers. The difference between cellulose and amylose lies in the bonding between the glucose units. The bonding angles around the oxygen atoms connecting the glucose rings are each 180° in cellulose, and 120° in amylose. This subtle structural difference is the reason we cannot digest cellulose. Human beings do not have the necessary enzymes to break down cellulose to glucose. On the other hand, termites, a few species of cockroaches, and ruminant mammals such as cows, sheep, goats, and camels, are able to digest cellulose.

Chitin, a polysaccharide similar to cellulose, is Earth's second most abundant polysaccharide (after cellulose). It is present in the cell walls of fungi and is the fundamental substance in the exoskeletons of crustaceans, insects, and spiders. The structure of chitin is identical to that of cellulose, except for the replacement of the OH group on the C-2 carbon of each of the glucose units with an $–NHCOCH_3$ group. The principal source of chitin is shellfish waste. Commercial uses of chitin waste include the making of edible plastic food wrap and cleaning up of industrial wastewater.

All proteins are condensation polymers of amino acids. An immense number of proteins exists in nature. For example, the human body is estimated to have 100,000 different proteins. What is amazing is that all of these proteins are derived from only twenty amino acids. In the condensation reaction whereby two amino acids become linked, one molecule of water forming from the **carboxylic acid** of one amino acid and the amine group of the other is eliminated. The result is a peptide bond; hence, proteins are **polypeptides** containing from approximately fifty to thousands of amino acid residues.

The primary structure of a protein is the sequence of the amino acid units in the protein. The secondary structure is the shape that the backbone of the molecule (the chain containing peptide bonds) assumes. The two most common secondary structures are the α-**helix** and the β-pleated sheet. An α-helix is held together by the intramolecular **hydrogen bonds** that form between the N-H group of one amino acid and the oxygen atom in the third amino acid down the chain from it.

The α-helix is the basic structural unit of hair and wool, which are bundles of polypeptides called α-keratins. The helical structure imparts some

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

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

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

Chitin, the earth's second most abundant polysaccharide, is the fundamental substance in the exoskeletons of crustaceans.

elasticity to hair and wool. The polypeptides in silk, on the other hand, are β-keratins with the β-sheet structure, in which several protein chains are joined side-to-side by intermolecular hydrogen bonds. The resulting structure is not elastic.

Nucleic acids are condensation polymers. Each monomer unit in these polymers is composed of one of two simple sugars, one phosphoric acid group, and one of a group of heterocyclic nitrogen compounds that behave chemically as bases. Nucleic acids are of two types: deoxyribonucleic acid (**DNA**), the storehouse of genetic information, and ribonucleic acid (RNA), which transfers genetic information from cell DNA to cytoplasm, where protein **synthesis** takes place. The monomers used to make DNA and RNA are called nucleotides. DNA nucleotides are made up of a phosphate group, a deoxyribose sugar, and one of four different bases: **adenine**, **cytosine**, **guanine**, or **thymine**. The nucleotides that polymerize to produce RNA differ from DNA nucleotides in two ways: they contain ribose sugar in place of deoxyribose sugar and **uracil** instead of thymine.

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

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

cytosine: heterocyclic, pyrimidine, amine base found in DNA

guanine: heterocyclic, purine, amine base found in DNA

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

uracil: heterocyclic, pyrimidine, amine base found in RNA

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

Natural rubber is an addition polymer made up of thousands of **isoprene** monomer repeating units. It is obtained from the *Hevea brasiliensis* tree in the form of latex. The difference between natural rubber and another natural polymer, gutta-percha (the material used to cover golf balls), is the geometric form of the polyisoprene molecules. The CH_2 groups joined by double bonds in natural rubber are all on the same sides of the double bonds (the *cis* configuration), whereas those in gutta-percha are on opposite sides of the double bonds (the *trans* configuration). This single structural difference changes the elasticity of natural rubber to the brittle hardness of gutta-percha. SEE ALSO DEOXYRIBONUCLEIC ACID; NUCLEIC ACIDS; POLYMERS, SYNTHETIC; PROTEINS.

Melvin D. Joesten

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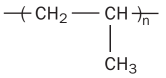
Polymers, Synthetic

Polymers are large molecules composed of repeated chemical units. The smallest repeating unit is called a mer. The term polymer is derived from the Greek words *poly* and *mers* meaning “many parts.” Linear polymers are like ropes. For a polymer chain of 10,000 units (a typical length), a standard half-inch-thick rope would be about 128 meters (140 yards) long to represent the length-to-thickness ratio. Polymers are synthesized naturally and artificially to perform a wide variety of specialized tasks.

Basic Polymer Science

A polymer is generally described in terms of a single repeat unit, such as the following example:

Figure 1.

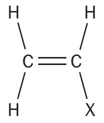


$$-(\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}})_n-$$

The number of repeat units in a chain is called the degree of polymerization (DP) or chain length. Thus, a poly(propylene) chain 5,000 units long would have a DP of 5,000 and an “n” value of 5,000. Because most polymer mixtures contain chains of varying lengths, the chain length is often referred to in terms of average chain length or average DP.

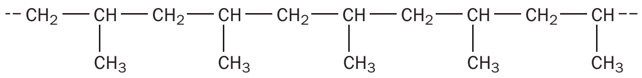
At either end of the polymer chain are end groups. (Because the chain is often thousands of units long, the end groups are usually omitted.) For (poly)propylene (shown in Figure 1) the repeating carbons (C-C-C-C-C-C-C-C) form the polymer backbone and represent the atoms that connect the chain together. In vinyl polymers, so called because they are generally derived from substituted vinyl reactants or monomers (Figure 2), the polymer backbone is composed of only carbon atoms. An example is poly(propylene), which has five mers represented (Figure 3).

Figure 2.



Vinyl Monomer

Figure 3.



$$--\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{CH}}}--$$

Poly(propylene)

Condensation polymer backbones include non-carbon atoms. For example, polyesters have oxygen atoms and nylons have nitrogen atoms in the backbone in addition to carbon atoms (Figure 4).

Figure 4.

$$-(\mathrm{O}-\mathrm{R}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R'}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_n-$$

Polyesters

$$-(\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\mathrm{R}-\overset{\mathrm{H}}{\overset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{R'}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_n-$$

Nylons

Unsymmetrical reactants, such as substituted vinyl monomers, react almost exclusively to give what are called “head-to-tail” products where the substituents occur on alternative carbon atoms:

Figure 5. $-CH_2-CHX-CH_2-CHX-CH_2-CHX-CH_2-CHX-$

Occasionally a "head-to-head, tail-to-tail" configuration occurs. For most vinyl polymers this structure occurs less than 1 percent of the time in a random manner throughout the chain.

Figure 6. $-CH_2-CHX-CHX-CH_2-CH_2-$

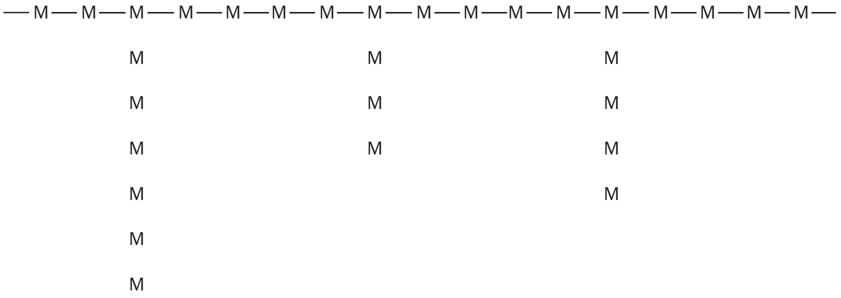
Even with the head-to-tail configuration, a variety of structures are possible. These include a simple linear homopolymer structure

Figure 7.

—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—M—

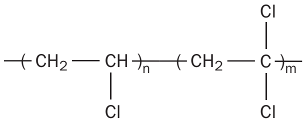
and branched structures with varying amounts and lengths of branching.

Figure 8.



Copolymers are polymers derived from two different monomers (M and N). Saran, a component of Saran Wrap, is one example (Figure 9). Other examples of copolymer structures are depicted in Figure 10.

Figure 9.



$$-\left(CH_2-\underset{Cl}{CH}\right)_n\left(CH_2-\overset{Cl}{\underset{Cl}{C}}\right)_m-$$

Repeat units of vinyl chloride and vinylidene chloride, Saran copolymer

Figure 10. —M—N—M—N—M—N—M—N—M—N—M—N—M—N—M—N—

Alternating

—N—N—M—N—M—M—N—M—N—N—M—N—M—M—N—

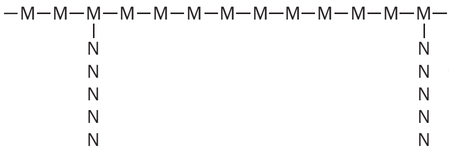
Random

—M—N—M—M—M—M—M—M—M—M—M—M—M—N—

Block in "M"

—N—N—N—N—N—N—M—M—M—M—M—M—M—N—N—

Block in both "M" & "N"

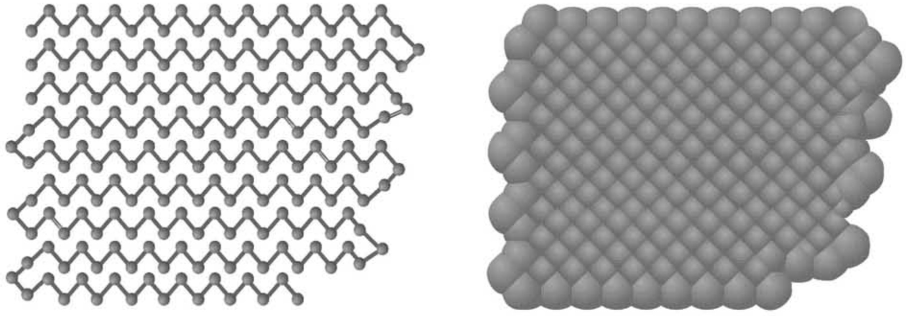


Graft

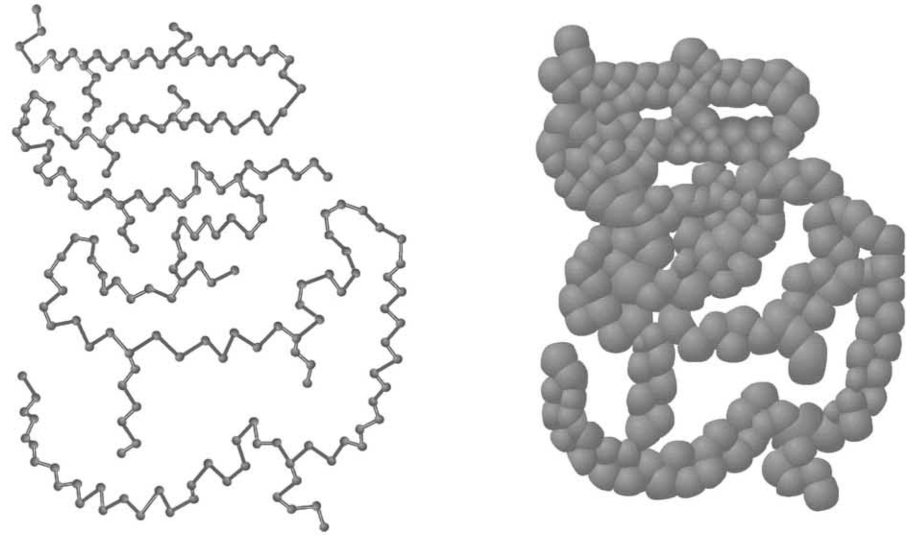
Some linear chains have extensions (beyond the substitution) coming off the polymer backbone. These extensions are called branches and influence a polymer's properties. Branches may be long or short, frequent or infrequent. For example, so-called low density polyethylene (LDPE) has between forty and one hundred short branches for every 1,000 ethylene units, whereas high density polyethylene (HDPE) has only one to six short branches for every 1,000 ethylene units (Figure 11). Branching discourages the chains from fitting close together so that the structure will be **amorphous** with relatively large amounts of empty space. Regular structures with little or no branching allow the polymer chains to fit close together, forming a crystalline structure. Crystalline structures are generally stronger, more brittle, of higher density, more resistant to chemical penetration and degradation, less soluble, and have higher melting points. For example, HDPE has a density of 0.97 gram per milliliter and a melting point of about 130°C (266°F), whereas LDPE has a density of about 0.92 gram per milliliter and a melting point of about 100°C (212°F).

amorphous: containing chains that are arranged in less than a well-ordered, crystalline manner

Figure 11.



High-density polyethylene, 200 units, without branching in a crystalline structure (ball-and-stick model to the left and space-filling model on the right. Only carbon atoms are shown.)

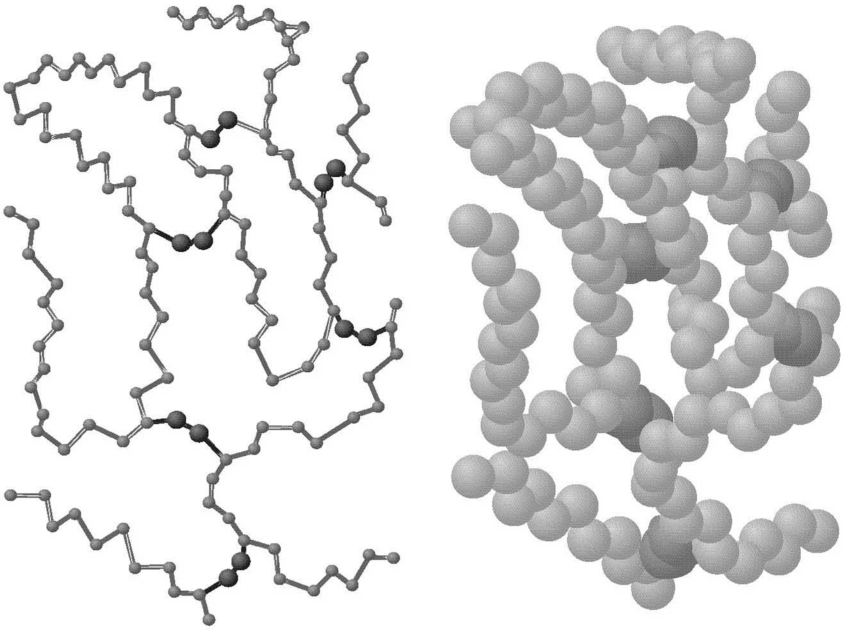


Low-density polyethylene, 200 units, with branching occurring about every 20 carbons, in an amorphous arrangement

Polymer chains can be connected to one another chemically or physically, much like a knot can connect two pieces of string. These connections are called crosslinks and cause the connected chains to act as a single unit

(Figure 12). Some materials can have only a few crosslinks, such as permanent press materials where the fabric contour is locked into place with crosslinks. Others materials such as Bakelite and ebonite are heavily crosslinked; these are hard, brittle, non-flexible materials.

Figure 12.



Low-density polyethylene, 200 repeat units, with crosslinks at 5 percent of the carbon atoms

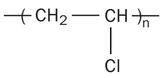
Physical Properties of Polymers

The properties of polymers are dependent on many factors including inter- and intrachain bonding, the nature of the backbone, processing events, presence/absence of additives including other polymers, chain size and geometry, and molecular weight distribution.

While most materials have melting/freezing and boiling/condensing points, polymers do not boil because the energy necessary to put a polymer into the vapor state is greater than the bond energies of the atoms that hold the polymer together, thus they degrade prior to boiling. In order for a polymer to be flexible, its various units or segments must be able to move. The glass transition temperature (T_g) is the temperature where polymer units or segments can move but the entire chain cannot. Most vinyl polymers have T_g values below room temperature so that they appear to be flexible and act as rubber and plastic materials. Most condensation polymers have T_g values above room temperature and are used as hard plastics and fibers. The temperature where entire chain movement occurs is called the melting point (T_m) and is greater than the T_g.

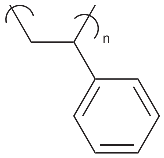
Many polymers are themselves brittle at room temperature. For these polymers to become more pliable, additives called plasticizers that allow segmental mobility, and consequently segmental flexibility, are added. For synthetic polymers such as poly(vinyl chloride) (PVC) and polystyrene (Figure 13), plasticizers are added that allow the polymers to be flexible.

Figure 13.



$-(\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}})_n-$

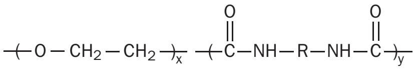
Poly(vinyl chloride), PVC



Polystyrene

The inflexible regions of a polymer, such as crystalline regions, are often referred to as "hard" regions. Conversely, the flexible regions of a polymer, where segmental mobility occurs, are referred to as "soft" regions. This combination of hard and soft can be illustrated with so-called segmented polyurethanes (Figure 14). The urethane portion of such polymers is involved in hydrogen bonding and is considered "hard," while the polyether portion, flexible at room temperature, is considered "soft." These segmented polyurethanes are sold under a number of trade names including Spandex.

Figure 14.



$-(\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2})_x-(\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\mathrm{R}-\mathrm{NH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}})_y-$

Soft **Hard**

Segmented Polyurethane

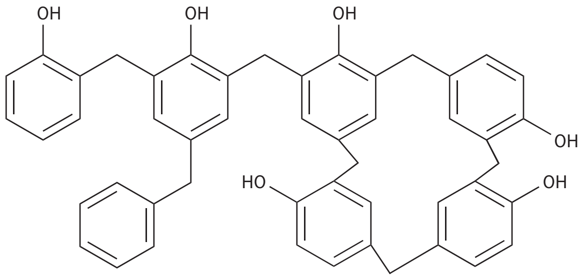
History of Synthetic Polymers

While polymers form the basis of life, the history of synthetic polymers is relatively recent. Some of the key polymers that have been developed since the early days of polymer science include:

Vulcanized rubber. In the mid-1800s, American scientist Charles Goodyear began working with rubber to try to make it more temperature stable. After many unsuccessful attempts, he accidentally allowed a mixture of sulfur and pre-rubber to touch a hot stove. The rubber did not melt but only charred a little. By 1844 Goodyear had been given a patent for a process he called "vulcanization" after the Roman god of fire, Vulcan. Vulcanization is the crosslinking reaction between the rubber chains and the sulfur.

Bakelite. After years of work in his chemistry lab in Yonkers, New York, Leo Baekeland announced in 1907 the synthesis of the first truly synthetic polymeric material, later dubbed "Bakelite." It was generally recognized by leading organic chemists of the nineteenth century that phenol would condense with formaldehyde, but because they did not understand the principles of the reaction, they produced useless crosslinked materials. Baekeland's main project was to make hard objects from phenol and formaldehyde and then dissolve the product to reform it again in a desired shape. He circumvented the problem by placing the reactants directly in a mold of the desired shape and then allowing the reactants to form a hard, clear solid—Bakelite (Figure 15). It could be worked (i.e., cut, drilled, and sanded), was resistant to acids and organic liquids, was stable at high temperatures, and did not break down when exposed to electrical charge. By adding dyes to the starting materials the objects became available in different colors. Bakelite was used to make bowling balls, phonograph records, telephone housings, cookware, and billiard balls. Bakelite also acted as a binder for textiles, sawdust, and paper, forming a wide range of composites including Formica laminates. Many of these combinations are still in use in the twenty-first century.

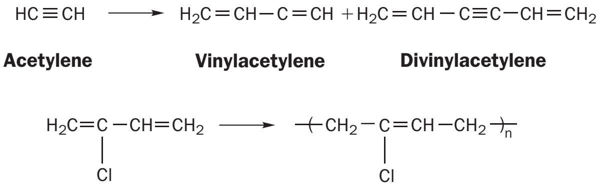
Figure 15.



Representative structure of the complex three-dimensional, highly crosslinked structure of Bakelite.

Neoprene. Chemist and Catholic priest Julius A. Nieuwland did extensive work in the 1920s on acetylene. He found that acetylene could be made to add to itself forming dimers and trimers. Arnold Collins, a chemist at the Dupont Company in the lab of Wallace Carothers, continued work on the project and in 1930 ran the reaction described by Nieuwland, purifying the reaction mixture. He found a small amount of material that was not vinylacetylene or divinylacetylene. After setting the liquid aside, it solidified into a material that seemed rubbery and even bounced. This new rubber was given the name Neoprene (Figure 16). Neoprene has outstanding resistance to gasoline, ozone, and oil in contrast to natural rubber and is used in a variety of applications including electrical cable jacketing, window gaskets, shoe soles, industrial hose, and heavy-duty drive belts.

Figure 16.



$HC\equiv CH \longrightarrow H_2C{=}CH{-}C{=}CH + H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$

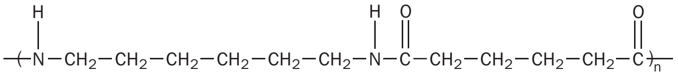
Acetylene **Vinylacetylene** **Divinylacetylene**

$H_2C{=}\underset{\mathrm{Cl}}{\underset{|}{C}}{-}CH{=}CH_2 \longrightarrow \left(CH_2{-}\underset{\mathrm{Cl}}{\underset{|}{C}}{=}CH{-}CH_2\right)_n$

Chloroprene **Polychloroprene (Neoprene)**

Nylon. In the early 1930s Wallace Carothers and his team of chemists at Dupont were investigating synthetic fibers in order to find a synthetic alternative to silk. One promising candidate was formed from the reaction of adipic acid with hexamethylenediamine and was called fiber 66 because each monomer-containing unit had six carbons. It formed a strong, elastic, largely insoluble fiber with a relatively high melting temperature. DuPont chose this material for production. Such polyamides were given the name "nylons"; thus was born nylon 6,6 (Figure 17).

Figure 17.



$\left(\overset{\mathrm{H}}{\overset{|}{N}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\mathrm{H}}{\overset{|}{N}}{-}\overset{\mathrm{O}}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\mathrm{O}}{\overset{\|}{C}}\right)_n$

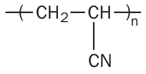
Nylon 6,6

Poly(vinyl chloride). While PVC was initially formed by German chemist Eugen Baumann in 1872, scientists at B. F. Goodrich discovered in 1926 how to make sheets and adhesives from it, starting the "vinyl age." PVC's many applications include water pipes and joints, building materials, food packaging, wire insulation, and medical components.

Polystyrene. While polystyrene was probably first formed by German apothecary Eduard Simon in 1839, it was almost 100 years later, in 1930, that the German chemical company I. G. Fraben placed polystyrene on the market. Polystyrene-molded parts became common place by 1935. Applications of polystyrene include loose-fill packaging "peanuts," shape-molded packaging, and disposable utensils.

Polyacrylonitrile. Rohm and Haas Company bought out Plexiglas (polyacrylonitrile [Figure 18]; also known as acrylic and as a fiber sold under tradenames such as Orlon) from a British firm in 1935 and began production of clear plastic parts and goods, including replacements for glass in camera lenses, aircraft windows, clock faces, and car tail lights.

Figure 18.

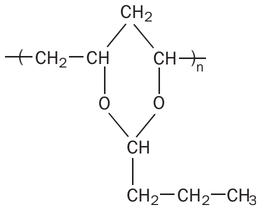


$$\left(CH_2-\underset{CN}{\underset{|}{CH}} \right)_n$$

Polyacrylonitrile

Poly(vinyl butyral). The polymer poly(vinyl butyral) (PVB) was first used in automotive safety glass in 1938 to prevent flying glass resulting from automobile accidents and continues to be utilized in the twenty-first century for this purpose (Figure 19).

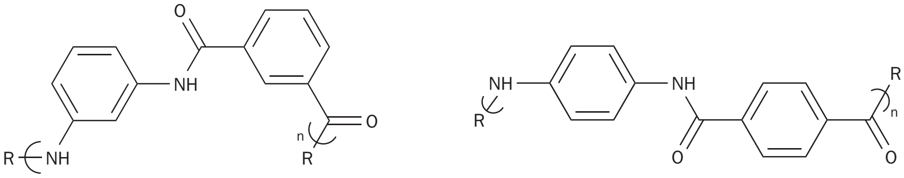
Figure 19.



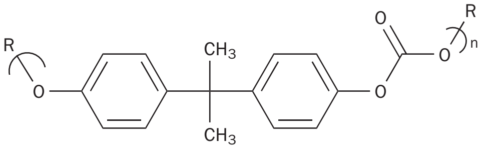
Poly(vinyl butyral), PVB

Other important synthetic polymers. World War II helped shape the future of polymers. Wartime demands and shortages encouraged scientists to seek substitutes and materials that exceeded currently available materials. During and after the war new materials were developed, spurred by needs in the electronics, medical, communications, food, aerospace, and other industries. The aromatic nylons (armids) Kevlar (capable of stopping a speeding bullet and used as tire cord) and Nomex (used in constructing fire-resistant garments) were developed. Polycarbonates sold under the trade names of Merlon and Lexon were developed that substituted for glass in many automotive products such as tail lights. Other key developments included polytetrafluoroethylene, a slick material also known as Teflon; polysiloxanes, also know as silicones, which have an extremely wide temperature-use range and were a component of the soles of the shoes that first touched the moon; and polyester fibers and plastics such as poly(ethylene terephthalate) (PET), used in carbonated drink bottles (Figure 20).

Figure 20.

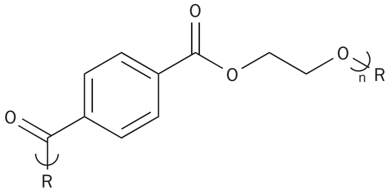


Nomex **Kevlar**



Polycarbonate

Polytetrafluoroethylene **Polydimethylsiloxane**



Even with this early commercial activity, little was actually known about polymers. German chemist Herman Staudinger studied the polymerization of isoprene (a five-carbon hydrocarbon containing a double bond that is obtained as a product of the degradation of natural rubber by heating) as early as 1910. Intrigued by the difference between this synthetic material and natural rubber he began to study giant molecules. Many of his fellow scientists told him there was no such thing as giant molecules and that he was wasting his time. By 1920 he published a summary of his studies and correctly proposed linear structures for polystyrene and polyoxymethylene. X-ray studies were used to support the concept of macromolecules.

Wallace Hume Carothers is considered to be the father of synthetic polymer science. In 1927 the DuPont Company began a program of fundamental research in the areas of colloid chemistry, catalysis, organic synthesis, and polymer formation. Carothers, then a Harvard instructor, was persuaded to join the DuPont group. Carothers looked at the construction of giant molecules from small molecules to form synthetic polymers. His intention was to prepare molecules of known structure through the use of known organic chemistry and to "investigate how the properties of these substances depended on constitution." Over the course of his career, Carothers filed for over fifty patents and was involved in the discovery of nylon and the synthetic rubber neoprene.

From his studies Carothers established several concepts. First, polymers could be formed by employing already known organic reactions but with reactants that had more than one reactive group per molecule. Second, the forces that bring together the individual polymer units are the same as those that hold together the starting materials: namely, primary covalent bonds. Much of the polymer chemistry names and ideas that permeate polymer science were standardized through his efforts.

Types of Synthetic Polymers

Elastomers. Elastomers are polymers possessing chemical and/or physical crosslinks (Table 1 and 2). These crosslinks allow the stretched, deformed segments to return to their original locations after the force is removed. The "use" temperature must be above the T_g to allow ready chain slippage as the rubbery material is flexed and extended. The forces between the chains should be minimal to allow easy movement of these chain segments. Finally, the chains must be present in an amorphous, disorganized fashion. As force is applied and the material distorts or elongates, the randomly oriented chains are forced to align and take more ordered positions with the chains, forming crystalline regions that resist ready movement. As the force is removed the material has a tendency to return to its original disorganized state and therefore its pre-stretched shape. The formation of the crystalline regions as the material is stretched gives the material a greater tensile strength (i.e. an increased force is necessary for further elongation) at high extensions. Crosslinked vinyl polymers are ideal materials to be used in elastomers: the attractive forces between chains is low and their T_g is below room temperature.

MAJOR SYNTHETIC ELASTOMERS

Polychloroprene	Epichlorohydrin Copolymers
Styrene-Butadiene, SBR	Polybutadiene
Nitrile	Ethylene-Propylene
Neoprene	Polyfluorocarbon
Silicone	Polyurethane (Segmented)
Polyisoprene	Butadiene-Acrylonitrile
Styrene-Isoprene	

Table 1.

Thermosets and thermoplastics. Thermosets are materials that have sufficient crosslinking present so that they are prevented from being soluble and melting when heated. Such materials are therefore difficult to recycle. Thermoplastics are materials that melt on heating and generally contain little or no crosslinking. They can be recycled more easily through heating and reforming. Linear polymers are thermoplastic materials.

Fibers. Fibers require materials with a high tensile strength and high modulus (high force required for elongation). This requires polymers with strong forces between the chains and chains that are symmetrical to allow for good crystalline formation. Condensation polymers exhibit these properties and so are most utilized as fibers. Fibers are normally linear and drawn (pulled) in one direction, producing higher mechanical properties in that direction. If the fiber is to be ironed, its T_g should be above 200°C. Branching and crosslinking are undesirable since they inhibit crystalline formation. Even so, some crosslinking may be present to maintain a given orientation, such as desired in permanent press clothing. While most fibers are made from condensation polymers, new treatments allow some fibers to be made from olefinic materials such as polypropylene (Table 3).

Plastics. Plastics require properties that are intermediate between elastomers and fibers. Engineering plastics can be readily machined, cut, and drilled. Condensation polymers are typically engineering plastics while vinyl polymers are typically plastics. Table 4 contains a listing of the most common engineering plastics and plastic materials and Table 5 the volume of engineering plastics and plastics produced in the United States.

U.S. PRODUCTION OF ELASTOMERIC MATERIALS IN 2000

Elastomer	Production (millions of pounds)
Ethylene-Propylene	700
Nitrile	180
Polybutylene	1,210
Styrene-Butadiene	1,750
Other	1,100

Source: International Institution of Synthetic Rubber Producers.

Table 2.

U. S. PRODUCTION OF FIBERS IN 2000

Fiber	Production (millions of pounds)
Cellulosic, Acetate and Rayon	350
Fiber Glass	2,000
Acrylics	340
Polyesters	3,870
Nylons	2,610
Olefins	3,180

Source: Fiber Economics Board

Table 3.

Coatings. Coatings and adhesives are generally derived from polymers that are considered to be plastics, although there are major groups that do not. For instance, silicone rubbers are elastomers that can be used as adhesives. Coatings, or coverings, are generally highly viscous (low flowing) materials. Coatings protect surfaces from the degradative effects of oils, oxidative chemical agents, extreme temperatures, rain, snow, and ionizing radiation. Coatings must adhere to the surface they are applied to. Coatings are typically a mixture of a liquid (vehicle or binder/adhesive) and one or more colorants (pigments). Coatings often also contain a number of so-called additives that can furnish added protection against ionizing radiation, increase the rate of drying and/or curing (crosslinking), and prevent microorganism growth. Coatings are specially formulated for specific purposes and locations and can be divided into five groups:

- Oil paints consist of a suspension of pigment (colorant) in a drying oil such as linseed oil.
- Oil varnishes consist of a polymer, either natural or synthetic, dissolved in a drying oil together with the necessary additives such as catalyst that promotes crosslinking of the drying oil.
- Enamels are oil varnishes with pigment added.
- Lacquers are polymer solutions to which pigments have been added.
- Latex paints are polymer latexes, often poly(methyl methacrylate) and polyacrylonitrile, to which pigments have been added. They account for well over one half of the commercial paint used.

Hardening or drying consists of removal of solvent (evaporation) and/or crosslinking of a drying oil that contains C=C units.

Adhesives. In contrast to coatings that must adhere to only one surface, adhesives are used to join two surfaces together (Table 6). Adhesion for both adhesives and coatings can occur through a number of mechanisms including physical interlocking, chemical adhesion where primary bonding occurs between the adhesive and the surfaces being joined, secondary bonding where hydrogen bonding or polar bonding occurs, and viscosity adhesion where movement is restricted because of the viscous nature of the adhesive material. Adhesives can be divided according to the type of delivery of the adhesive or by the type of polymer:

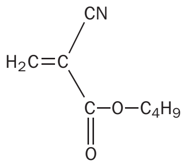
INDUSTRIALLY IMPORTANT ENGINEERING PLASTICS AND PLASTICS

Epoxies	Polyesters
Urea-Formaldehydes	Melamine-Formaldehydes
Phenolics (Phenol-Formaldehydes)	Polyethylenes
Polypropylene	Styrene-Acrylonitriles
Polystyrene	Polyamides
Poly(vinyl chloride) and Co-polymers	
Polytetrafluoroethylene	Poly(methyl methacrylate)
Polycarbonates	Silicons
Polysulphone	Poly(phenylene oxide)
Polyimides	

Table 4.

- Solvent-based adhesives like model airplane glue contain a volatile solvent that dissolves part of the plastic and when dry forms a solvent weld.
- Pressure-sensitive adhesives like those used on Post-It-Notes often contain the same adhesive material used in more permanent adhesives like Scotch Tape except in lesser amounts.
- Reactive adhesives are short chained polymers or monomers that solidify through polymerization or crosslinking after application.
- Plywood is formed from the impregnation of thin sheets of wood with resin that dries after the sheets are pressed together. Phenolic thermosets such as those developed by Bakelite are often used as the resins for plywood.
- Adhesives made from cyanoacrylates are among the best known adhesives, sold under trade names such as Super Glue and Crazy Glue. Monomers such as butyl-alpha-cyanoacrylate (Figure 16) polymerize spontaneously in the presence of moisture. The presence of the cyano and acrylate groups, both quite polar, makes this a particularly good adhesive; it is used in surgery and for mechanical assemblies.

Figure 21.



Butyl-alpha-cyanoacrylate

Sealants and caulks. Sealants and caulks provide a barrier to the passage of gases, liquids, and solids; maintain pressure differences; and moderate mechanical and thermal shock. While adhesives are used for "load transfer" and require high tensile and shear strengths, sealants act as insulators and shock attenuators and do not require high tensile and shear strengths.

Films and sheeting. Films are two-dimensional forms of plastic, thick enough to be coherent, but thin enough to be flexed, creased, or folded without cracking. Most films are produced from materials from the elastomeric and plastic categories. Sheeting is a two-dimensional form of plastic that is thicker (generally greater than 250 micrometers) than film and is generally not easily flexed, creased, or folded without cracking.

U.S. PRODUCTION OF PLASTICS AND ENGINEERING PLASTICS IN 2000

Plastic	Production (millions of pounds)
Nylons	1,400
Polyesters	4,400
Acrylonitrile-Butadiene-Styrene, ABS	3,100
Polyethylene, high density	15,400
Polyethylene, low density	17,900
Styrene-Acrylonitrile	125
Polystyrene	6,600
Polypropylene	15,400
Poly(vinyl chloride) & Copolymers	14,300

Source: C & E News

Table 5.

INDUSTRIALLY IMPORTANT ENGINEERING PLASTICS AND PLASTICS

Epoxies	Polyesters
Urea-Formaldehydes	Melamine-Formaldehydes
Phenolics (Phenol-Formaldehydes)	Polyethylenes
Polypropylene	Styrene-Acrylonitriles
Polystyrene	Polyamides
Poly(vinyl chloride) and Co-polymers	
Polytetrafluoroethylene	Poly(methyl methacrylate)
Polycarbonates	Silicons
Polysulphone	Poly(phenylene oxide)
Polyimides	

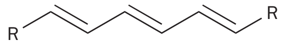
Table 6.

Composites. Composites are materials that contain strong fibers or reinforcement embedded in a continuous phase called a matrix. They are found in jet fighters such as stealth fighters and bombers, in the "reusable" space shuttle, in graphite golf clubs, in synthetic human body parts, and for many years in marine craft (fibrous glass).

Laminates. The combination of an adhesive and an adherent is a laminate, a type of composite. Commercial laminates are produced on a large scale with wood as the adherent and phenolic, urea, epoxy, resorcinol, or polyester resins as the adhesive. Plywood is an example of a laminate. Laminates of paper or textile include Formica and Micarta. Laminates of phenolic, nylon, or silicone resins with cotton, asbestos, paper, or glass textiles are used as mechanical, electrical, and general purpose structural materials.

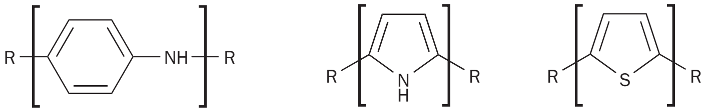
Conductive polymers. Most polymers are nonconductive and polymers such as polyethylene, polypropylene and polytetrafluoroethylene (Teflon) are used as insulators. Even so, some polymers have been found to conduct electricity. An example is polyacetylene; oxidation with chlorine, bromine, or iodine vapor makes polyacetylene film10^9 (1,000,000,000) times more conductive than the non-treated film (Figure 17). This treatment with a halogen is called "doping." Other polymers including polyaniline, polythiophene, and polypyrrole have been found to be conducting after doping and these materials are now being used in a variety of applications (Figure 18). Doped polyaniline is employed as a conductor and as an electromagnetic shielding for electronic circuits. Polythiophene derivatives are used in field-effect transistors. Polypyrrole is used in microwave-absorbing "stealth" screen coatings and in sensing devices. Poly(phenylene vinylidene) derivatives are used in the production of electroluminescent displays.

Figure 22.



Segment of trans-polyacetylene

Figure 23.



Polyaniline **Polypyrrole** **Polythiophene**

Polymer Synthesis

The process by which polymers are formed from monomers is called polymerization. Polymerization occurs by one of two basic reactions: addition or condensation. In addition polymerization, entire monomers are linked together to form long chains. In condensation polymerization, some small molecules (such as water) are released as polymer is formed.

Polymerization reactions may be divided into two major categories: step-wise processes and chain-type processes. In the step-wise process, reactants are brought together and heated. Initially short chains are formed and only at the end of the reaction are long chains formed. Reactions generally require hours to form the polymers. It is by this process that condensation polymers are generally made.

Vinyl polymers are formed using a chain-type process that involves three steps:

- Initiation. This first step requires that the monomer's double bond is broken. This can occur by means of heat or light, or by the addition of other chemical compounds that have less stable bonds. The decomposition products of these chemical compounds add to the vinyl monomer, causing the double bond to break. These materials are called initiators because they start the polymerization process.
- Propagation. This second step involves growth of the polymer chain by the addition of monomer units. This occurs rapidly, within fractions of a second.
- Termination. Finally, the growth of the chain is stopped (terminated).

The process of initiation, growth, and termination continues until the monomer is consumed. Reactions often occur at or below room temperature.

Synthetic Routes

Starting materials are often referred to as feedstocks. Most of the starting materials (monomers) employed in the synthesis of synthetic polymers like polystyrene, polyethylene, and nylons are derived indirectly from fossil fuels. The term fossil fuels refer to materials formed from the decomposition of once-living matter.

There are four basic routes by which polymers are synthesized industrially:

Melt process. Also referred to by other names including high melt, bulk melt, bulk, or neat. The melt process is an equilibrium-controlled process in which polymer is formed by driving the reaction toward completion, usually through removal of the byproduct or condensate. Thus, in the reaction of a diacid and a diol to form a polyester, water is removed, causing the reaction to proceed towards polymer formation. The reactants are employed "neat" (without solvent); any other needed materials such as catalysts are added to the reaction vessel. Heat is applied to melt the reactants, permitting them to come into contact with one another. Additional heat can be added and the pressure reduced, but heat control is important since most of these reactions are exothermic. These reactions typically take several hours to days before the desired polymer is formed. The product yield is necessarily high.

Solution process. Solution polymerizations are also equilibrium processes, with the reaction also often driven by removal of the small byproduct. The product may be recovered from the reaction system through addition of the reaction liquid to a non-solvent, removal of the solvent, or direct precipitation of the polymer from the reaction system. Because the reaction is often run at a lower temperature, more reactive reactants are generally required.

Suspension process. Water-insoluble monomers can be polymerized as suspended droplets in a process called suspension polymerization. Coalescing of the droplets is prevented by use of small amounts of water-soluble polymers such as poly(vinyl alcohol).

Emulsion process. The emulsion process differs from suspension polymerization in the size of the suspended particles and in the mechanism.

Polymer Companies

About 10,000 companies in the United States are active in synthetic polymers. These companies can be divided into three groupings:

Manufacturers. Over 200 companies produce the "bulk" polymers that are used by the other two groupings of companies. While most of these produce the bulk polymers in large quantities, some produce what are called "specialty polymers," those used in special applications on a small scale.

Processors. While some companies produce their own polymers, most purchase the raw polymer material from a manufacturing company. Processors may specialize in the use of selected polymers, such as polypropylenes, polyethylenes, or nylons; in a particular mode of processing; or in the production of particular markets such as films, sheets, laminates, adhesives, or coatings.

Fabricators and finishers. The large majority of companies are involved in the fabrication and finishing of polymer-containing products. Fabrication can be divided into three broad areas: machining, forming, and fashioning. SEE ALSO ADHESIVES; FIBERS; NYLONS; PLASTICS; POLYESTERS; POLYMERS, NATURAL.

Charles E. Carraher Jr.

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Polypeptide ***See Proteins.***

Polysaccharides

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

Polysaccharides are long polymers of **monosaccharides** and their derivatives. Unlike proteins or nucleic acids, these polymers can be either linear or branched, and they can contain only one type of monosaccharide (homopolysaccharides), or more than one (heteropolysaccharides). Polysaccharides can also be roughly divided into groups according to their two main functions: energy storage and their contributions to structural components of cells.

Starch is the main energy reserve in plants; glycogen is the main energy reserve in animals. Starch is a homopolysaccharide and has two forms: amylopectin and α-amylose. In nature, starch is approximately 10 to 30 percent α-amylose. Alpha-amylose is a linear chain polymer composed of **glucose** residues in α (1→4) linkages. Its molecular weight varies from several thousand to more than one million grams (2,205 pounds) per mole. In contrast to amylopectin, which comprises 70 to 90 percent of natural starch, α-amylose is a branching polysaccharide. Although amylopectin, like α-amylose, is composed entirely of α-glucose, its α-glucose residues are joined not only in α (1→4) linkages but also at α (1→6) branch points. Branches occur at every twelve to thirty residues along a chain of α (1→4) linked glucoses. As a result, amylopectin has one reducing end and many nonreducing ends. Amylopectin and α-amylose are broken down by the enzyme amylase. In animals, salivary α-amylase begins the digestion process in the mouth. Pancreatic α-amylase continues the process in the intestine.

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

Glycogen is the energy storage carbohydrate in animals. Glycogen is found mainly in the liver (where it is responsible for up to 10 percent of liver mass) and skeletal muscle (1 to 2 percent of skeletal muscle mass). Like amylopectin, it consists of α-glucose residues in α (1→4) linkage, with α (1→6) branch points. However, glycogen branches more abundantly than amylopectin, with branches at every eight to twelve residues. As a result, it has many more nonreducing ends. Glycogen is broken down at these nonreducing ends by the enzyme glycogen phosphorylase to release glucose for energy. Having many reducing ends, glycogen is more readily broken down in cases in which an animal needs a sudden burst of energy.

The primary structural homopolysaccharides are cellulose and chitin. Cellulose, a major component of plant cell walls, is the most abundant natural polymer on Earth. It is responsible for much of the mass of wood. Cotton is almost pure cellulose. Like α-amylose, cellulose is a linear polysaccharide composed entirely of glucose. However, in cellulose the glucose residues occur in β(1→4) linkage rather than α (1→4) (see Figure 1). This change in linkage has profound effects on the chemical and structural properties of cellulose. The glucose molecules in cellulose are alternately inverted (every other one inverted) such that each chain has a highly extended and rigid conformation. In addition, individual cellulose strands can form **hydrogen bonds** with one another to provide additional strength. Most animals, including humans, lack the enzymes necessary to dissolve β(1→4) linkages and so cannot digest cellulose. The animals that can (such as ruminants) do so via a symbiosis with bacteria that secrete cellulose-degrading enzymes.

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

The second most abundant polymer on Earth is chitin. Chitin comprises much of the exoskeletons of crustaceans, insects, and spiders, as well as the cell walls of fungi. Structurally, chitin is very similar to cellulose, except that its basic monosaccharide is N-acetylglucosamine. Chitin, like cellulose, has its repeating units joined in β(1→4) linkages. SEE ALSO CARBOHYDRATES; DISACCHARIDES.

Stephanie E. Dew

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Postactinides ***See Transactinides.***

Potassium

19
K
POTASSIUM
39.0983

MELTING POINT: 63.38°C
BOILING POINT: 759°C
DENSITY: 0.862 g/cm^3
MOST COMMON IONS: K^+

Potassium is a soft, silvery alkali **metal** that reacts strongly with water to produce hydrogen gas. The word "potassium" is derived from "potash" or "pot ashes," as Humphry Davy isolated the element in 1807 via the electrolysis of caustic potash, KOH. The element's symbol is derived from *kalium* (Latin), which originated from *qali* (Arabic for "alkali"). Currently, potassium metal is generated by the reduction of molten potassium chloride, KCl, with sodium and the use of **fractional distillation** to separate the resulting mixture. In nature it is never found in its elemental form. Compounds of potassium are found primarily in the minerals sylvite, carnallite, langbeinite, and polyhalite, as well as in the brines of the Dead Sea in Jordan and the Great Salt Lake in Utah. Potassium is the second most abundant alkali metal and the eighth most abundant element in Earth's crust (18,400 ppm). Potassium burns violet in the flame test.

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

The industrial demand for potassium metal is much smaller than that for sodium. Potassium-sodium **alloys** (which are liquid at room temperature) serve as heat-exchange liquids in the cooling systems of **nuclear** reactors. Strong bases such as potassium amides and alkoxides are formed from the reaction of potassium with amines and alcohols, respectively.

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

nuclear: having to do with the nucleus of an atom;

Compounds of potassium are economically more important than the metal. KCl is used extensively in fertilizers. KOH is used to make liquid soaps and detergents. Potassium nitrate, KNO_3, serves primarily as an oxidizing agent in gunpowder and pyrotechnics. Potassium superoxide, KO_2, is used in backup ventilation equipment as it generates oxygen gas in the presence of CO_2. Potassium ions are essential to plants and animals as many metabolic reactions and pathways depend on their presence. SEE ALSO ALKALI METALS.

Nathan J. Barrows

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Praseodymium

MELTING POINT: 935°C
BOILING POINT: 3,017°C
DENSITY: 6.475 g/cm^3
MOST COMMON IONS: Pr^{3+}, Pr^{4+}

59
Pr
PRASEODYMIUM
140.908

In 1885 C. A. von Welsbach isolated two elements as oxides, praseodymium (the word meaning "green twin") and neodymium (meaning "new twin"), from a mixture of **lanthanide** oxides called didymia. The oxides can be transformed to fluorides by reaction with HF at 700°C (1,292°F), or with NH_4HF_2 at 300°C (572°F). The hydrated fluorides are then dehydrated in vacuo in a current of HF gas. The **metals** praseodymium and neodymium are obtained via metallothermic reduction with calcium at approximately 1,450°C (2,642°F), or via electrolytic reduction of the melts. The metals can also be obtained from anhydrous chlorides, obtained via reaction of the oxides with ammonium chloride at 350°C (662°F), which are then reduced with lithium-magnesium at approximately 100°C (212°F).

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

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

Praseodymium halides (except the fluoride), nitrate, and acetate are soluble. The hydroxide, carbonate, oxalate phosphate, and oxide compounds are insoluble. Praseodymium's solutions and most of its solids are green.

When oxo-compounds of Pr(III) are ignited in the atmosphere, a black oxide of composition Pr_6O_{11} (approximately) is obtained. Fluorocomplexes of Pr(IV) that have the compositions Na_2PrF_6, $Na_7Pr_6F_{31}$, and PrF_4 have been obtained.

Pr(III) salts and complexes are weakly luminescent. The salts are used to color some special glasses and as pigments in ceramics. The compound $Zr_{1-x}Pr_xSiO_4$ is used often as a yellow pigment in the ceramic industry; it is very stable in color and resistant to high temperatures. Pr(III), in Pr_2S_3, is an excellent pigment for plastics and paints. Other uses of praseodymium include tires (Pr-doped $ZrSiO_4$), photographic filters (Pr_2O_3), and welding masks (Pr-Nd). SEE ALSO LANTHANIDES.

Lea B. Zinner
Geraldo Vicentini

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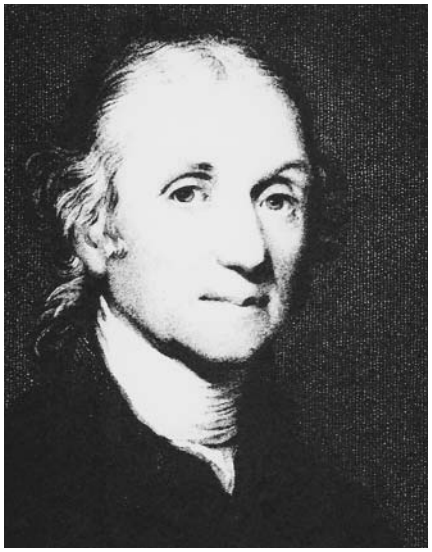
Precious Metals ***See Gold; Palladium; Platinum; Silver.***

Priestley, Joseph

ENGLISH THEOLOGIAN AND CHEMIST
1733–1804

Joseph Priestley was a dissenting Unitarian minister in England at a time when adherence to the established Church of England was of great importance. Preaching was a difficult career for Priestley—because his Unitarian views were unpopular and because he spoke with a stammer. Priestley published widely in a variety of subjects, including theology, education, history, politics, and science. Most often, Priestley is remembered as one of the discoverers of oxygen, but his impact on other lives went much further than this.

His first major science publication was *The History and Present State of Electricity* (1767), which gained him admission to the **Royal Society**; it was followed by *The History and Present State of Discoveries Relating to Vision, Light and Colours* (1772). Both light and electricity were regarded as aspects of the **Newtonian** "imponderable fluid" or "ether." They were called "imponderable fluids" (or subtle fluids) because they had no detectable weight (no "poundage"), but still had some fluidlike characteristics. Another form of this "ether" was "phlogiston." Phlogiston was the postulated substance of fire, the active principle of acids, and the driving force behind chemical reactions.



English chemist Joseph Priestley, the first person to isolate a number of gases, including oxygen.

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

Newtonian: based on the physics of Isaac Newton

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

As Priestley expanded his studies in chemistry he became active in the field of pneumatic chemistry, the study of air and gases. Priestley was the first to isolate and characterize a number of gases, including oxygen, nitrogen, hydrogen chloride, ammonia, sulfur dioxide, carbon monoxide, **nitric oxide**, and nitrous oxide. Priestley's names for these compounds were different from the modern names, in part because he never adopted the oxygen theory of chemistry. The names he used were in terms of the older "phlogiston theory." Priestley did this work using very simple apparatuses, such as saucers, glasses, tubes, cylinders, and tubs of water or mercury.

Among the chemical phenomena he investigated was the behavior of a gas or other substance in contact with fire. If fire was the visible escape of phlogiston from a burning substance, then some gases had a greater affinity for phlogiston than ordinary air and encouraged the flame. Other gases had a lesser affinity for phlogiston than ordinary air (or no affinity at all) and would extinguish the flame.

calx: substance produced by roasting or burning a mineral, taken as the essence of the mineral

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

One gas was found to be especially able to support a flame. Priestley called this gas "eminently respirable air." He later called this same substance "dephlogisticated air," reasoning that because it had a large affinity for phlogiston, it must be particularly devoid of it, or dephlogisticated. Priestley found that the heating of a sample of "red precipitate" (a **calx** of mercury) to produce pure mercury generated very pure dephlogisticated air. Priestley's discovery of the large amount of "air" generated during the heating of red precipitate was similar to Joseph Black's discovery of "fixed air." The production of dephlogisticated air also fit Priestley's belief that a **metal** is phlogiston compounded with a calc. The dephlogisticated air liberated from red precipitate also fit well with the observation that when a candle burned out in a closed vessel, the volume of the air was diminished. It was thought that the presence of phlogiston decreased the "springiness" of air. Thus, adding phlogiston to air would cause it to contract, and removing phlogiston from air would cause it to expand. Priestley also found that air saturated with phlogiston could be "revivified" (or dephlogisticated) by green plants in the presence of sunlight. Dephlogisticated air would be renamed "oxygen" by Antoine Lavoisier, who made it the cornerstone of his theory of chemistry.

Priestley resisted the oxygen theory of chemistry to the end of his life. For Priestley, phlogiston was more than just the active principle of fire—it

PHLOGISTON

There never was a widespread coherent theory of phlogiston. German chemist Johann J. Becher (1635–1682) brought the term "phlogiston" into use among European chemists in the middle 1600s. The word is based upon a Greek word used by Aristotle in his writings on matter. German chemist Georg Stahl (1660–1734) further articulated the phlogiston theory in the early 1700s.

According to the phlogiston theory, a flame was thought to be the visible escape of matter called phlogiston from a burning substance. Another key feature of the theory was that a metal was thought to be composed of phlogiston and earth. Luster, high heat conductivity, malleability, and ductility are all unusual characteristics for metals, but according to the theory, metals share these features because of their postulated phlogiston content. If the phlogiston was removed from a metal, the result was an earth called calc (plural, calx), often the metal's naturally occurring ore. Under certain conditions, phlogiston might even exhibit a negative weight! This anomaly became problematic after Sir Isaac Newton's 1687 Law of Universal Gravitation.

—David A. Bassett

was the active principle of life. Here Priestley's scientific theory merged with some of his religious beliefs. If phlogiston were the active principle of fire, heat, light, electricity, acids, chemical reactivity, and life, then it might also be the active principle of spirit. This accorded well with his Unitarian belief in one omnipresent active principle in the universe. In his book *Disquisition on Matter and Spirit* (1777), he asserted that there was only matter and void in the universe—there were no immaterial spiritual influences. Thus, the material existence of phlogiston corresponded well with his religious beliefs.

Priestley also had strong convictions in favor of broad-based democratic reforms and freedom of thought. He advocated wider religious toleration in England. He supported the American colonists in their revolution against the British Crown and supported the French Revolution, even in the face of atrocities such as the Reign of Terror. Priestley made enemies as a result of his political beliefs, and in 1791 his house and laboratory in Birmingham were attacked and burned by a mob. Priestley fled to London and was able to emigrate from there to the United States in 1794. In the United States he was a renowned international figure. When he landed in New York, both the mayor and the governor greeted him. When he arrived in Philadelphia, he was received by President Washington.

In 1794 Priestley declined an offer to be a professor of chemistry at the University of Pennsylvania. He retired from public life in Northumberland, Pennsylvania, and died there in 1804. His home in Northumberland is now preserved as a historical landmark. According to Peter Miller (1993), "A work entitled 'Joseph Priestley in Context' would . . . far surpass the competence of any single chronicler." SEE ALSO Gases; Lavoisier, Antoine; Nitrogen; Oxygen.

David A. Bassett

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Primary Structure

There are four recognized levels of protein structure: primary, secondary, tertiary, and quaternary. The primary structure refers to the **amino acid sequence** of a protein. The primary structure is important to the protein's unique three-dimensional structure, its mechanism of action, and its relationship to other proteins with similar physiological roles. The amino acids in a protein✷ are linked together by a specific type of **covalent bond**, called a peptide bond, that exists between adjacent amino acids in the **polypeptide** chain. Another important aspect of the primary structure is the sequence or order of amino acids in the polypeptide chain. The sequence of amino acids in a protein is specified by the nucleotide sequence of the segment of **DNA** containing the gene that codes for that protein. Each protein has a characteristic number and sequence of amino acid residues. The primary structure of a protein determines how the protein folds into a unique three-dimensional structure (further described by the secondary, tertiary, and quaternary structures), which in turn determines the biological function of the protein. SEE ALSO Peptide Bond; Proteins; Quaternary Structure; Secondary Structure; Tertiary Structure.

Elizabeth S. Roberts-Kirchhoff

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

✷See the Amino Acids article for a table of the amino acids.

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

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

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

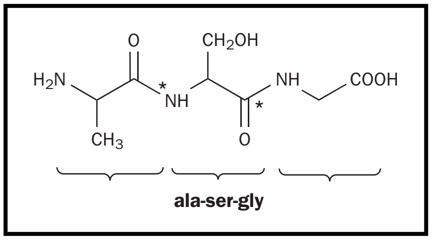

Figure 1. Structure of a tripeptide with the peptide bonds marked with an asterisk. The primary sequence is the order of amino acids, and in this example the primary sequence is ala-ser-gly.

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Promethium

MELTING POINT: 1,100°C
BOILING POINT: 3,000°C
DENSITY: 7.22 g/cm^3
MOST COMMON IONS: Pm^{3+}

61
Pm
PROMETHIUM
145

The existence of promethium was first theorized in 1902 by Bohuslav Brauner, who predicted that an element between neodymium and samarium was missing from the periodic table. Because only minuscule amounts of promethium are naturally present in Earth's crust, full confirmation of this prediction was not made until 1945. Working at the Oak Ridge National Laboratory in Oak Ridge, Tennessee, Jacob Marinsky, Lawrence Glendenin, and Charles Coryell produced promethium by the **nuclear fission** of uranium and by neutron irradiation of neodymium, chemically identifying the new element using **ion exchange chromatography**.

In compounds, promethium is known to exist in the tripositive **oxidation** state only (Pm^{3+}), which is the most stable oxidation state for all of the **rare earth elements**. Consequently, its chemistry is like that of other rare earth elements and of the tripositive actinide ions, especially Am^{3+}, which is almost the same size as Pm^{3+}. When enough material is present to see, promethium compounds are generally a pale pink color under white light. In the dark, however, the intense radioactivity of all promethium **isotopes** causes macroscopic amounts of promethium compounds to glow pale blue or green. The isotope ^{145}Pm has the longest half-life (17.7 years), but ^{147}Pm (half-life 2.6234 years) is produced in significant quantities from the fission of uranium and plutonium in nuclear reactors, and convenient methods for isolating gram amounts of ^{147}Pm by displacement **chromatography** have been described. The availability, high specific activity (928 Ci/gram), and pure β-particle emission of ^{147}Pm lend it to industrial applications in thickness gauges, nuclear batteries, and emergency lights that operate without an external power source. SEE ALSO CERIUM; DYSPROSIUM; ERBIUM; EUROPIUM; GADOLINIUM; HOLMIUM; LANTHANUM; LUTETIUM; NEODYMIUM; NUCLEAR FISSION; PRASEODYMIUM; SAMARIUM; TERBIUM; YTTERBIUM.

Mark Jensen

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

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

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

rare earth elements: older name for the lanthanide series of elements, from Lanthanum to Lutetium

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

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

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Protactinium

MELTING POINT: 1,568°C
BOILING POINT: Unknown
DENSITY: 15.37 g/cm^3
MOST COMMON IONS: Pa^{4+}, $PaO(OH)2^{+}$

91
Pa
PROTACTINIUM
231.036

An **isotope** of protactinium (having mass number 234 and a half-life of 1.1 minutes) was first identified by Kasimir Fajans and O. Gohring in 1913 as a short-lived member of the naturally occurring ^{238}U decay series and was given the name *brevium*, meaning brief. The existence of protactinium was confirmed in 1918 when another isotope of protactinium (of mass 231 and a half-life of 3.3×10^4 years) was studied independently by Otto Hahn and

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

Lise Meitner in Germany, and by Frederick Soddy and John Cranston in Great Britain. The current name of the element is a shortened version of the original *protoactinium*, derived in part from the Greek *protos*, meaning parent; protoactinium thus meant parent of actinium (its decay product). There are twenty-four known isotopes of Pa, having mass numbers ranging from 214 to 238, the most stable isotope being ^{231}Pa. Protactinium **metal** is silvery and relatively nonreactive. It occurs at ppm levels in uranium ores and is extracted from these ores. There are about 125 grams (4.4 ounces) of protactinium in the world today. Its ground state electronic configuration is [Rn]$5f^2 6d^1 7s^2$, placing it in Group IIIB. Its **principal oxidation state** is +5, but there is no stable Pa^{5+} ion because it is hydrolyzed so quickly to species such as $PaO(OH)^{2+}$, or forms complexes with **anions** such as fluoride. Protactinium in its +4 state may exist in **aqueous solution** or in compounds. The most important solid compound of protactinium is Pa_2O_5. SEE ALSO ACTINIUM; BERKELIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; RUTHERFORDIUM; THORIUM; URANIUM.

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

principal oxidation state: oxidation state that is most important

anion: negatively charged chemical unit, like Cl^-, CO_3^{2-}, or NO^{3-}

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

Walter Loveland

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Proteins

Excluding the water present in the human body, about one half of the remaining mass is composed of a class of molecules called proteins. It should therefore be of no surprise that proteins carry out many important biological processes.

Amino Acids

Proteins are essentially natural polymers composed of long chains of subunits. These smaller units are called amino acids. One "end" of an amino acid has acidic character because it has a carboxyl (COOH) **functional group**. The other end has basic character because it has an amino (NH_2) functional group. When two amino acids react, they form what is called a peptide bond. The resulting molecule, called a dipeptide, still has one end that is acidic and another that is basic (Figure 1). With this fundamental reactive pattern, it is possible to string together many amino acids to form a **polypeptide**. For such a chain, the end that has the **carboxyl group** is referred to as the C-terminus; the amino end is referred to as the N-terminus.

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

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

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

Some proteins, including a number of hormones, have only a relatively small number of amino acid units, while others have literally thousands. Once an amino acid is incorporated into the polypeptide, it is referred to as a residue. When biochemists identify a particular portion of a protein, they usually refer to the residue with its name and a number, referring to how far from the N-terminus that residue is located.

In the human body, there are twenty different amino acids that are found in proteins✷. The body is capable of synthesizing most of the amino acids it needs, but there are eight molecules that cannot be made. These are called

✷See table of amino acids in the Amino Acids article.

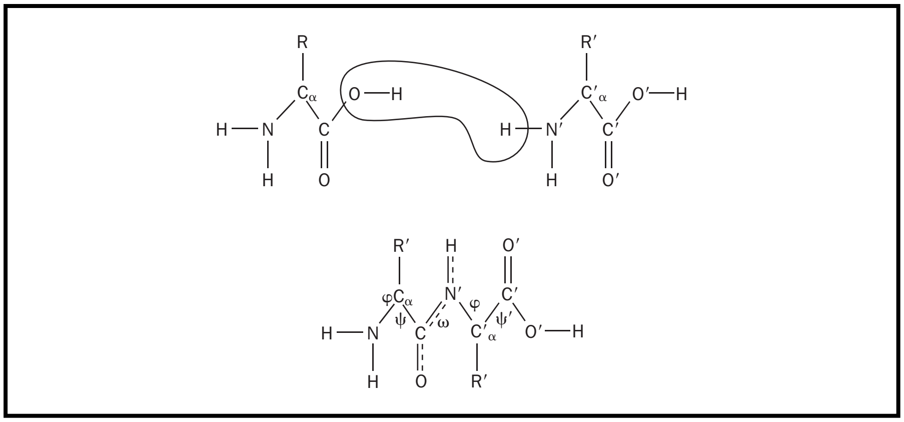

Figure 1. When amino acids react, they form what is called a peptide bond. The resulting molecule, called a dipeptide, has one end that is basic and another that is acidic.

the essential amino acids, and they must be present in the diet or a person will develop malnutrition. Many people gain the amino acids they need by eating a diet that contains complete proteins. Most meats (such as beef, poultry, or fish) have complete proteins. The body metabolizes (breaks down) these ingested proteins and in so doing provides the raw materials needed for making the proteins.

People who do not eat meat must be careful to eat a diet that includes the essential amino acids. This can be accomplished by eating complementary proteins. For example, corn has many essential amino acids but is low in tryptophan. Beans, however, have ample tryptophan; cultures that use cornmeal often complement this food source with beans. Similarly, cultures in Asia often eat rice with soy sauce; this combination provides complementary proteins in the diet.

Protein Structure

The order of the amino acids in a protein dictates the primary structure of the protein. While other levels of structure are important, they all follow from the order of the residues. The primary structure is dictated by genetic information found in a cell; deoxyribonucleic acid (**DNA**) contains the **code** that directs which amino acids are linked together. The processes by which the genetic code is read and proteins are synthesized are called **transcription** and translation.

The next level of protein structure is called the secondary structure. The side chains of the residues have various functional groups that can have different types of forces: some are **hydrophobic** and others are **hydrophilic**; some participate in **hydrogen bonding** interactions while others do not. These forces lead to conformations (geometric arrangements of the residues) that result in lower energies. Two specific arrangements that are found regularly are shown in Figure 2: a **helix** (which looks like a corkscrew) and a pleated sheet (which looks like a paper that has been folded and opened).

The secondary structure of the protein is the result of interactions of side chains that are located within a few residues of each other. Proteins are sufficiently long that they can eventually fold back on themselves, allowing residues that are farther apart in the primary structure to interact with each other. These interactions give rise to the tertiary structure of the protein

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

code: mechanism to convey information on genes and genetic sequence

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

hydrophobic: a part of a molecule that repels water; if an entire molecule is hydrophobic, it will not dissolve in water

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

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

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

Figure 2. The secondary structure of protein. Darker grey portion is the helix and lighter grey portion is the pleated sheet.

(Figure 2). Some proteins can form structures with multiple units (dimers, trimers, or tetramers). These collections of units provide yet another level of structure called the quaternary structure.

Solubility is one property that can be used to classify the proteins that result from the various levels of structure. For example, fibrous proteins are not soluble in water. Many familiar components of tissues are composed of fibrous proteins, including keratin (the protein present in hair), collagen (a structural protein found in tendons and cartilage), myosin (a protein found in most muscle tissue), and fibrin (the protein that allows blood to clot and form scabs). Conversely, globular proteins are soluble in water. For example, albumins are water-soluble proteins that provide a familiar example of what happens when a protein loses its secondary and tertiary structure, a process called denaturation. When an egg is cooked, the egg white changes from translucent to white; this color change is indicative of the change in structure that has taken place in the albumin proteins.

In many cases, the structure of a protein defines a key location called the active site, the region that is associated with the primary activity of a protein, even though it is often made up of only a small number of residues.

Biological Functions

The variety of structures associated with proteins suggests the large number of biological tasks that they carry out. It is possible to classify proteins based on their biological functions.

Enzymes are proteins that catalyze chemical reactions that take place in living systems. A **catalyst** is a molecule that speeds up a reaction but is not consumed by that reaction. Enzymes are particularly interesting because they often are quite specific, capable of catalyzing only one type of biochemical reaction. Learning about the structure of the active site is often a

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

crucial component of studies that look at the **catalytic** properties of an enzyme.

Many hormones are proteins, often containing only a relatively small number of residues. Insulin is perhaps the most well known peptide hormone; because of its role in the **metabolism** of carbohydrates, it plays an important role in the control of diabetes. Growth hormone is another example of a protein.

Some neurotransmitters are closely related to proteins, differing from them only because they have relatively few residues. There are many known neurotransmitters; endorphins and enkephalins are examples of peptides that carry out this role.

Many **antibodies** and other components of the immune response system are proteins. One important component of a body's defenses is the ability to form clots to stop bleeding from cuts. A protein called fibrinogen plays a key role in this.

Proteins comprise a majority of muscle tissue. Two classes of protein, actin (which makes moving filaments) and myosin (which remains stationary), are primary components of the muscles in the body.

Proteins are often involved in the storage of nutrients in the body. For example, iron is stored (mostly in the spleen) in a protein called ferritin. In plants, nutrients needed for the growth of a new plant are a major component of seeds, and storage proteins carry out this task.

In addition to storing nutrients, proteins can transport them. Perhaps the most critical transport protein is hemoglobin, which transports oxygen and carbon dioxide in the bloodstream. In the lungs the percentage of oxygen is high, so it binds to the protein in an **equilibrium** process. When hemoglobin reaches tissue that has produced carbon dioxide, the oxygen is released and used by cells in metabolism. The hemoglobin can then bind carbon dioxide and carry it to the lungs to be released.

There are several ways that proteins contribute to the structure of living things. Glycoproteins play a major role in the structures of cell membranes. While **lipids** are more numerous in the membrane, many of the key functions that occur at the membrane level, such as transport of materials, are carried out by transmembrane proteins. **Receptors**, including those in nerve cells, are proteins that help cells interact with their external environment. Some tissues like cartilage have proteins that help provide structure on a larger scale.

Proteins can also be dangerous or unhealthy. For many who suffer from allergies to agents like pollen, it is proteins on the surface of the pollen that cause an immune response that triggers the allergic reaction. More seriously, many natural **toxins** are proteins. Snake venom is one example of a naturally occurring protein-based toxin. SEE ALSO ACTIVE SITE; AMINO ACID; DENATURATION; ENZYMES; FIBROUS PROTEINS; GLOBULAR PROTEINS; NEUROTRANSMITTERS; PEPTIDE BOND; PROTEIN SOLUBILITY; PROTEIN SYNTHESIS; PROTEIN TRANSLATION; RNA SYNTHESIS; SECONDARY STRUCTURE; TERTIARY STRUCTURE; TRANSMEMBRANE PROTEINS; VENOM.

Thomas A. Holme

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

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)

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

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

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

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

toxin: poisonous substance produced during bacterial growth

CARBON MONOXIDE POISONING

Carbon monoxide, CO, poisons the body by combining with hemoglobin some 250 times more tightly than O_2, thus hindering the transport of O_2 to the body's tissues. In an environment of 0.1 percent CO (within the lung), more than half the binding sites of hemoglobin become occupied with CO, and the victim dies within an hour.

—N. M. Senozan

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Protein Solubility

hydrophilic: a portion of a molecule that attracts water

At the surfaces of proteins are amino acid residues that interact with water. The amino acids are referred to as **hydrophilic** amino acids and include arginine, lysine, aspartic acid, and glutamic acid. At pH 7 the side chains of these amino acids carry charges—positive for arginine and lysine, negative

A scientist adjusts equipment used in fast protein liquid chromatography, which is used to isolate specific proteins from sample mixtures. Soluble proteins have a charge on their surfaces.

for aspartic acid and glutamic acid. As the pH increases, lysine and arginine begin to lose their positive charge, and at pHs greater than about 12 they are mainly neutral. In contrast, as pH decreases, aspartic acid and glutamic acid begin to lose their negative charges, and at pHs less than 4 they are mainly neutral.

The surface of a protein has a **net charge** that depends on the number and identities of the charged amino acids, and on pH. At a specific pH the positive and negative charges will balance and the net charge will be zero. This pH is called the isoelectric point, and for most proteins it occurs in the pH range of 5.5 to 8. A protein has its lowest solubility at its isoelectric point. If there is a charge at the protein surface, the protein prefers to interact with water, rather than with other protein molecules. This charge makes it more soluble. Without a net charge, protein-protein interactions and precipitation are more likely.

net charge: total overall charge

The solubility of proteins in blood requires a pH in the range of 7.35 to 7.45. The bicarbonate–carbonic acid buffer system of blood ($HCO_3^- + H^+ \longleftrightarrow H_2CO_3$), in which the bicarbonate is in excess of the carbonic acid, helps to maintain the correct pH. Exhalation of carbon dioxide from the lungs causes some of the bicarbonate ions in blood to combine with protons, and this would raise the pH. However, because there is an excess of bicarbonate ions and protons, the loss of a small number of protons does not influence the pH significantly.

The proteins of protein mixtures can be separated using a technique known as isoelectric focusing. A mixture is placed in a polyacrylamide gel that has a pH gradient. An anode (positive electrode) and a cathode (negative electrode) are positioned at the low and high ends of the pH gradient, respectively. If a protein is located in the high pH region, it will be negatively charged and will move toward the anode. As the protein moves to a lower pH region, its surface charge will become less negative, and a pH region will be reached at which the protein net charge is zero (the isoelectric point). The protein will stop moving and, because different proteins have different isoelectric points, separation can be achieved. SEE ALSO PROTEINS.

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Protein Synthesis

There is no task more important to the function of living cells than the **synthesis** of proteins. Because proteins carry out so many different tasks, the mechanism to synthesize them is intricate. There are several stages involved in the synthesis process, including transcription and translation.

synthesis: combination of starting materials to form a desired product

Transcription

The primary role of deoxyribonucleic acid (**DNA**) is to direct the synthesis of proteins. DNA, however, is located in the nucleus of the cell, and

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

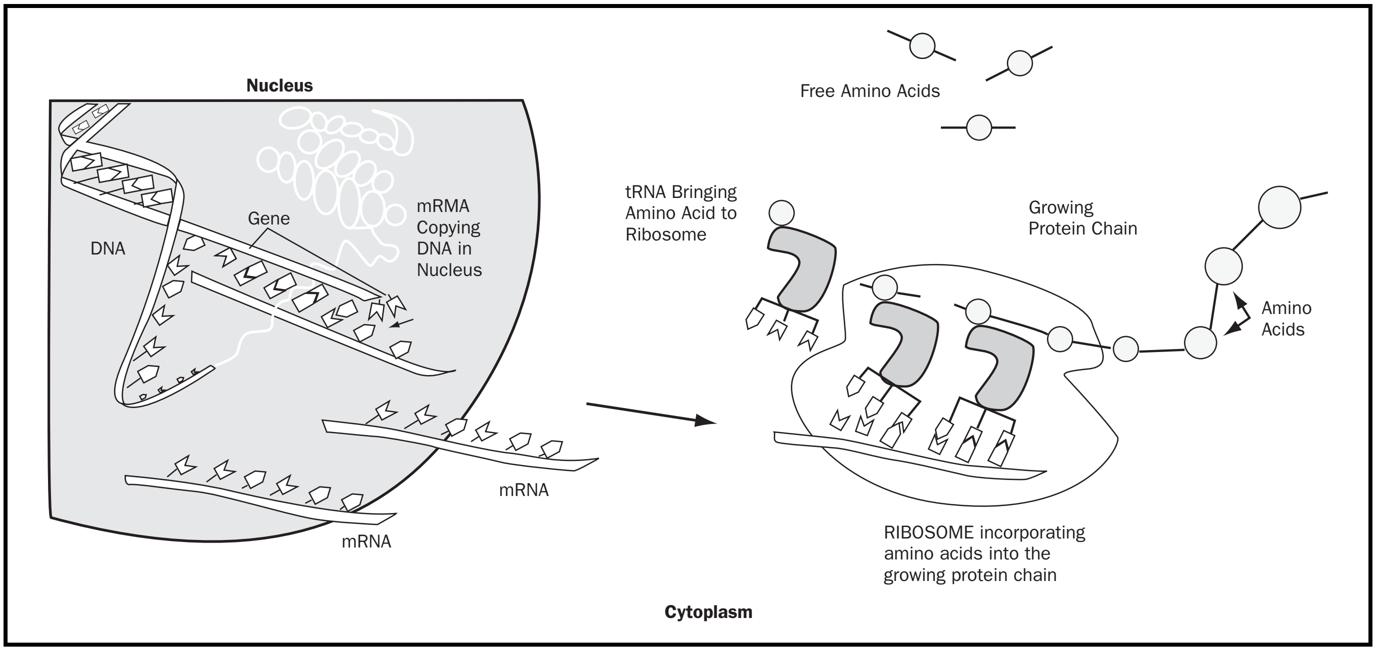

Figure 1. Protein synthesis requires transcription (shown on the left side of the figure) and translation (shown on the right side of the figure).

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

protein synthesis occurs in cellular structures called **ribosomes**, found outside the nucleus. The process by which genetic information is transferred from the nucleus to the ribosomes is called transcription. During transcription, a strand of ribonucleic acid (RNA) is synthesized. This messenger RNA (mRNA) is complementary to the portion of DNA that directed it—it has a complementary nucleotide at each point in the chain.

RNA polymerase: enzyme used to make RNA using DNA as a template

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

A specialized protein called an enzyme controls when transcription occurs. The enzyme called **RNA polymerase** is present in all cells; **eukaryotic cells** have three types of this enzyme. DNA has a section called the promoter region that identifies the sites where transcription starts and must be recognized by one subunit of the RNA polymerase called the sigma (σ) factor. Recognition between the promoter and the σ-factor helps to regulate how often a particular gene is transcribed. Once bound, the polymerase initiates the construction of mRNA (or other RNA molecules).

Initiation of the synthesis of a new RNA molecule does not always lead to a complete synthesis. After roughly ten nucleotides have been strung together, the continued addition of complementary base pairs takes place more readily in a process called elongation. The speed of addition of new nucleotides is remarkable—between twenty and fifty nucleotides per second can be added at body temperature.

uracil: heterocyclic, pyrimidine, amine base found in RNA

Eventually the elongation process must stop. There are certain sequences of nucleotides that stop elongation, a process called termination. Often, termination occurs when the newly formed section of RNA loops back on itself in a tight formation called a hairpin. Once the hairpin structure has formed, the last component is then a string of **uracil** residues.

After transcription has taken place, the mRNA produced is not necessarily ready to direct the subsequent protein synthesis. Depending on the type of cell, segments of nucleotides may be removed or appended before the actual synthesis process takes place. This type of post-transcriptional processing often occurs in human cells.

Translation

Once the mRNA has been synthesized, and perhaps modified, the next step of protein synthesis, translation, takes place. For this stage, additional forms of RNA are needed.

Transfer RNA (tRNA) plays the role of carrying an amino acid to the synthesis site at the ribosome. tRNA molecules are relatively small, with around seventy-five nucleotides in a single strand. They form several loops, one of which is an anti-codon, a three-residue series that is complementary to the codon present in the mRNA (Figure 2). The opposite end of the tRNA is where an amino acid is bound. The correct binding of an amino acid to a specific tRNA is every bit as important as the anti-codon in ensuring that the correct amino acid is incorporated in the **polypeptide** that is synthesized. There are different tRNA molecules for each of the twenty amino acids that are present in living systems; some amino acids have more than one tRNA that carry them to the synthesis site.

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

When translation begins, mRNA forms a complex with a ribosome to form an assembly site. This complex requires the assistance of proteins called initiation factors, so the existence of an mRNA does not mean that a protein will always be synthesized. The first tRNA that takes part in the initiation always carries the same amino acid, methionine. When the protein is completely synthesized, this initial methionine is often removed.

With the initial methionine in place, another tRNA with its amino acid joins the assembly site as dictated by the codon on the mRNA. With two amino acids present, a peptide bond can be formed and the polypeptide can begin forming. The new amino acid is added to the carbon end of the polypeptide (the C-terminus) with the peptide bond forming between the C-O of the polypeptide and the amine of the new amino acid. This structural specificity is enforced by the nature of the binding between the amino acid and the tRNA. The portion of the amino acid that is unbound in the tRNA complex is the amine.

Elongation ultimately requires the repetition of several steps: (1) The tRNA–amino acid complexes must be made. (2) This complex must bind to the mRNA-ribosome assembly site. The correct amino acid is assured by the matching of the anti-codon on the tRNA to the codon on the mRNA. (3) A peptide bond is formed between the new amino acid and the growing polypeptide chain. (4) The amino acid is **cleaved** from the tRNA, which can be cycled back to form another complex with an amino acid for a later synthesis. (5) The growing polypeptide forms a fiber-like tendril. (6) The ribosome essentially moves along the mRNA, reopening the initiation site for additional protein synthesis. In this way, proteins are synthesized by several ribosomes acting on the same mRNA molecule.

cleave: split

The structure of the ribosome plays an important role in this elongation process. There must be two sites available for synthesis to occur. One site, called the P site (for peptide), is where the growing (or nascent) polypeptide is located. Adjacent to this location is another site where the tRNA with

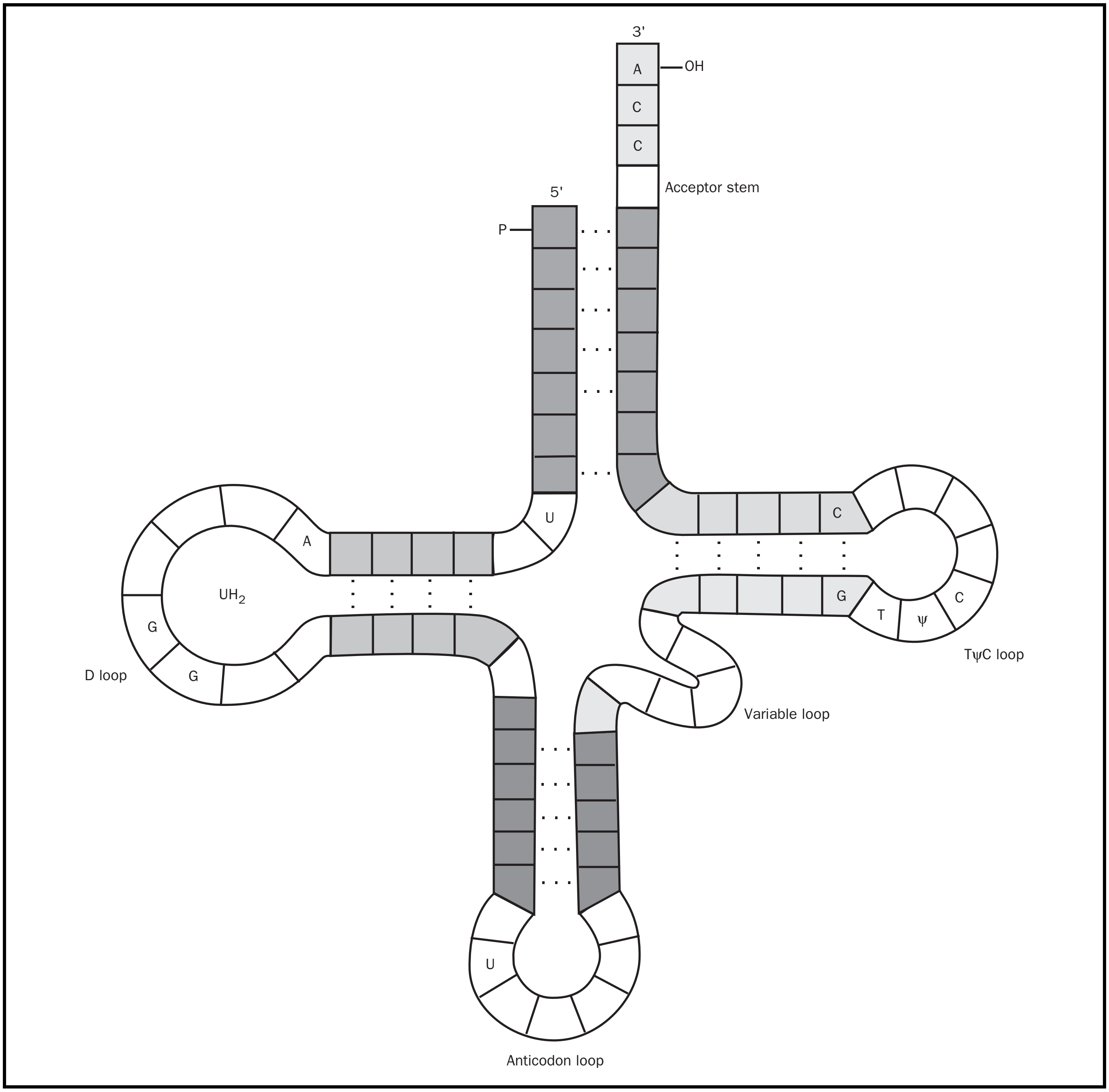

Figure 2. A tRNA molecule. tRNA carries amino acid to the synthesis site at the ribosome.

its new amino acid can bind. This site is called the A site (for the amino acid that is delivered there along with the tRNA).

As was the case in the elongation of mRNA noted earlier, somehow the emerging polypeptide must stop adding amino acids. The termination is actually part of the coding present in the codons. Three specific codons are known as stop codes, and when they are present in mRNA, the elongation is stopped.

Despite the overall complexity of this process, it occurs with remarkable accuracy. The rate of error is roughly one in every 10,000 amino acids.

Using the processes of transcription and translation, the body makes an amazing number and variety of proteins.

The transcription and translation processes provide the correct primary structure of the protein. The protein must fold to obtain the correct secondary and tertiary structures. Protein folding remains an active research area.

Medical Applications

Protein synthesis is critical to the growth of cells; medicines that work by killing cells often target this process. A majority of antibiotics work by disrupting the translation process. Tetracycline is an antibiotic that inhibits the binding of tRNA to the assembly site. **Streptomycin** works by causing the translation process to make more mistakes than usual—as high as one mistake for every 100 amino acids. Proteins with this many errors are not capable of performing their tasks, and the cells (in this case, bacteria) die. Streptomycin also inhibits the initiation of the synthesis process. SEE ALSO PEPTIDE BOND, PROTEINS.

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

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Protein Transcription *See* ***RNA Synthesis.***

Protein Translation

Protein translation is the process of synthesizing proteins from amino acids. This series of reactions translates the **code** provided to messenger ribonucleic acid or RNA (mRNA) by deoxyribonucleic acid or **DNA** into a sequence of amino acids that makes up the active protein molecule. Protein **synthesis** begins with a strand of mRNA synthesized in response to the genetic code located in a gene on a strand of DNA. The process of translation is slightly different in **eukaryotic cells** from that in **prokaryotic** cells; for the sake of simplicity, translation in prokaryotes will be discussed here.

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

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

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

Proteins are made up of combinations of the twenty common amino acids. Placement of each amino acid is specified by a three-nucleotide codon. Four different nucleotides are available to code; taken three at a time, they can form sixty-four combinations. Some amino acids have more than one codon (a phenomenon known as redundancy). Translation also requires a start codon and stop codon.

Four general actions comprise protein translation: The mRNA binds to a **ribosome**; amino acids are carried to the ribosome by transfer RNA (tRNA); the amino acids are joined, forming peptide bonds; and the completed protein molecule is released from the ribosome. The synthetic processes are called initiation, elongation, and termination and are assisted by protein factors essential for each step.

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

Adenosine triphosphate (ATP) provides energy for the attachment of amino acids by specific enzymes to tRNA. For reference, the ends of DNA and RNA strands are designated 5′ and 3′. Translation begins with attachment of the 5′-end of mRNA to the small unit of a ribosome. A tRNA molecule carrying formylmethionine attaches to the ribosome at a location matching the initiation codon (AUG) on mRNA. The large subunit of the ribosome then attaches to this complex, forming a complete, active ribosome. During periods of rapid translation, a number of ribosomes may cluster together with mRNA, forming polyribosomes. A second tRNA brings another amino acid to the ribosome, matching the codon on mRNA for the second amino acid. A peptide bond forms between the two amino acids, and the first tRNA is released.

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

Guanosine triphosphate (GTP) provides energy to move the growing peptide chain along as mRNA passes through the ribosome. As more amino acids are added, the **polypeptide** chain grows longer until the ribosome reaches the stop codon of mRNA.

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

When the growing peptide chain approaches the **carboxylic acid** end (at the stop codon on mRNA), protein termination factors help to disassemble the ribosome and release the completed protein chain. Protein translation is interrupted by antibiotics such as tetracycline or chloramphenicol that interfere with protein synthesis. SEE ALSO CODON; PROTEINS; PROTEIN SYNTHESIS; RIBONUCLEIC ACID.

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

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Protons *See Atomic Nucleus; Atomic Structure.*

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Quantum Chemistry

Quantum chemistry is the application of **quantum mechanical** principles and equations to the study of molecules. In order to understand matter at its most fundamental level, we must use quantum mechanical models and methods. There are two aspects of quantum mechanics that make it different from previous models of matter. The first is the concept of wave-particle duality; that is, the notion that we need to think of very small objects (such as electrons) as having characteristics of both particles and waves. Second, quantum mechanical models correctly predict that the energy of atoms and molecules is always quantized, meaning that they may have only specific amounts of energy. Quantum chemical theories allow us to explain the structure of the periodic table, and quantum chemical calculations allow us to accurately predict the structures of molecules and the **spectroscopic** behavior of atoms and molecules.

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

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

Background: Wave-Particle Duality for Light

Quantum mechanical ideas began with studies of the physics of light. By the late nineteenth century, virtually all scientists believed that light behaved as a wave. Although some earlier scientists, such as Isaac Newton in the seventeenth century, had thought of light as consisting of particles, the early nineteenth-century experiments of Thomas Young and Augustin Fresnel demonstrated that light has wavelike properties. In these experiments, light was passed through a pair of slits in a screen, and produced alternating light and dark regions (interference patterns) on a second screen. This phenomenon, known as diffraction, cannot be explained using a particle model for light. In the late nineteenth century, James Clerk Maxwell derived a set of equations based on the wave model for light, which beautifully explained most experimental results.

Despite this apparent certainty that light was a wave, Max Planck and Albert Einstein, at the beginning of the twentieth century, showed that some experiments required the use of a particle model for light, rather than a wave model. Since both models were necessary for an accurate description of all of the properties of light, scientists today use mathematical equations appropriate to both waves and particles in describing the properties of light.

Waves and particles are fundamentally different: a particle exists at a particular point in space, whereas a wave continues on for (sometimes) a great distance. It defies intuition to think that both of these models might describe the same thing. Nevertheless, an accurate description of light requires the use of both wave and particle ideas.

The Wave Nature of Matter

The success of wave-particle duality in describing the properties of light paved the way for using that same idea in describing matter. Experiments in the early twentieth century showed that the energy in atoms is quantized✷; that is, a given atom can have only specific amounts of energy. For hydrogen, the simplest of the atoms, an accurate formula for the possible energies had been experimentally determined but was unexplainable using any particle model for the atom. The best picture that the particle model could give, consistent with experiments on atoms, put the electron in a sort of "orbit" around the nucleus. Unfortunately, the particle model predicts that the electron should collide with the nucleus, releasing energy in the process. Obviously there was a need for a different model for the electron.

✷One example of quantization would be to think of your distance from the ground when standing on a ladder—your distance from the ground can only change one rung at a time.

In 1924 Louis de Broglie presented a theory for the hydrogen atom that modeled the electron as a wave. Calculations made for this model give the quantization of energy that is experimentally observed in this atom. De Broglie also postulated a general formula for obtaining the wavelength of a moving object. His formula, which is analogous to that used for light, states that the wavelength of a moving object is inversely proportional to its momentum (mass times velocity). When one uses de Broglie's formula to determine wavelengths of macroscopic objects, one discovers that the wavelengths of even the smallest objects visible to the naked eye are too small for the wavelike characteristics of these objects to be significant in any real situation. For the electron, however, the wavelength is large enough to be measurable. Diffraction experiments have been performed using electrons, demonstrating conclusively that they have wave properties.

It is contrary to our intuition that electrons might behave as waves. The repercussions of this notion are that the electron does not have a definite size, but is spread out over a region in space. We are more comfortable with the thought of the electron being a microscopic particle, moving around in an orbit near the nucleus of an atom. As with light, however, we do not abandon the particle model for electrons; rather, we employ mathematical equations arising from both particle and wave models. For quantum chemical calculations, the wave model turns out to be more useful.

The Heisenberg Uncertainty Principle

One consequence of the wave nature of matter is that the position and momentum of small objects are not well known, as they would be for a particle model. In some circumstances, a wave may be confined to a very narrow region in space; however, there is still some uncertainty as to its position. Additionally, the value of the momentum of a quantum object is often not known precisely. In 1927 Werner Heisenberg showed that the product of the uncertainty in position and the uncertainty in momentum is greater than or equal to a certain constant (Planck's constant divided by 4π). This constant is very small; accordingly, quantum mechanical uncertainty in position and momentum of objects that are large enough to see is not noticed experimentally. For electrons, however, quantum mechanical uncertainties in position and momentum are important considerations in interpreting both theoretical models and experimental results. The relationship between the uncertainties in position and momentum is known as the Heisenberg Uncertainty Principle. It tells us that the more we know about the position of a small object, such as an electron, the less we know about its momentum (and vice versa).

Calculating the Wavefunction

For a scientist, knowing that matter behaves as a wave is useful only if one knows something about that wave. The wavefunction is a mathematical function describing the wave. For example, $y(x) = A \sin(kx)$ might be the wavefunction for a one-dimensional wave, which exists along the x-axis. Matter waves are three-dimensional; the relevant wavefunction depends on the x, y, and z coordinates of the system being studied (and sometimes on time as well). We conventionally label the wavefunction for a three-dimensional object as $\psi(x, y, z)$. In 1926 Erwin Schrödinger introduced a mathematical equation whereby, if one knows the potential energy acting on an object, one can calculate the wavefunction for that object. Heisenberg had already introduced a mathematical formalism for performing quantum mechanics calculations, without explicitly including the concept of waves. It was later shown that, although the approaches of Schrödinger and Heisenberg looked very different, they made exactly the same predictions. In practice, the Schrödinger formalism is more useful for explaining the problem being studied, and the Heisenberg methodology allows for more straightforward computation. Accordingly, a mixture of the two approaches is typically used in modern quantum chemistry. Once we know the wavefunction of the atom or molecule under study, we can calculate the properties of that atom or molecule.

Quantum Mechanics of Atoms

An exact solution for Schrödinger's wave equation can be obtained for the hydrogen atom; however, for larger atoms and molecules (which contain more than one electron), Schrödinger's equation can be solved only approximately. Although this may sound so restrictive as to make the equation useless, there are well-established approaches that allow for practical and accurate calculations on atoms and molecules. This is done by making some assumptions about larger systems based upon the hydrogen atom, as explained below.

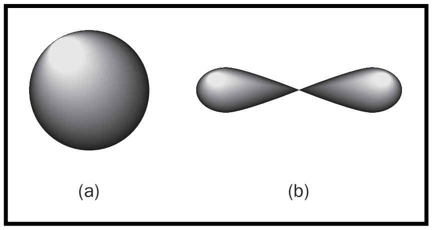

Figure 1.

When the Schrödinger equation is solved for the hydrogen atom, the resulting wavefunctions for the various possible energies that the atom can have are used to determine **atomic orbitals**. An orbital is a region in space where an electron is most likely to be found. For example, the lowest-energy wavefunction for a hydrogen atom is the so-called 1s orbital (see Figure 1), which is a spherical region in space surrounding the nucleus. For some higher-energy states, the orbitals are not necessarily spherical in shape (e.g., the 2p orbital pictured in Figure 1).

atomic orbital: mathematical description of the probability of finding an electron around an atom

For atoms larger than hydrogen, one assumes that the orbitals occupied by the electrons have the same shape as the hydrogen orbitals but are differing in size and energy. The energies corresponding to these orbitals may be found by solving an approximate version of Schrödinger's equation. These atomic orbitals, in turn, may be used as the building blocks to the electronic behavior in molecules, as we shall see below. As it happens, two electrons may share an atomic orbital; we say that these electrons are paired. Chemists have developed a system of rules for determining which orbitals are occupied in which atoms; calculations can then be done to determine the energies of the electrons in the atoms.

Quantum Mechanics of Molecules

Molecules are held together by **covalent bonds**. The simplest definition of a covalent bond is a shared pair of electrons. There are two basic approaches to modeling covalent bonds in molecules: the **valence** bond model and the molecular orbital model. In the valence bond model, we think of atomic orbitals on each of two atoms combining to form a bond orbital, with one electron from each atom occupying this orbital. Both the bond orbital and the electron pair now "belong" to both of the atoms. This sharing of electrons brings about a lowering in the energy, which makes the formation of molecules from atoms an energetically favorable process. The valence bond model gives the simplest quantum mechanical picture of chemical bonding, but it is not the best method for accurate calculations on molecules containing more than two atoms.

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

valence: combining capacity

Molecular orbital theory differs from valence bond theory in that it does not require the electrons involved in a bond to be localized between two of the atoms in a molecule. Instead, the electron occupies a molecular orbital, which may be spread out over the entire molecule. As in the valence bond approach, the molecular orbital is formed by adding up contributions from the atomic orbitals on the atoms that make up the molecule. This approach, which does not explicitly model bonds as existing between two atoms, is somewhat less appealing to the intuition than the valence bond approach. However, molecular orbital calculations typically yield better predictions of molecular structure and properties than valence bond methods. Accordingly, most commercially available quantum chemistry software packages rely on molecular orbital methods to perform calculations.

SCHRÖDINGER'S WAVE EQUATION

Schrödinger's Wave equation may be written (in abbreviated form) as:

$$\hat{E}_K\psi\,(x,\,y,\,z) + \hat{E}_P\psi\,(x,\,y,\,z) = \hat{E}\psi\,(x,\,y,\,z)$$

The first term, $\hat{E}_K\psi\,(x, y, z)$, represents the kinetic energy of the system being studied. The second term, $\hat{E}_P\psi\,(x, y, z)$, represents the potential energy of the system. E and $\psi(x, y, z)$ are the total energy of the system and wavefunction describing the system, respectively. Once the wavefunction is determined, virtually any property of the molecule may be calculated.

A lot of the modern research in quantum chemistry is focused on improving the valence bond and molecular orbital methods for calculating molecular properties. Different underlying approximations and different orbital functions are tried, and the results are compared with previous calculations and with experimental data to determine which methods give the best results. It is often the case that the best choice of quantum chemical method depends on the particular molecule or molecular property being studied. SEE ALSO Atomic Structure; Computational Chemistry; Molecular Structure; Theoretical Chemistry.

Wayne B. Bosma

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Quaternary Structure

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

hydrophobic: water repelling

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

electrostatic interaction: force that arises between electrically charged particles or regions of particles

Many proteins are made up of a single, continuous **polypeptide** chain and are thus called monomeric. Other proteins are composed of two or more polypeptide chains called subunits. The quaternary structure describes the arrangement and position of each of the subunits in a multiunit protein. The stabilizing forces that hold the polypeptide subunits together are the same forces that are responsible for tertiary structure stabilization. A major force stabilizing the quaternary structure is the **hydrophobic** interaction among **nonpolar** side chains at the contact regions of the subunits. Additional stabilizing forces include interactions between side chains of the subunits, including **electrostatic interactions** between ionic groups of opposite charge:

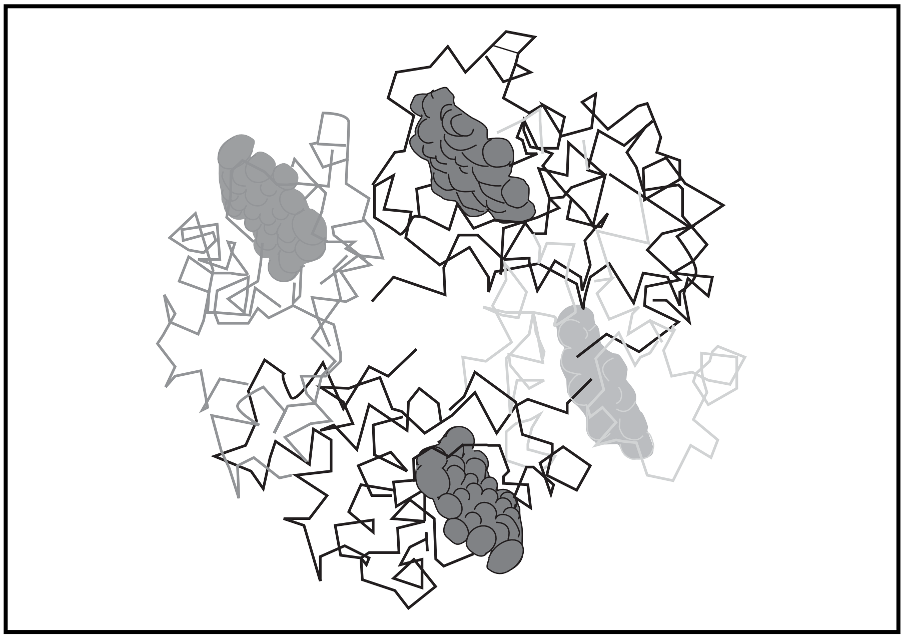

Figure 1. Hemoglobin.

hydrogen bonds between polar groups; and **disulfide bonds**. An example of a protein with quaternary structure is hemoglobin. Hemoglobin, an oxygen transport protein, is a tetrameric (four unit) protein consisting of two α and two **β subunits**. SEE ALSO Primary Structure; Proteins; Secondary Structure; Tertiary Structure.

Elizabeth S. Roberts-Kirchhoff

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

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

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 a, b, etc.

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Radiation

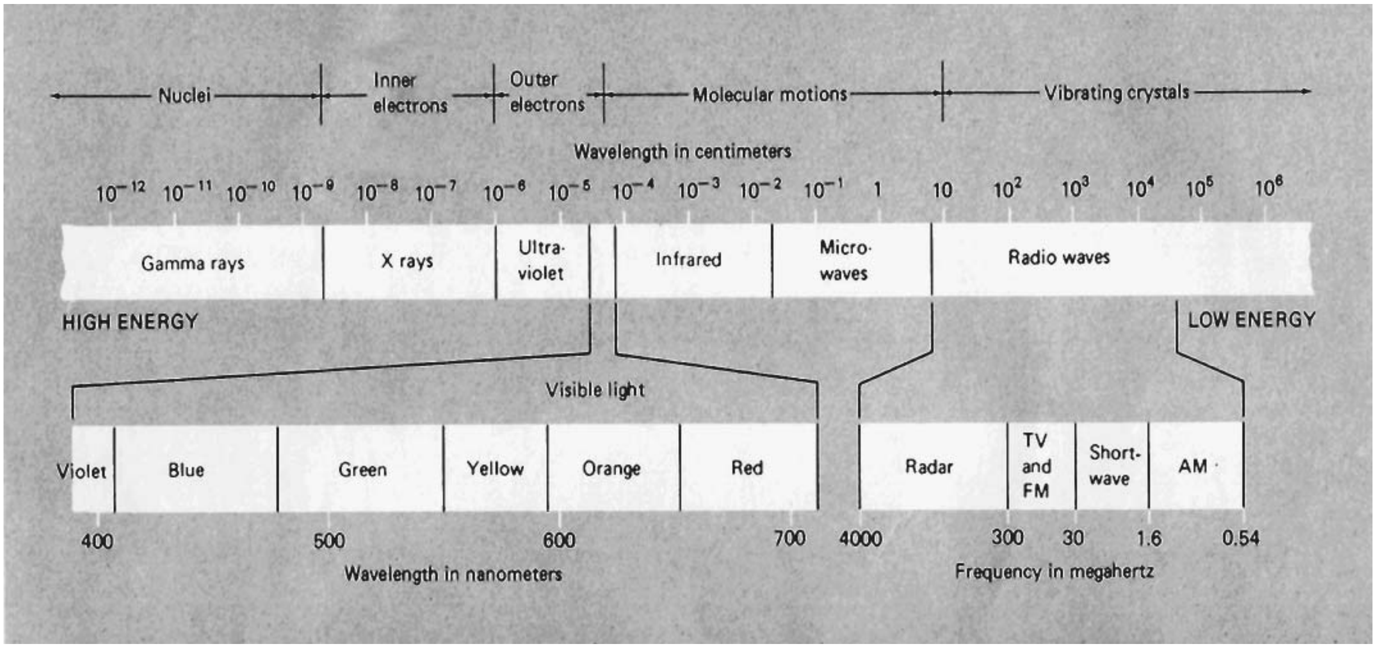
Radiation takes many forms, including both electromagnetic waves and subnuclear particles. The electromagnetic spectrum consists of light waves ranging in length from very short (10^{-16} meters, or 3.937×10^{-15} inches) to very long (10^{8} meters, or 621,400 miles). The product of the velocity of electromagnetic waves and their wavelength is a constant equal to the velocity of light, 3×10^{8} meters per second (m/s); therefore, as the length of waves increases, the frequency decreases. Thus, if the waves were 1 meter (3.3 feet) long, the frequency would be 3×10^{8} hertz (Hz) or 300,000,000/s (meaning 300,000,000 light waves would pass by each second). The electromagnetic spectrum consists of light waves ranging in length from very short γ (gamma) rays through x rays, ultraviolet (UV) rays, the spectrum of visible light, infrared (IR) rays, and microwaves, to very long radio and television waves.

Forms of Radiation

The shortest electromagnetic waves are classified as γ rays. One of the forms of energy emanating from natural sources of radioactivity here on Earth and also from energy sources in space, γ rays can be thought of as very short x rays. Discovered by the German physicist Wilhelm Conrad Röntgen in 1895, the remarkable penetrating effect of γ rays and x rays results from their very short wavelength (from about 10^{-12} to 10^{-8} meters, or 3.28×10^{-11} to 3.28×10^{-7} feet). The waves are so small that they can pass through many substances with little interaction. X rays pass through skin and organs with little effect but are diffracted somewhat when they pass through denser materials such as bone; the resulting pattern enables technicians to make x-ray images of bones and of the contents of packages in airport scanners.

The energy of electromagnetic radiation is directly proportional to the frequency. Since both x rays and γ rays have very high frequencies, they carry large amounts of energy, and high intensities of x rays and γ rays can damage many materials (including living tissue). The rays may be focused by special lenses and used to kill cancer cells or organisms that might cause disease or hasten spoilage in food.

Bonds between atoms in chemical compounds vibrate at characteristic frequencies. Some molecules possess bonds capable of absorbing electromagnetic



The electromagnetic spectrum, showing wavelengths and kinds of light.

energy, causing the bonds to bend, stretch, or vibrate and sometimes break. Certain bonds in particular (e.g., that between carbon and oxygen atoms) capture energy at specific frequencies of IR radiation, allowing technicians to use instruments called spectrophotometers to detect the presence of these bonds in chemical compounds. UV, visible, and IR **spectroscopy** are tools that permit chemists to readily identify and characterize small amounts of chemical substances.

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

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

Most animals, including humans, have visual **receptors** that detect light in the visible spectrum ranging from 400 nanometers (15.75×10^{-6} inches) for blue light to 700 (27.56×10^{-6} inches) for red light. (A nanometer equals 10^{-9} meters.) Just below the visible spectrum lies UV light, ranging in wavelength from about 10 to 400 nanometers (3.937×10^{-7} to 157.5×10^{-7} inches). UV light is more energetic than visible light; UV radiation in the sunlight can damage molecules in the skin and is the cause of sunburn. Green plants carry out **photosynthesis** by using **chlorophyll** molecules that readily capture light energy in the visible spectrum.

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

chlorophyll: active molecules in plants undergoing photosynthesis

Microwave radiation consists of electromagnetic waves somewhat longer than infrared waves (from about 10^{-3} meters, or 0.3937 inches, to 1 meter, or 39.37 inches, long) and having a lower frequency, ranging from about 1,000 to 300,000 megahertz (MHz). Waves in this range are readily absorbed by bonds in water molecules. Microwave ovens take advantage of the fact that foods usually contain large amounts of water, and dishes do not. The waves of IR or microwave radiation are usually too long to pass through the small holes in the doors of microwave ovens; thus, one can use a microwave oven to heat food without heating the dish or being harmed by the radiation. Magnetron tubes generate radiation that can be used for radar or for the microwave transmission of electronic signals.

An immense amount of radiation passes undetected through the environment. Our surroundings contain large amounts of radio waves, generally from one to thousands of meters long. X rays and γ rays also pass through us and the space around us with little effect. From time to time, fears have been raised concerning the electromagnetic radiation emanating from power lines, cathode ray terminals such as television sets and computer monitors, and the earphones of personal transistor radios or CD players, but there is little actual evidence of injury or illness from low intensity radiation. However, workers have been injured or killed by high intensity microwave radiation, and technicians working with radioactive materials must take special precautions.

Much radiation arrives on Earth from the Sun, and some of the energy of this radiation exists in the form of UV light. UV light waves can damage skin and would be much more hazardous were it not for the layer of ozone that exists in Earth's upper atmosphere. In a process known as the Chapman cycle, UV radiation splits oxygen molecules (O_2) in the **stratosphere** to form free oxygen atoms (O). Some of these atoms combine with oxygen molecules to form ozone molecules (O_3). The O_3 molecules are especially sensitive to UV radiation; the absorption of UV photons converts the ozone back into oxygen atoms and oxygen molecules:

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

$$O_2 \xrightarrow{UV} 2\ O \tag{1}$$

$$O + O_2 \longrightarrow O_3$$

$$O_3 \xrightarrow{UV} O_2 + O$$

In recent years the amount of O_3 in the stratosphere over the South Pole has decreased periodically, resulting in an ozone "hole" in the atmosphere. The decrease is most pronounced during the summer months of the Southern Hemisphere. If the amount of ozone continues to decrease, more UV light will reach the surface of Earth, probably causing some skin damage and increasing the incidence of cancer. Chlorine atoms react with and destroy ozone:

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{2}$$

Increasing atmospheric amounts of chlorine atoms or free radicals probably result in the destruction of ozone; the source of the chlorine atoms is thought to be synthetic substances known as **chlorofluorocarbons (CFCs)**. Some CFCs may be released from air-conditioning equipment or aerosol spray cans, and some may result from the production of plastic foams. Several international agreements, including the Montréal Protocol of 1987 and the Copenhagen amendment of 1992, have been established to limit the production of CFCs.

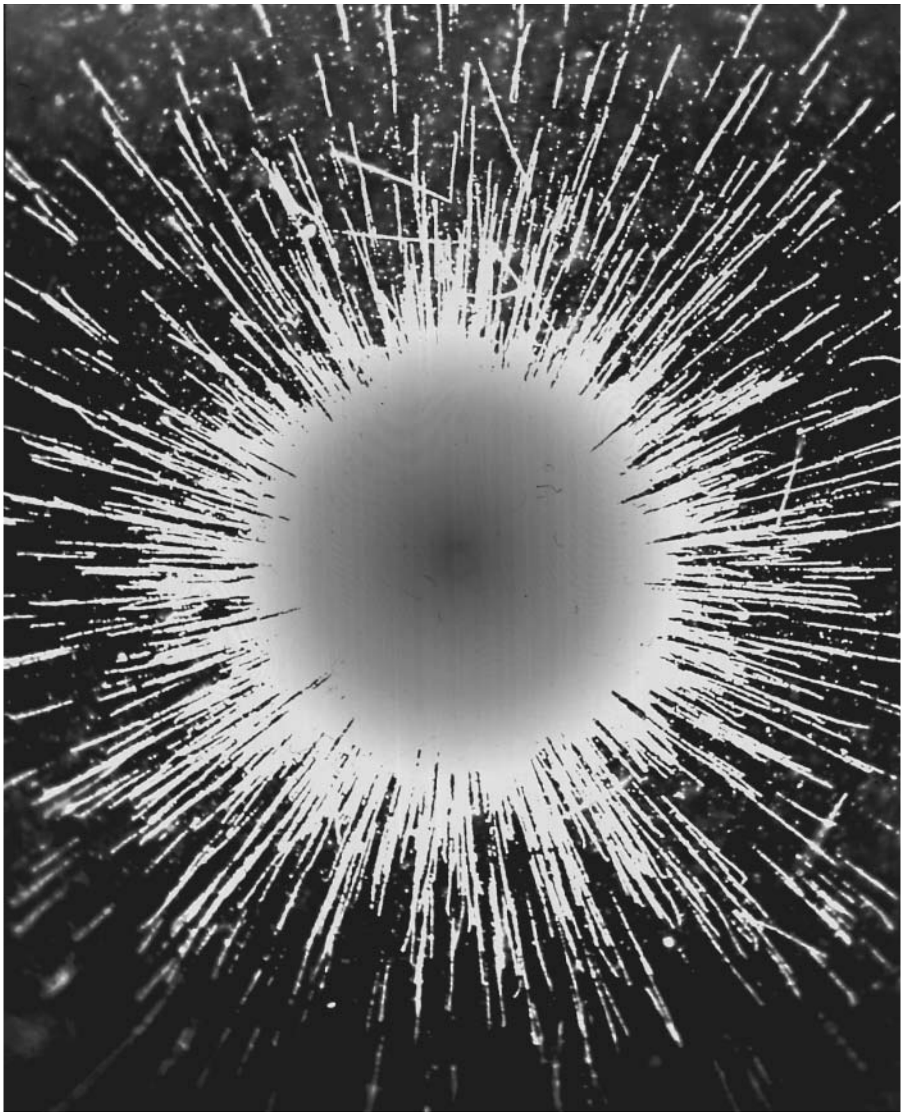
chlorofluorocarbon (CFC): compound that contains carbon, chlorine, and fluorine atoms, which remove ozone in the upper atmosphere

Radioactivity

Although many forms of electromagnetic radiation exist, special consideration is often given to radiation from unstable (radioactive) atomic nuclei. This radiation is usually one of three types, α- and β-particles or γ rays, but some nuclear reactions may also result in the emission of neutrons. **α-particles** are relatively large and highly charged particles identical with the nuclei of helium atoms. Each has a mass of four **atomic mass units** (AMU) and a charge of +2. Radioactive ores containing sources of α-particles often produce helium gas as a result of the capture of electrons by the

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

atomic mass units: a unit of mass used to indicate the relative mass of an atom; abbreviated as AMU, and equal to 1.674×10^{-24}g



The radioactive emission of alpha particles from radium, captured on photographic film.

α-particles. β-particles are high-speed electrons, having a mass of about 1/1,800 amu and a charge of -1. γ rays are similar to x rays.

X rays, γ rays, and neutron beams are considered ionizing radiation. Ionizing radiation may break molecules into pieces, creating ionic free radicals that can be very damaging to tissue. Contaminated food or dust containing radionuclides that emit α- and β-particles may be very dangerous if the sources of radiation are ingested. Strontium-90 (^{90}Sr) present in fallout from nuclear weapons testing may be absorbed from soil, incorporated in plant tissues, eaten by cows, and eventually find its way into milk. Strontium is chemically similar to calcium. The ^{90}Sr may then be absorbed from the digestive tract and deposited in bone, where α-particles released by radionuclide decay damage the blood-producing reactions in bone marrow.

Several methods are used to detect radiation; the earliest of these, also discovered by Röntgen, is exposure of photographic film. Since x rays can pass through solid materials, they expose photographic film sealed in lightproof envelopes. Workers in industrial settings today often wear film badges that contain a sheet of photographic film inside a plastic container fitted with aluminum and lead shields. In order to determine the amount and type of radiation exposure, the badges are collected periodically and the film developed. Darkening of the film indicates exposure. Workers may also wear dosimeters, pencil-like tubes that are examined daily for exposure. For large-scale operations or as survey monitors at factory gates, Geiger-Mueller counters are utilized. These devices detect radiation by using a tube consisting of a metal can containing a charged wire. The tube is sealed with a thin plastic or mica window. Radiation penetrating the can or window ionizes molecules of gas inside the tube, and the ions allow an electrical discharge, which can be detected and registered by an electrical circuit. Civil defense and military personnel often carry Geiger counters to survey large areas for contamination by radioactivity.

Uses of Radiation

Radiation is a versatile tool for the diagnosis and treatment of disease, as well as a means of industrial testing and treating foods to avoid spoilage. Many common metabolic substances can be labeled by replacing atoms such as carbon or hydrogen with radioactive atoms such as ^{14}C or ^{3}H. The resulting molecules are absorbed by the body and react in the same way as nonradioactive molecules, but the decay of the radioisotope releases tiny amounts of radioactivity that can be detected with sensitive instruments. Some compounds are absorbed more rapidly by diseased tissue (a cancerous organ, for example, might rapidly absorb **glucose** from blood), and the use of substances such as radioactive iodine can help diagnose tumors of the thyroid gland without invasive surgery. Some diseases such as cancer can be treated by administering a preparation containing radionuclides within molecules that are taken up by an organ and release their radioactivity within the diseased tissue.

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

Cells that are growing and dividing rapidly are the most sensitive to radiation. In the human body, these include gonadal tissue, hair follicles, the immune system, bone marrow, **intestinal epithelium**, and cancer cells. Cancer may be treated by external beam radiation, using γ-type radiation to deliver energy to abnormal cells, in the hope of killing them. Normal tissues are protected by lead shielding, and also by rotating the radiation source, passing the beam of γ rays through a larger range of tissue, and avoiding the intense irradiation of nontumorous tissues. In some cases, malignant cells can be treated with brachytherapy, the implantation of tiny metallic seeds containing radioisotopes that emit small amounts of radiation, killing the cancer from the inside. Radioisotopes decay at a known rate; often a nuclide that decays rapidly may be chosen, allowing the patient to be radiation-free upon discharge.

intestinal epithelium: layer of cells in the intestines that allows the passage of water and solutes

Gamma radiation is widely used in manufacturing to make images of welds in pipes. A recent application of radiation in the food industry involves the use of radiation (usually either γ rays or high-energy beams of electrons) to irradiate food, killing organisms that cause spoilage. The irradiation of food presents several advantages: foodstuffs may last weeks longer with little refrigeration; the use of dangerous chemical preservatives can be avoided; and foods may be prepared, wrapped, and preserved with less contact by human workers, lessening the chances of spreading disease-producing organisms.

In recent years, especially virulent and damaging strains of *Escherichia coli* have caused outbreaks of illness among persons who consumed contaminated hamburger, and some cases of salmonella poisoning have been associated with the consumption of poultry products. Food irradiation may help to make such foods much safer.

Our environment contains many sources of radiation, such as cosmic rays that constantly bombard Earth. The atmosphere filters out some cosmic rays, so exposure is greater at higher altitudes than at sea level. Radiation sources also include smoke detectors, luminous watch dials, television and computer monitors, and medical x rays. We are exposed daily to electromagnetic radiation in the form of radio waves as well as α- and β-particles and γ rays emanating from radioactive carbon, hydrogen, and potassium, which are part of all living things. A small amount of radiation is probably harmless and may, in fact, be helpful. Radon in our homes is a potential cause of cancer. Although radon is a colorless, odorless gas, it decays to more chemically reactive and radioactive products that may bind in lung tissue. Like many dangerous gases, radon is much more hazardous in the presence of particulate matter such as the tiny particles present in cigarette smoke. SEE ALSO PHOTOSYNTHESIS; RADIOACTIVITY; RÖNTGEN, WILHELM.

Dan M. Sullivan

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Radition Exposure

All matter is potentially damaged when exposed to radiation. This article examines radiation exposure to living systems. Radiation exposure occurs when the energy associated with radiation is deposited in a living organism, which is said to "receive a radiation dose." In the United States, radiation doses are measured in "rems" or "millirems" (mrems); "rem" stands for *r*adiation *e*quivalent *m*an. The international unit of radiation is the Grey, and 100 rem = 1 Grey.

Natural Radioactivity

Radioactivity is a natural and spontaneous process that occurs when unstable atoms of an element emit or radiate excess energy in the form of particles or waves. Such emissions are called ionizing radiation. Ionization, the process by which molecules lose electrons, is a particular characteristic of the radiation produced when radioactive elements decay. The capacity of radioactive emissions to cause ionization of molecules is the basis for health hazards and provides the means by which radiation can be detected.

Low levels of radioactivity are commonly found in the air, the rocks, and the soil, in the water and oceans, and even in our building materials. Several important radioactive nuclides occur naturally, such as carbon-14 (C-14) and potassium-40 (K-40). These **isotopes** are generated by cosmic ray interactions and make their way into the food chain. Once ingested, they can decay and deposit an internal dose of radioactivity, however mild. Carbon-14 is a particularly useful isotope. All living organic material has a constant natural ratio of carbon-14 to nonradioactive carbon-12. Once an organism dies, the remaining organic material is no longer involved in the cycle of absorbing carbon and moving the carbon along the living metabolic chain. For example, plants absorb CO_2 and during their life processes produce a variety of carbohydrates $(C_6H_{12}O_6)_x$. As long as the plant lives, all of the carbon in the plant is in the naturally occurring ratio and is in equilibrium with the natural ratio of carbon-14 to carbon-12 in the atmosphere. When the plant dies, that ratio in the dead plant starts changing because the carbon-14 decays, whereas the carbon-12 does not. By measuring that ratio of C-14 to C-12 in the dead plant, the approximate date of death can be determined. This process of establishing the date of the death of a living organism is called “carbon dating.” Potassium-40 is naturally found in the soil and taken up by plants such as bananas. This fruit with the incorporated K-40 then becomes part of a food chain cycle.

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

Radiation in small doses, usually below 10 rem, generally does not have demonstrable biological effects. And there are suggestions that small doses may provide a health benefit in the form of radiation hormesis. Hormesis is a modification of the word hormone that describes stimulation induced at low doses of agents that are harmful or even lethal at high doses. Generally, hormesis is any stimulatory or beneficial effect, induced by low doses of an agent that cannot be predicted by the extrapolation of detrimental or lethal effects induced by high doses of the same agent.

Large doses of radiation, at the level of several hundred rems, may cause serious injury if received in a short time period (days or hours). This condition is called “acute radiation syndrome.” Much larger doses can cause death. Doses between the large doses and small doses increase the risk of cancer.

Types of Radiation

Common types of ionizing radiation are alpha (α), beta (β), neutron, x-ray, and gamma (γ) radiation. Radioactive elements are often called radioactive isotopes or “radionuclides.” An alpha particle consists of 2 protons and 2 neutrons; since there are no electrons in the alpha particle, it carries a charge of +2. Beta particles are electrons and carry a −1 charge. Both are referred to as “charged particles.” Neutrons carry no charge. Gamma and x rays have neither mass nor charge. They are electromagnetic waves and are sometimes referred to as “photons.” Cosmic radiation is divided into two types: primary and secondary. Primary cosmic radiation consists of high-energy particles, such as protons, that come from the Sun or other sources outside our solar system. The Sun-derived cosmic radiation is produced during solar flares. Only a small fraction of the primary cosmic radiation penetrates to Earth's surface; most interacts with the atmosphere, producing the secondary cosmic radiation, which produces other lower-energy radiation in the form of photons, electrons, neutrons, and muons that eventually reach the surface.

Earth's atmosphere and magnetic field act as shields against cosmic radiation, reducing the amount that reaches Earth's surface. The average radiation dose from cosmic radiation in the United States is 27 mrem per year. This dose roughly doubles with every increase of 6,000 feet of elevation. Traveling at high altitudes in an airplane increases exposure to cosmic radiation. A typical exposure obtained from flying in a commercial jet across the United States (coast to coast) provides a radiation dose of approximately 0.5 rem for each hour traveled.

Cosmic radiation can cause genetic changes. Some scientists believe that this radiation has been important in driving the development of life on our planet. While cosmic radiation can cause some damage to individuals, it also may have played an important role in the development of humans.

Earth's atmosphere is a natural shield against the harmful effects of primary cosmic radiation. If humans were to leave Earth and travel to some distant planet, exposure to high levels of primary radiation is a serious potential risk. Future space travelers will have to be shielded from exposure to cosmic rays. SEE ALSO RADIATION; RADIOACTIVITY.

John Pickering

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Radioactivity

In 1896 Henri Bequerel, a French physicist, was studying the fluorescence of uranium compounds. He placed crystals of potassium uranyl sulfate on top of photographic film wrapped in dark paper and exposed the crystals to sunlight. Bequerel interpreted darkening of the film to be the result of penetration of the paper by the fluorescence of the uranium. A second experiment on this uranyl fluorescence was delayed for some days due to cloudy, wintry weather in Paris, leading Bequerel to decide to repeat the experiment, using new film. However, he developed the earlier film, expecting to see little, if any, darkening. To his surprise the film was as dark as if sunlight had been striking the uranium throughout the whole cloudy period. He concluded that uranium was spontaneously emitting high-energy rays that caused the observed darkening of the photographic plate and asked Madame Marie Curie, a research assistant in his laboratory, to join him in further studies of this new phenomenon. Curie named the spontaneous, high-energy radiation "radioactivity."

By 1898 Madame Curie and her husband Pierre, in collaboration with Bequerel, had isolated two new elements from the **radioactive decay** of uranium in pitchblende ore. Both were more radioactive than uranium itself. They named the first element polonium (Po) after Madame Curie's native land (Poland), and the second was named radium (Ra). Isolation of these two elements required chemical separation of very small amounts of Po and Ra from tons of pitchblende. Radium was found to be over 300,000 times more radioactive than uranium.

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

The French experiments attracted the attention of Ernest Rutherford, a physicist at the University of Manchester in England. Using an electrical field, Rutherford demonstrated that the radiation emitted from a radioactive sample could be separated into three types of rays, which he named alpha, beta, and gamma rays. The α rays (alpha rays) were positively charged, as they were deflected strongly to the negative side, whereas the negative β rays (beta rays) were deflected to the positive side. The γ rays (gamma rays) were not deflected and are uncharged high-energy electromagnetic radiation, similar to x rays and light rays. Gamma rays are the result of rearrangements of neutrons and protons in nuclei that yield lower-energy states and usually accompany other forms of radioactive decay.

Emission of an **α-particle** produces a new nucleus with a reduction in **atomic number** by two and in mass number by four. When a nucleus emits a β-particle, the atomic number of the new nucleus increases by one (over that of the decaying nucleus), but the mass numbers are unchanged. Some radioactive nuclei do not increase in atomic number in decay, but decrease by one unit of mass number due to the emission of a positron (a positively charged β ray). For example, in β decay with electron emission, ${}^{14}_{6}\mathrm{C}$ is converted to ${}^{14}_{7}\mathrm{N}$, whereas in positron β decay, ${}^{22}_{11}\mathrm{Na}$ is converted to ${}^{22}_{10}\mathrm{Na}$. An alternative process to β decay involves the absorption of an orbital electron by the nucleus in a process known as electron capture, which results in a decrease in the atomic number of the product nucleus, for example, ${}^{195}\mathrm{Au}$ decaying to ${}^{195}\mathrm{Pt}$. Gamma-ray decay results in no change in either mass number or atomic number.

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

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

fission: process of splitting an atom into smaller pieces

Another type of radioactive decay that is observed in the heaviest elements is spontaneous **fission**. In this process, a nucleus splits into two roughly equal parts, simultaneously releasing a large amount of energy. For example, for the nuclide ${}^{252}_{98}\mathrm{Cf}$, of every 100 nuclei that decay, approximately 97 do so by α decay and 3 undergo spontaneous fission.

The rate of radioactive decay is directly proportional to the amount of radioactive species present. A radioactive nucleus is characterized by its half-life, which is the amount of time it takes for 50 percent of the atoms present initially to decay. The half-life of ${}^{131}\mathrm{I}$ is eight days: an original sample of 1 gram (0.035 ounces) of ${}^{131}\mathrm{I}$ after eight days has only 0.5 grams (0.018 ounces) remaining; after sixteen days, only 0.25 grams (0.0088 ounces), and so on. The half-life is unaffected by differences in temperature, pressure, or chemical state. This constancy has made study of the half-lives of radioactive nuclei very useful to scientists engaged in dating archaeological and geological materials.

Since the discovery of radioactivity, radioactive nuclei serving as "tracers" have been of immense value to science, agriculture, medicine, and industry.

HANS GEIGER (1882–1945)

Hans Geiger worked in Ernest Rutherford's laboratory manually and meticulously counting **α-particle** scintillations for the famous experiments that led to the discovery of the nucleus. Because of this work, he developed an α-particle detector. After World War I, Geiger developed the modern Geiger–Mueller counter and worked until his death to increase its speed and sensitivity.

—Valerie Borek

These radiologists are measuring radioactivity levels in the soil near the Chernobyl nuclear plant, Ukraine.

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

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

chlorophyll: active molecules in plants undergoing photosynthesis

synthesis: combination of starting materials to form a desired product

In the use of radioactive tracers it is assumed that the radioactive **isotopes** studied are identical in chemical behavior to the nonradioactive isotopes. The first experiments that used radioactive tracers were carried out in 1913 in Germany and were designed to measure the solubility of lead salts via the use of a radioactive isotope of lead. In industry, radionuclides have been used for analytical purposes, for measurements of flow in pipes, and as part of many other applications. Another example of an important tracer study has been the investigation of **photosynthesis** of carbohydrates from atmospheric CO_2 in the presence of light and **chlorophyll**. Scientists used $^{14}_{6}C$, $^{32}_{15}P$, and $^{3}_{1}H$ to identify the intermediate steps involved in the photosynthesis of carbohydrates in plants that had been placed in an atmosphere composed of $^{14}_{6}C$-labeled CO_2 and had been irradiated with light. The presence of the radioactive carbon in the synthesized carbohydrate was evidence that O_2 was involved in the **synthesis**.

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

The process of **neutron activation analysis**, in which radioactivity is induced in stable nuclei by their bombardment with neutrons, has allowed measurement of impurities on the level of less than one part per billion. Neutron activation analysis has been used in determining the authenticity of paintings, in criminology, in analyzing lunar soil, and in many other areas.

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

The largest single use of radionuclides has been in medical science. If a radioactive compound, such as a radioactively labeled amino acid, **vitamin**, or drug, is administered to a patient, the substance is incorporated in different organs to varying degrees. The substance undergoes chemical change within the body, and the movement of the radioactive atoms in the body can be followed with radiation detectors. Such information is of great diagnostic value toward identifying the presence of tumors and other diseases in different organs in the body. Radioactivity has also been used in medicine for therapeutic purposes (radiotherapy); for example, it attacks cancerous cells more efficiently than normal cells. SEE ALSO Nuclear Fission; Nuclear Medicine; Transactinides; Transmutation.

Gregory R. Choppin

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Radium

MELTING POINT: **700°C**
BOILING POINT: **1,140°C**
DENSITY: **5.00 g/cm^3**
MOST COMMON IONS: **Ra^{2+}**

88
Ra
RADIUM
226.03

Radium is the last of the alkaline earth **metals** comprising the second column of the Periodic Table. While there are twenty-five known **isotopes** of radium (only four of which are found naturally), all of them are radioactive. Of these isotopes, radium-226 is the most common, with a half-life of about 1,600 years.

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

Radium was first isolated in 1898 by Marie Sklodowska Curie and her husband, Pierre Curie. They were studying the radioactivity of pitchblende, a uranium-rich ore, and noticed that the ore was still radioactive with all the uranium removed. After years of painstaking work, the Curies eventually isolated radium and named it for the Latin word *radius*, meaning "ray." For this work, Madame Curie was awarded the Nobel Prize in Chemistry in 1911, her second such honor (the first one, in physics, shared with her husband and Henri Becquerel in 1903 for their initial studies of radioactivity).

Radium is rare in nature, being only the eighty-fifth most abundant element in Earth's crust. When the Curies and their assistant, Gustave Bemont, first isolated radium, they had to reduce many tons of pitchblende ore to obtain only a few grams of the element. As a metal, radium has a silvery white color and is luminous due to its inherent radioactivity. In the past, radium salts were mixed with phosphorescent zinc sulfide into a paint that was placed on the faces of some clocks and watches so that they could be seen at night. However, the workers who painted the clocks suffered and often died of radiation poisoning and cancer, and so the practice was ended. These days, the uses for radium are as rare as the element itself, with annual world production totaling less than 1 kilogram (2.2 pounds). SEE ALSO Curie, Marie Sklodowska.

David A. Dobberpuhl

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86
Rn
RADON
222

Radon

MELTING POINT: −71°C
BOILING POINT: −61.8°C
DENSITY: 9.73 g/cm^3
MOST COMMON IONS: None

Radon is a member of the **noble gas** family and was the first radioactive gas to be discovered. It is colorless, odorless, and chemically **inert** (like the other noble gases), but it is a highly radioactive **α-particle** emitter.

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

inert: incapable of reacting with another substance

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

Radon was discovered in 1899 by the McGill University professors Ernest Rutherford and Robert Owens, who found that radioactive thorium produced radioactive gas. They named this gaseous substance thorium emanation, later to become thoron. It was found that radium gave off a similar emanation (radon), as did actinium (actinon), in 1900 and 1904, respectively. Once the structure of the atom and the elemental transmutation process became better understood, it was determined that thoron, radon, and actinon were different **isotopes** of the same element (radon)—^{220}Rn, ^{222}Rn, and ^{219}Rn, respectively.

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

Radon has a tiny natural abundance as the product of uranium and thorium decay; it has a background concentration of 6 × 10^{-14} parts per million by volume in air. Because radon is a short-lived α-emitter, the **synthesis** of compounds that contain radon has been limited to just fluorides and oxides. Radon saw considerable therapeutic use between 1920 and 1950 in the irradiation of tumors, but its modern usages stem from its being an easily detected radioactive gas. It is used to trace gas flow and air movement, and

synthesis: combination of starting materials to form a desired product

Radon is radioactive and is responsible for 10 percent of all lung cancer deaths. Many homes are equipped with radon detectors, such as the one at the far left in this photograph.

its presence below Earth's surface can yield information about tectonic movement, earthquake potential, and mineral deposits.

During the 1980s it became recognized that there was widespread contamination of households by radon, which is now estimated to cause 10 percent of all lung-cancer deaths. The primary source of household radon is surrounding bedrock rich in uranium and also present in a permeable matrix that permits diffusive and convective transport of the radon isotopes derived from the uranium. The U.S. Environmental Protection Agency encourages corrective action when household radon levels surpass 4 picoCuries per liter, yet in some parts of the country more than 40 percent of the residences exceed this value. SEE ALSO Noble Gases.

Laurence E. Welch

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Raman, Chandrasekhara

INDIAN PHYSICIST
1888–1970

Chandrasekhara Venkata Raman described himself as a "child of nature"; he was indeed a profound student of nature all his life, a keen and resourceful observer of the world around him. In addition to discovering the physical effect that bears his name, he can also be considered the father of modern Indian experimental science.

Raman was born near Trichinopoly (now Tiruchipalli) in southern India on November 7, 1888. His father, whose family had been farmers in the area for many generations, turned to teaching and became a lecturer in physics and mathematics at a small college in Vizagapatam when Raman was four years old. During Chandrasekhara's childhood, his father conveyed to him not only an interest in science but also a love of music. He attended Presidency College at the University of Madras, where he excelled in science and graduated in 1904 at the age of sixteen. Although his teachers urged him to go to England for graduate study, he was prevented from doing so for health reasons and remained at Presidency College to work on his master's, which he obtained in 1907. During this time Raman began his longtime interest in optical phenomena, publishing a paper in the *Philosophical Magazine* on the diffraction patterns of reflected light. At that time, modern scientific research was practically unknown in India, especially from someone who had not attended school outside the country.

Since there was scarce opportunity for Raman to pursue a scientific career when he graduated, he entered the civil service, becoming an accountant in the Indian Finance Department. During his ten years of service in this capacity, spent mostly in Calcutta, he continued to conduct scientific research under the auspices of the Indian Association for the Cultivation of Science, a small, privately endowed organization. Using simple and inexpensive equipment, and working outside his regular office hours, Raman published thirty papers in ten years, mostly in the area of sound. His work attracted the attention of the officers of the University of Calcutta, and in 1917 he was offered a professorship in physics, becoming the first Indian-educated scientist to hold such a post. He was then able to pursue his research more actively and to supervise graduate students.

While traveling to England in 1921 to attend a scientific congress, Raman was struck by the blue color of the Mediterranean Sea, caused by the scattering of sunlight in the clear water. This observation prompted the studies that culminated in his discovery of the characteristic changes in wavelength of scattered light caused by certain materials—the so-called Raman effect. Although previously predicted by others as a consequence of the interaction of light **quanta** with molecules, the actual effect was very weak and required long and careful measurements to establish. It represented a significant advance in chemical analysis, since at that time, other **spectroscopic** methods such as infrared spectroscopy were difficult and inexact without expensive instrumentation. On the contrary, only relatively simple equipment was necessary to observe the shifts in wavelength (the "Raman shifts") exhibited by a wide variety of chemical substances. Raman was knighted for this work in 1929 and received the Nobel Prize in physics in 1930, becoming the first Asian to receive the award.

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

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

Raman left Calcutta in 1933 to become the director of the Indian Institute of Science, in Bangalore, where he remained until 1948. He continued his research on optical and electromechanical phenomena but also worked on a wide range of problems that reflected his fascination with the natural world—diamonds, seashells, and the coloration of flowers and feathers. In 1948 he established the Raman Research Institute in Bangalore, where he continued to carry out research until almost the end of his life. He died on November 21, 1970. SEE ALSO SPECTROSCOPY.

Bartow Culp

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Ramsay, William

SCOTTISH CHEMIST
1852–1916

William Ramsay, the only child of civil engineer and businessman William Ramsay and his wife Catherine, was born on October 2, 1852, in Glasgow, Scotland. Despite the scientific background of his family, he was expected to study for the ministry. He completed his secondary education at the Glasgow Academy and in 1866 entered the University of Glasgow, where he pursued a standard course of study in the classics. He became interested in chemistry when he read about gunpowder manufacture in a textbook, and he began attending lectures on chemistry and physics as a result. Starting in 1869, he also worked as a chemical apprentice to Glasgow City Analyst Robert Tatlock.

From April 1871 to August 1872, Ramsay worked on toluic and **nitrotoluic acids** under Rudolf Fittig at the University of Tübingen; these research efforts earned him a Ph.D. at the age of nineteen. In 1872 he became an assistant in chemistry at the Anderson College (now the Royal Technical College) in Glasgow and in 1874 a tutorial assistant at the University of Glasgow. He was appointed a professor of chemistry at University College, Bristol, in 1880. In 1887 he became a professor of inorganic chemistry at University College, London, where he remained until his retirement in 1913.

Scottish chemist Sir William Ramsay, recipient of the 1904 Nobel Prize in chemistry, "in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system."

nitrotoluic acid: benzoic acid molecule with methyl and nitro groups attached

Ramsay was a scientist of exceptionally wide interests and talents. His earliest works centered on organic chemistry. Beginning in the 1880s, he pursued topics related to physical chemistry, such as stoichiometry, thermodynamics, surface tension, density, molecular weights, and the critical states of liquids and vapors. However, his most important achievements involved inorganic chemistry.

In 1785 English chemist Henry Cavendish suggested that, in addition to nitrogen, oxygen, carbon dioxide, and water vapor, air might contain another gas. In 1892 Lord Rayleigh (John William Strutt) found that nitrogen prepared from ammonia (NH_3) was less dense than nitrogen prepared from air. He reported his results in the journal *Nature* and asked readers to suggest an explanation for the discrepancy, which was beyond experimental error. At an 1894 meeting of the **Royal Society**, Lord Rayleigh posited that chemically prepared nitrogen might be contaminated with a less dense gas.

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

Ramsay believed that, on the contrary, atmospheric nitrogen might contain a denser gas. In large-scale experiments he passed atmospheric nitrogen over hot magnesium, which reacted to form solid magnesium nitride (Mg_3N_2) and left behind a small amount of unreactive gas. When he analyzed the gas spectroscopically, he observed, in addition to the lines of nitrogen, lines of a gas at that point still unknown. Simultaneously, Rayleigh repeated Cavendish's experiments and confirmed the presence of an unknown gas (1/107 of the original volume).

On August 13, 1894, Rayleigh and Ramsay announced their discovery of a new element in the atmosphere to the British Association at Oxford. Because of its unreactivity, they later called the gas argon, from the Greek word meaning "lazy." Ramsay suggested that argon be placed within a new group of zero-valent elements in the Periodic Table, between chlorine and potassium. In 1895 Ramsay and, independently, Per Theodor Cleve and Nils Abraham Langlet in Sweden, discovered helium, previously known from its solar spectrum, in a radioactive mineral. Also in 1895, Ramsay and the English chemist Morris W. Travers discovered the **inert** gases krypton (from the Greek, meaning "hidden"), neon (from the Greek, meaning "new"), and xenon (from the Greek, meaning "stranger"). From 1962, when English-born American chemist Neil Bartlett prepared xenon hexafluoroplatinate(V), $XePtF_6$, inert gases became known as **"noble gases."**

inert: incapable of reacting with another substance

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

In 1904 Ramsay received the Nobel Prize in chemistry "in recognition of his services in the discovery of the inert gaseous elements in air, and his determination of their place in the periodic system," becoming the first British recipient of this award. SEE ALSO ARGON; CLEVE, PER THEODOR; STRUTT, JOHN (LORD RAYLEIGH).

George B. Kauffman

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Rayleigh, Lord ***See Strutt, John.***

Reaction Rates

In chemistry, there is much interest in how quickly reactant molecules are transformed into product molecules and in the reaction steps or "mechanism" by which the chemical transformation occurs. We focus here on the speed with which chemical transformations occur, hence the title "reaction rates."

To calculate the impact of changing reactant concentrations, temperature, or pressure on a chemical reaction rate, a reliable quantitative measure of the change in the concentration of a reactant or product chemical species versus the change in time is needed. The first quantitative reaction rate study, carried out by Ludwig Wilhelmy in 1850, illustrates this. He followed the course of the "inversion of sucrose" in **aqueous solution**

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

$$sucrose + H_2O \xrightarrow{\text{dilute acid}} glucose + fructose$$

by observing a gradual rotation of the plane of polarized light passed through the solution over time. Sucrose rotates the plane of polarized light clockwise, whereas fructose rotates the plane of polarized light more strongly counterclockwise. Wilhelmy thus found that the concentration *c* of sucrose decreases with time *t* according to the following equation

$$-dc/dt = k_1c$$

where k_1 is the rate constant, a factor that has a temperature and pressure dependence but does not have a concentration dependence. This is called a first-order rate expression and k_1 is called a first-order rate constant, because the concentration *c* is raised to the first power in this rate equation. The half-line of this reaction, the time required for half of the sucrose

Half-lives of Some Radioactive Isotopes.

Radionuclide	Half-life (Days)	Radionuclide	Half-life (Days)
3H	4.50×10^3	90Sr	1.00×10^4
14C	2.09×10^6	99Mo	2.79
32P	14.3	99mTc	0.250
35S	87.1	99Tc	7.70×10^6
42K	0.52	109Pd	0.570
45Ca	16.4	111In	2.81
47Ca	4.90	129I	6.30×10^9
59Fe	45.1	131I	8.00
57Co	270	135I	0.280
72Ga	0.59	207T1	3.33×10^{-3}
58mCo	0.38	207Bi	1.53×10^{-3}
58Co	72.0	226Ra	5.84×10^5
60Co	1.9×10^3	235U	2.60×10^{11}
64Cu	0.538	236U	8.72×10^{-5}
67Cu	2.58		

initially present in solution to react, is given for a first-order reaction by the expression

$$t_{1/2} = \ln 2/k_1$$

where the first-order rate constant k_1 has the units of reciprocal time. This is a general expression for all first-order reactions.

Overall Reaction Order

When the sucrose inversion reaction was later run in nonaqueous solvents it was recognized that a better description of the rate of disappearance of sucrose S is given by the following equations:

$$S + H^+ \rightleftharpoons SH^+$$

$$Kc = [SH^+]/[S][H^+]$$

$$SH^+ + H_2O \xrightarrow{\text{slow}} glucose + fructose + H^+$$

$$-d[S]/dt = k[SH^+][H_2O] = kK_c[S][H^+][H_2O]$$

Thus, the reaction rate is first-order in sucrose, first-order in the **catalyst** H^+, and first-order in H_2O. The reaction is said to be "third-order overall," third because of the sum of the powers on the three concentration factors.

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

The "initial rate method" is usually used to deduce reaction order from experimental rate data. This means that the reaction rate is determined over a short range of times after mixing reactants to avoid the complicating effects of reaction products undergoing further reactions. The initial reaction rate $R = k[A]^a[B]^b[C]^c \ldots$ is measured several times, with the concentrations of the reactants A, B, C, and so on systematically varied. Then, taking the logarithm of both sides of each rate equation $\log R = \log k + a \log[A] + b \log[B] + c \log[C] \ldots$ the several resulting simultaneous linear equations for the values of a, b, c, and so on can be solved. Often, all but one of the reactant concentrations are kept constant, and the concentration dependence of the variable reactant is then most easily determined.

Temperature Dependence of Rates

In 1889 Svante Arrhenius noted that an increase in Kelvin temperature T caused the rate constant k of many reactions to increase according to the relation

$$k = Ae^{-Ea/RT}$$

or

$$\ln/k = \ln A - Ea/RT$$

where the activation energy E_a is related to the minimum amount of energy that a reactant molecule must acquire from collisions or some other form of excitation to go on to form reaction products. R is the perfect gas (ideal gas) constant.

If the rate constant k for a reaction is determined at several different temperatures, all that one needs to do to obtain a numerical value of E_a is to construct a plot of ln k on the vertical axis versus $1/T$ on the horizontal axis. If the chemical reaction obeys the Arrhenius equation, a straight line plot of the experimental data having a negative slope is obtained. The slope of this line is equal to $-E_a/R$. Readers living in temperate climates will recall that the rate at which crickets chirp gradually declines in autumn as outside temperatures become cooler. If the natural logarithm of the frequency of the chirping of crickets is plotted versus the reciprocal of the Kelvin temperature, the observer deduces from the slope of the resulting straight line that the activation energy for chirping is about $E_a = 5 \times 10^4$ joules/mole.

If k_1 is the rate constant for a given reaction at a Kelvin temperature T_1, we may estimate the magnitude k_2 of the rate constant of that reaction at some other temperature T_2 from the following alternative form of the Arrhenius equation:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)$$

A familiar rule in chemistry states that "the rate of a chemical reaction doubles for each increase in temperature of ten degrees." From this second form of the Arrhenius equation it becomes clear that the moderate success of this rule of thumb proceeds from the fact that for many chemical reactions the activation energy E_a has a magnitude in the general ballpark area of 5×10^4 joules/mole.

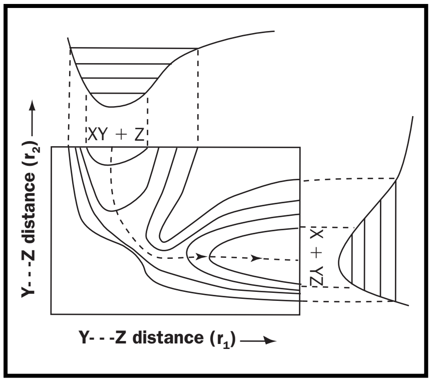

Figure 1. Typical potential energy surface for the reaction XY + X → x + YZ.

phase: homogeneous state of matter

The Activated Complex

A chemical reaction in which a diatomic molecule A–B collides end-on with an atom C, to form a diatomic molecule B–C and an atom A, can be depicted as occurring on a surface within a theoretical three-dimensional space in which the vertical axis is potential energy and the other two axes are the A–B and the B–C bond distances. In 1931 Henry Eyring and Michael Polanyi took reaction rate studies to the individual molecule level by calculating a potential energy surface for the colinear gas **phase** reaction

$$D + H_2 \rightarrow DH + H$$

where D denotes the deuterium **isotope** of hydrogen. They visualized the passage of the system from reactants to products as occurring via a linear configuration of the three atoms corresponding to the top of a potential energy barrier that they called the "activated complex." This entity had a presumed lifetime of only 10^{-13} seconds or less, and no one in the 1930s foresaw that activated complexes would finally be observed experimentally (in 1987) by Ahmed Zewail using femtosecond duration (10^{-15} seconds) laser pulses.

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

In 1935 Eyring and Polanyi independently formulated a "transition state theory" expression for the A-term in the Arrhenius equation pertaining to the rate constant of a gas phase reaction. Their work was based on the idea that a chemical **equilibrium** exists between the reactant species and the activated complex, even though some of the activated complex species must be "leaking" over the top of the potential energy barrier and forming products. Powerful concepts that still have wide application in explaining reaction rates emerged from transition state theory. For instance, gas phase reactions between two large molecules are typically slower than one would predict using a billiard ball collision model of reaction rates. This is because much of the collision energy can be stored unreactively in the internal vibrations of a collisionally excited molecule.

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

Pressure Dependence of Rates

Another application of transition state theory is its explanation of the effect of pressure on reaction rates. Increasing pressure by a factor of 10^3 decreases the rate constant for a ring-closure reaction

$$Mo(\mathrm{CO})_5L \xrightarrow{k} \mathrm{Mo}(CO)_4L + CO$$

by a factor of 1.3 (where L is the bidentate **ligand** 1,10-phenanthroline and the solvent is liquid toluene at 25°C). The change in volume in going from reactants to activated complex is $\Delta V^{\neq} = +6.1\ \mathrm{cm^3 mol^{-1}}$. Applying le Chatelier's principle to the quasi-equilibrium between reactants and activated complex molecules, the transition state theory point of view maintains that the increase in pressure favors formation of reactants over formation of activated complexes, because the reactants are more compact. With fewer activated complexes present, the reaction-yielding product from activated complexes slows down.

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

Reaction Time Scales

Many important reactions, such as the conversion of atmospheric nitrogen and hydrogen into ammonia, are very slow and remain that way until a catalyst (in this case iron oxide) is identified. In our bodies, enzymes can function as catalysts to speed up essential reactions. In order to understand reaction mechanisms, chemists focus on discrete reaction steps and often need very short-term experimental methods to follow rates of individual reaction steps. For instance, Manfred Eigen and Leo De Maeyer (1955) used an electrical conductance "relaxation method" to measure the rate of the reaction

$$H^+(\mathrm{aq}) + OH^-(\mathrm{aq}) \xrightarrow{k} H_2O(\mathrm{l})$$

in liquid water. They found a rate constant $k = 1.4 \times 10^{11}$ liters $mol^{-1}s^{-1}$ at 25°C (77°F) by measuring relaxation times (roughly reaction half-lives) on a time scale of tens of microseconds. In recent years femtosecond laser pulses have proved to be the most powerful experimental tool for elucidating the details of chemical reaction steps and their rates. Zewail has speculated that attosecond (10^{-18} second) laser pulses will be achieved that will enable scientists to track the paths of electrons within molecules as the molecules undergo chemical reactions. SEE ALSO CATALYSIS AND CATALYSTS.

Edward M. Eyring

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Reaction Speed ***See Kinetics.***

Recombinant DNA

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

Recombinant **DNA** (rDNA) is made of segments of DNA (polymers of deoxyribonucleotides) from two or more sources. Nature has been recombining DNA in living cells for eons, but humans have only recently discovered the means to carry out this operation in the test tube. DNA is the molecule of heredity, and the procedure used for preparing rDNA is referred to as genetic engineering. The biotechnology industry and much of modern medicine, basic research, and agriculture depend on the use of rDNA.

How the Technology Developed

cleave: split

hydrolyze: to react with water

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

The discovery of restriction endonucleases, enzymes that reproducibly **cleave** double-stranded DNA molecules at specific sequences, paved the way for the development of rDNA technology. Restriction endonucleases are produced in bacteria as a defense mechanism of that bacterium to restrict the growth of invading bacterial viruses; they act by destroying viral DNA. The enzymes **hydrolyze** or "cut" specific sites within a DNA molecule. In 1978, the Nobel Prize in medicine was awarded to Werner Arber, Daniel Nathans, and Hamilton O. Smith for the discovery and investigation of restriction endonucleases. The cuts made by these enzymes often leave single DNA strands with sticky ends due to the asymmetry of the cut (made to a double-stranded molecule) and the tendency of the bases in DNA to form **hydrogen bonds** with complementary bases on another strand. Scientists realized that these enzymes could serve as a powerful tool for manipulating DNA in a controlled way. The 1980 Nobel Prize in chemistry was awarded to Paul Berg for constructing the first recombinant DNA molecules.

When scientists became concerned about whether this new technology posed risks to humans and the environment, there was an unprecedented (and temporary) suspension of experiments using rDNA. In 1975, a conference was held in Asilomar, California, to assess such risks, and it was determined that most rDNA work should continue as long as appropriate safeguards were in place. A Recombinant DNA Advisory Committee was established through the auspices of the National Institutes of Health to set up guidelines and assess risks and benefits of proposed projects using rDNA. That committee, composed of scientists, physicians, ethicists, and legal experts, has met regularly since that time.

Preparing rDNA

When a DNA carrier, called a vector, and a targeted DNA sample are treated with the same restriction enzyme, the resulting fragments are left with matching, or complementary, sticky ends. When mixed, the two samples of treated DNA will "stick" together, and another enzyme, DNA ligase, will seal pieces of DNA together with the formation of **covalent bonds** (see Figure 1). Vectors are often plasmids, small extrachromosomal and circular DNA that are incorporated into bacterial DNA such as that of *E. coli*, so that the inserted or cloned genes can be reproduced manyfold and products of the inserted genes (protein molecules) can be manufactured, sometimes in large quantities. Some vectors are designed to induce protein **synthesis** from the information in the inserted genes. Other vectors are designed to deliver large segments of DNA to specific cells.

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

synthesis: combination of starting materials to form a desired product

Uses of rDNA Technology

Essentially every area of biological research has been affected by the use of rDNA technology. Protein structure/function relationship studies and gene expression and regulation research have been enormously enhanced by this powerful tool. Transgenic animals (into which DNA from another species has been inserted) have been bred to expand the study of human biochemical processes and diseases. Transgenic mice that are highly susceptible to breast cancer or Alzheimer's disease have furthered the understanding of those diseases.

Modern medicine is inextricably linked with rDNA technology. Gene therapy replaces defective genes with functional ones, delivered to the patient by way of a suitable vector, usually a disabled virus. The first moderately successful gene therapy was instituted to treat an inborn immune deficiency disease (ADA deficiency) caused by a defective enzyme, **adenine** deaminase. Cancer research and treatments as well as some vaccine development make use of rDNA technology. Attempts to modify animals genetically in such a way that organs suitable for transplant into humans may be harvested are now being made.

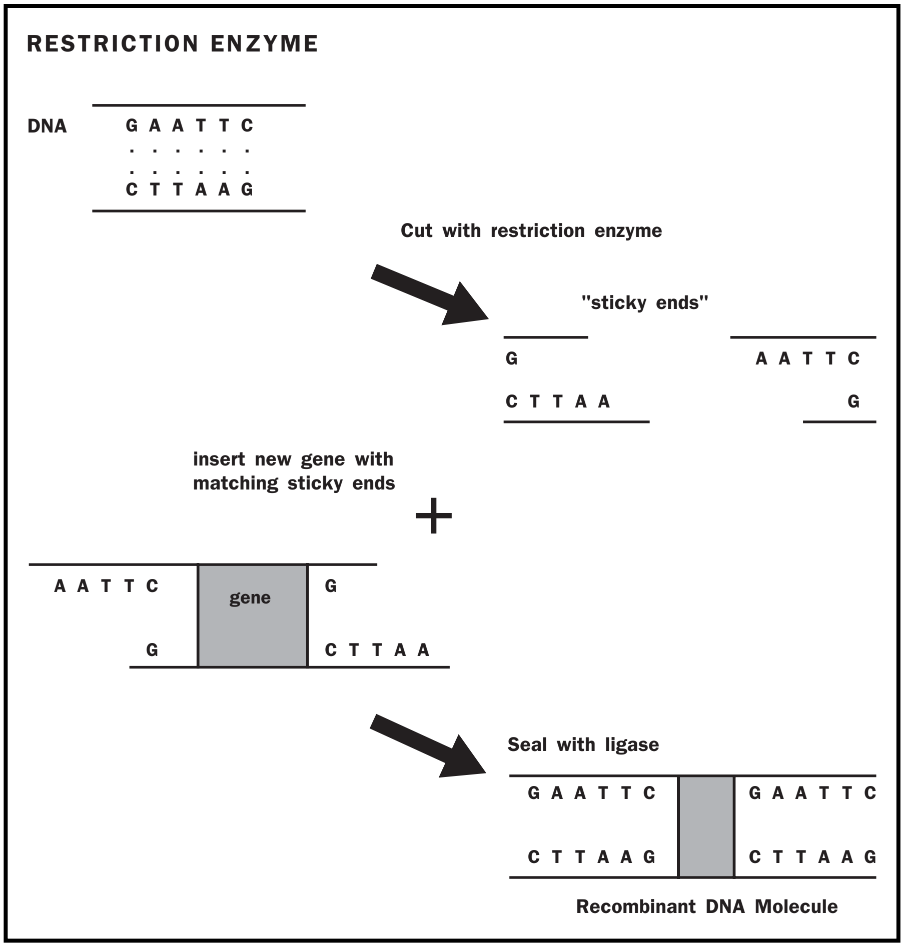
adenine: one of the purine bases found in nucleic acids, $C_5H_5N_5$

Agricultural uses of recombinant DNA technology are expanding. Genetically engineered bacteria sprayed onto strawberries protect the strawberries from freezing. Genes that promote herbicide resistance are incorporated into plants so that herbicides can be used for no-till farming. Some plant species have been transformed by rDNA containing genes that promote resistance to insects and pathogens.

The industrial use of rDNA technology includes the production of bleach-resistant enzymes that are used in laundry detergents to **degrade**

degrade: to decompose or reduce the complexity of a chemical

Figure 1. Scheme for producing an rDNA structure made from a plasmid and DNA to be cloned.



proteins. Transgenic cows that produce human milk for use in baby food have been bred. In 1980 the verdict of a landmark case heard before the U.S. Supreme Court stated that a genetically engineered bacterium, designed to digest oil in oil spills by researchers at Exxon, could be patented.

Recombinant DNA technology was used as an artist's tool in a macabre incident in which a jellyfish gene for a green fluorescent protein, often used in research as a marker for gene transfer, was inserted into a rabbit, making the rabbit fluoresce under green light. This and other dubious uses of rDNA technology have engendered a number of ethical, economic, safety, and legal debates. SEE ALSO CLONES; DNA REPLICATION; HYDROGEN; RESTRICTION ENZYMES.

Sharron W. Smith

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Recycling

Remains of human settlements through the ages are characterized by garbage. Early human encampments are surrounded by discarded bones, shells, and broken tools and weapons. While such material is a boon to archaeologists, the mountains of discarded materials produced by today's society threaten to consume available land near large cities, and they pollute the water supplies of both rural and urban environments. Nearly every object and material discarded by humans can be recycled, reducing the cost and danger of disposal and providing valuable resources for industry and the home. Recycling also restricts many dangerous substances to facilities designed to handle them.

The Emergence of Recycling

Many Americans remember when garbage disposal was as simple as placing the material in a can in the alley or, in the case of rural residents, feeding the pig, or tossing everything into a nearby ditch in the name, at least, of erosion control. Our ancestors lived lives much simpler and were much less encumbered by material possessions. Bottles, buttons, nails, and wood all passed through a progression of steps and were smelted, rewoven, reshaped, or burned. Few people anywhere lived in societies where many materials were simply thrown away. The largest furniture store now operating in the United States was founded by two immigrants who began their careers as rag and bottle pickers during the early 1900s.

Every bottle or jar in early America was recycled, and pieces were used for purposes as varied as arrowheads and grit for chickens. Birds, lacking teeth, must collect small rocks, or grit, in order to grind their food in the craw. Old-time farmers sometimes ground glass when oyster shell or other sources of grit were unavailable. Ground glass was also mixed with glue to make abrasives. The vast numbers of buffalo killed by Native American or European hunters left huge quantities of bones on the prairie, but early scavengers collected them and shipped them to plants where they were ground for fertilizer. Early-day cloth was collected and treated to reclaim fiber, which could be woven into string or rope. Most cities contain parks, and below many of these parks are landfills dating back as far as the 1800s. A lack of landfill space, increasing transportation costs, and tougher government regulations now diminish the use of landfills, and many smaller communities sport signboards denouncing the importation of waste from other cities or states.

Recycling falls into two categories: direct and indirect. Direct recycling is the reuse of components of manufactured materials before sale, often in the case of damaged or unsold products. Indirect recycling is the practice of recycling products or materials that consumers have used and discarded.

Shortages during World War I and World War II prompted scrap iron, fiber, and rubber drives, reclaiming many essential materials. The first items to be recycled through organized programs other than in wartime were milk and other beverage bottles. In days when milkmen placed bottles on doorsteps, the heavy bottles were returned, washed, and refilled dozens of times. During the 1940s and 1950s, families scavenged for soda and beer bottles and cans along highways, and many children supplemented or earned allowances by collecting bottles for the two-cent deposit. Plastic bottles and aluminum cans have largely replaced the reusable bottles of the twentieth century. Many states now mandate five- to ten-cent deposits on the plastic replacements. The scrap material drives of the World Wars brought the public's attention to the fact that many more fabrics, metals, and rubber items could be recycled.

Water

The most commonly recycled material is water. Seldom destroyed in use, water serves as a medium for chemical reactions and as a heat transfer mechanism in steam or hot water systems, car engines, and various industrial processes. Moderately dirty water may be dumped directly into streams, injected into wells, or, in the case of cooling water from power plants, allowed to pass through wetlands to cool.

Water containing sewage is given primary treatment consisting of settling and filtration and secondary aeration treatment to allow oxidative bacteria to reduce the bacterial oxidative demand (BOD). Tertiary treatment with chlorine, chloramines, or ozone is used if the water is needed for consumption. In rural areas, sewage may pass through a cesspool for sedimentation and anaerobic bacterial action, and the effluent may be distributed through a series of pipes into a disposal field. Water that has low BOD is usually purified by bacterial action in soil so that after passing some distance through the ground, biodegradable substances are removed. It is particularly important that detergents be biodegradable and contain minimal amounts of phosphates and nitrates, as these substances, along with high BOD water, contribute to eutrophication, a rapid growth of bacteria. Eutrophication may consume so much available oxygen that fish and other organisms die.

Farms, ranches, and feedlots provide food but often are major sources of pollution. Modern feedlots store sewage in lagoons where solids can be collected. Effluent water from lagoons often contains microorganisms that serve as food in fish farms, and solids from the lagoons can be processed into fertilizer. The effectiveness of these operations is often determined by the size of the operation and the need for cleanup. Larger operations can afford more complex remediation equipment and tend to be more cost-effective than small ones. Most large feedlots are located away from population centers whose residents often complain of the odors.

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

synthesis: combination of starting materials to form a desired product

Federal, state, and municipal laws mandate that industries reclaim most pollutants, such as **heavy metals** or organic chemicals, from wastewater. Prior to this legislation, toxic chemicals often made their way into the water table. Reclaiming toxic substances protects the environment and, in many cases, provides a valuable source of materials needed for **synthesis**. In many cases, industries are located near other manufacturing plants that pass their waste to another plant, which uses it as a raw material.

Paper, Steel, and Aluminum

Paper, in the form of used newspapers, packing materials, and telephone books, may be burned for energy, but it still makes up 30 percent to 45 percent of the average landfill. Landfilled paper requires decades to decay and may release methane, a greenhouse gas that is twenty times as deleterious as carbon dioxide. Most paper could be reused or converted to materials used for blown insulation. Nearly 40 percent of office paper and newspapers is now recycled. Two problems occur in recycling paper. Each time paper is reprocessed, the fibers break and become shorter. Office copiers work best with long-fiber paper that has higher tensile strength and produces less dust. Fiber from used paper is often blended with new fibers to produce the desired qualities. A second problem in recycling office paper is the demand for white paper. Used paper pulp often contains ink or other colored materials that must be removed. Some inks and adhesives can be removed by flotation, and bleaching then whitens the pulp. Older methods of chlorine bleaching produced toxic dioxin. Oxygen and hydrogen peroxide are now used to whiten paper and are considered less damaging to the environment. Use of colored papers for printing and copying greatly decreases the need for bleaching.

Steel is widely recycled. Soon after steel was first produced, damaged steel items were recycled into new products. Today, 68 percent of used steel is recycled. The basic oxygen process of steel manufacture uses 25 percent scrap as starting material, and nearly 100 percent of the starting material for steel production by the electric arc process is scrap. Many states have "clunker" laws that require that the purchase of a new car be accompanied by turning in a junked car, and most municipalities have programs for collecting and recycling used auto parts and furniture.

Aluminum is one of the most commonly recycled metals. Although many aluminum products are still discarded, 65 percent of aluminum materials are recycled; 95 percent less energy is needed to produce aluminum from recycled cans than from aluminum ore.

Plastics and Oil

Plastics make up only about 8 percent of the volume in the average landfill but represent a huge investment of energy and raw materials. Most plastics produced from petroleum materials by polymerization of monomers such as ethylene or vinyl chloride are thermoplastic materials and can be cleaned, melted, and re-formed. Thermosetting plastics can also be cut into pieces that are mixed with other plastics or used as fillers. High-density polyethylene (HDPE) and polyethylene terephthalate (PETE) are the most widely reused plastic materials, but polyvinyl chloride (PVC), polypropylene, and polystyrene account for 5 percent of the recycled plastics. In 2001 80 million pounds (36 million kilograms) of plastics were recycled in the United States. Recycled plastic materials are used in the production of bottles, fabrics, flowerpots, furniture, plastic lumber, injection molded crates, and automobile parts.

According to the Environmental Protection Agency, Americans discard 120 million gallons (454 million liters) of oil each year as a result of automobile oil changes. Virtually all this oil can be recycled, and most states require recycling. Used motor oil contains particulate matter and some chemical substances that must be removed during re-refining. As much as 80 percent of used motor oil is used with little change as a fuel for ships or industrial heating equipment, but this practice probably poses a greater danger to the environment than burning refined oil.

Batteries, Rubber, and Paint

Used lead-acid automobile batteries represent a major hazard to the environment. Most landfills accept batteries but place them aside for recycling, which includes collecting and neutralizing the acid, removing the cases, and resmelting the lead plates. Fragments of cases can be recycled into new battery cases, and resmelted lead is used to cast new battery plates. In New Zealand alone, 500,000 lead-acid storage batteries are recycled each year.

Rechargeable batteries from power tools, telephones, and most other devices can be recycled. Nonrecyclable batteries often contain mercury or other toxic metals that are harmful to the environment, but in the early twenty-first century, most were still discarded in landfills.

Rubber products pose a special problem in the environment, and their dumping in landfills usually requires a special fee. Discarded in piles or buried, they occasionally catch fire and produce noxious gases. In developing countries, many used or damaged automobile tires are repaired or disassembled to make other products. Granulated rubber produced from

Freon is being removed from a refrigerator. The Sacramento Municipal Utility District sells the freon to DuPont, drains the oil from the refrigerators, and sells the scrap metal.

discarded tires can be used to make floor mats and rubber wheels, and it can be used as a component of asphalt-paving materials. Used rubber can be heated to reclaim petroleum products, treated chemically to obtain components used as filler in manufacturing rubber products, or incinerated as a source of energy.

Many recyclable materials consist of mixed materials that pose special problems. Discarded automobile oil filters contain steel, fiber, and contaminated petroleum. Oil filters are crushed and heated to remove oil, and the metal reclaimed. Discarded household appliances contain large amounts of steel but must often be dismantled, with other materials removed. A special fee is charged at recycling centers to discard most appliances. Fluorescent lamps contain small amounts of mercury that can be reclaimed. Used computers and television sets contain usable materials and, often, some toxic materials that can be collected for safe disposal.

The small amounts of paint generated by the average household cannot be recycled economically, but most municipalities sponsor paint exchange programs and collect oil-based paints. Spent fuel rods from nuclear power plants can be recycled to reclaim unused uranium, and some spent uranium is used to produce armor-piercing bullets. Yard waste from households is often recycled and made into mulch for farming and gardening. Discarded Christmas trees are used to form mulch or are immersed in lakes as a habitat for fish. SEE ALSO Environmental Pollution; Water; Water Pollution; Water Quality.

Dan M. Sullivan

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Remsen, Ira

AMERICAN CHEMIST AND EDUCATOR
1846–1927

Most great chemists are remembered for their research. Ira Remsen, although he contributed significantly to the research of his time, is one of the few chemists remembered mainly for his teaching and mentorship. It was under his leadership that American chemical research came of age in the late nineteenth and early twentieth centuries.

Remsen was born in New York City on February 10, 1846, into a family that traced its lineage back to seventeenth-century Dutch colonial settlers. In his early schooling, he excelled in the classics and had almost no exposure to science. He attended the New York Free Academy (later the City College of New York), but in accordance with his father's wishes, he left before graduation to become an apprentice to a homeopathic physician.

He received an M.D. in 1867 from the Columbia College of Physicians and Surgeons. His prize-winning thesis, “The Fatty Degeneration of the Liver,” was written on the basis of information Remsen gleaned from books without ever seeing a liver. His interest in chemistry had been awakened during medical school, and Remsen resolved upon graduation to further pursue his studies in that field of science.

At that time, there were no American schools that engaged in serious chemical research; the epicenter of the chemical world was Germany, and Remsen embarked for Munich to study under Justus Liebig, the most renowned scholar of the time. Unfortunately, Remsen learned upon his arrival in Munich that Liebig had stopped supervising students. There was, however, no shortage of excellent teachers there. Remsen remained in the German university system for five years, studying under Jacob Volhard, Friedrich Wöhler, and Rudolph Fittig. He received his Ph.D. from Göttingen in 1870 in the newly organized field of organic chemistry.

Upon returning to the United States, Remsen accepted an appointment as a professor of chemistry and physics at Williams College in Massachusetts. There, despite a lack of facilities or administrative encouragement, he managed to continue the research that he had started in Germany. Recognizing the lack of chemistry textbooks in English, he translated Wöhler’s *Outlines of Organic Chemistry* and wrote the first of his eight textbooks, *Principles of Theoretical Chemistry.* The excellent quality of these books led to Remsen’s appointment to the newly founded Johns Hopkins University in Baltimore, Maryland, the first institution in the United States devoted primarily to research. Remsen remained there for thirty-six years, first as professor of chemistry and later as its president (1901–1912). During his tenure, he established the distinctly German tradition of chemistry research that he had learned in his studies in that country.

The research carried out in Remsen’s laboratories, although of less lasting import than his teaching, was significant in its time. These studies derived mostly from his earlier work and centered on the reactions of derivatives of substituted benzenes. The artificial sweetener saccharin was discovered, partially by accident, by one of his students. He was also noted for his clear and straightforward teaching style and for his devotion to his students. Under his tutelage, the first great generation of American academic chemists was established across the country.

In 1879 Remsen founded the *American Chemical Journal* in order both to promote the research being done at Johns Hopkins and elsewhere in the United States and to make this work widely available to American readers. It was the first American journal devoted to chemistry and quickly became recognized for its excellence both at home and abroad. It later merged with the *Journal of the American Chemical Society*.

Remsen retired in 1912 but remained active as a consultant to the chemical industry. He died on March 4, 1927, in Carmel, California. The next year his ashes were returned to Johns Hopkins and interred behind a bronze memorial tablet in the newly renamed Remsen Hall. SEE ALSO LIEBIG, JUSTUS VON; WOHLER, FRIEDRICH.

Bartow Culp

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Residue

A residue is a single molecular unit within a polymer. *Residue* is thus another term for monomer. Although the term *residue* is most often used to refer to a specific amino acid within a **polypeptide**, it is also used to refer to sugars within a carbohydrate molecule and nucleotides within deoxyribonucleic acid (**DNA**) or ribonucleic acid (RNA).

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

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

A protein or a polypeptide is composed of amino acids linked together by peptide bonds, with amino acids as the monomeric units of the polypeptide. The order of amino acids in a protein is known as the primary structure of that protein. The specific sequence of amino acids in the protein determines its three-dimensional structure and ultimately its function. The amino acids are numbered sequentially, beginning at the amino terminus of the polypeptide. For example, the 45th amino acid in the sequence would be identified as residue 45. Most often, scientists refer to an individual residue using both the name of the amino acid and its position. Therefore, if residue 45 in a particular polypeptide sequence is serine, that residue would be referred to as serine-45. SEE ALSO PEPTIDE BOND; PRIMARY STRUCTURE; PROTEINS.

Robert Noiva

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Restriction Enzymes

Restriction enzymes (also known as restriction endonucleases) are enzymes that cut double-stranded DNA at very specific recognition sites. They were originally discovered in bacteria that use them to restrict the growth of viruses but are now among the workhorse enzymes of biotechnology and recombinant DNA research.

It has long been known that bacteria are susceptible to attack by viruses known as *bacteriophages* ("eaters of bacteria"). The presence of restriction enzymes in bacteria is part of the defense system against bacteriophages that has evolved in these bacteria. These highly specific enzymes will scan DNA until a certain sequence of nucleotide bases is identified. The specificity is such that the sequence is apt to occur at only one or two sites in the viral DNA, with no such occurrence in the host bacterial DNA. Restriction enzymes recognize a sequence such as:

5′ G A A T T C 3′
3′ C T T A A G 5′

Interestingly, the enzyme can recognize the paired sequences from either strand because they are a palindrome (reading the same in either direction). The restriction enzyme can cut this palindromic sequence in one of two manners: across both strands at the same spot, or in a staggered manner that yields free single-stranded ends called "sticky ends." These sticky ends have proved most useful in recombinant DNA work.

The names of restriction enzymes are derived from their bacterial sources. One of the enzymes most widely used in recombinant DNA work is *Eco*R1, which is isolated from *Escherichia coli* RY13. Other examples include HindII (isolated from *Haemophilus influenza* Rd), and Xba I (isolated from *Xanthomonas badrii*). The specificity of each enzyme allows researchers to cut DNA in a predictable and reproducible manner. Using *Eco*R1 on the above sequence, one would always obtain the ends:

--------- 5′ G A A T T C 3′ ---------
--------- 3′ C T T A A G 5′ ---------

A small circular piece of DNA (such as a bacterial plasmid) with one *Eco*R1 site would yield a linear piece of DNA with the CTTAA sticky ends. Now suppose one could obtain the DNA (the gene) coding for a foreign protein such as human insulin. At each end of the insulin gene, one could attach complementary single-stranded sticky ends that would exactly "match" the ends of the cut plasmid. As if made of Velcro, the complementary ends would stick together, and if one were to use an enzyme called DNA ligase to form a stronger covalent bond between parts joined together, one would have incorporated a human (or other species) gene into bacterial DNA. This technique is known as recombinant DNA. The bacteria can now be grown in large batches and made to synthesize the foreign protein (insulin). SEE ALSO DEOXYRIBONUCLEIC ACID; ENZYME; RECOMBINANT DNA.

C. Larry Bering

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Retinoic Acid *See Retinol.*

Retinol

Retinol, or **vitamin** A, is a necessary nutrient in all higher animals. It plays an important role in vision, in the maintenance of epithelial cell layers, in spermatogenesis, and in fetal development. Retinol must be obtained from

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

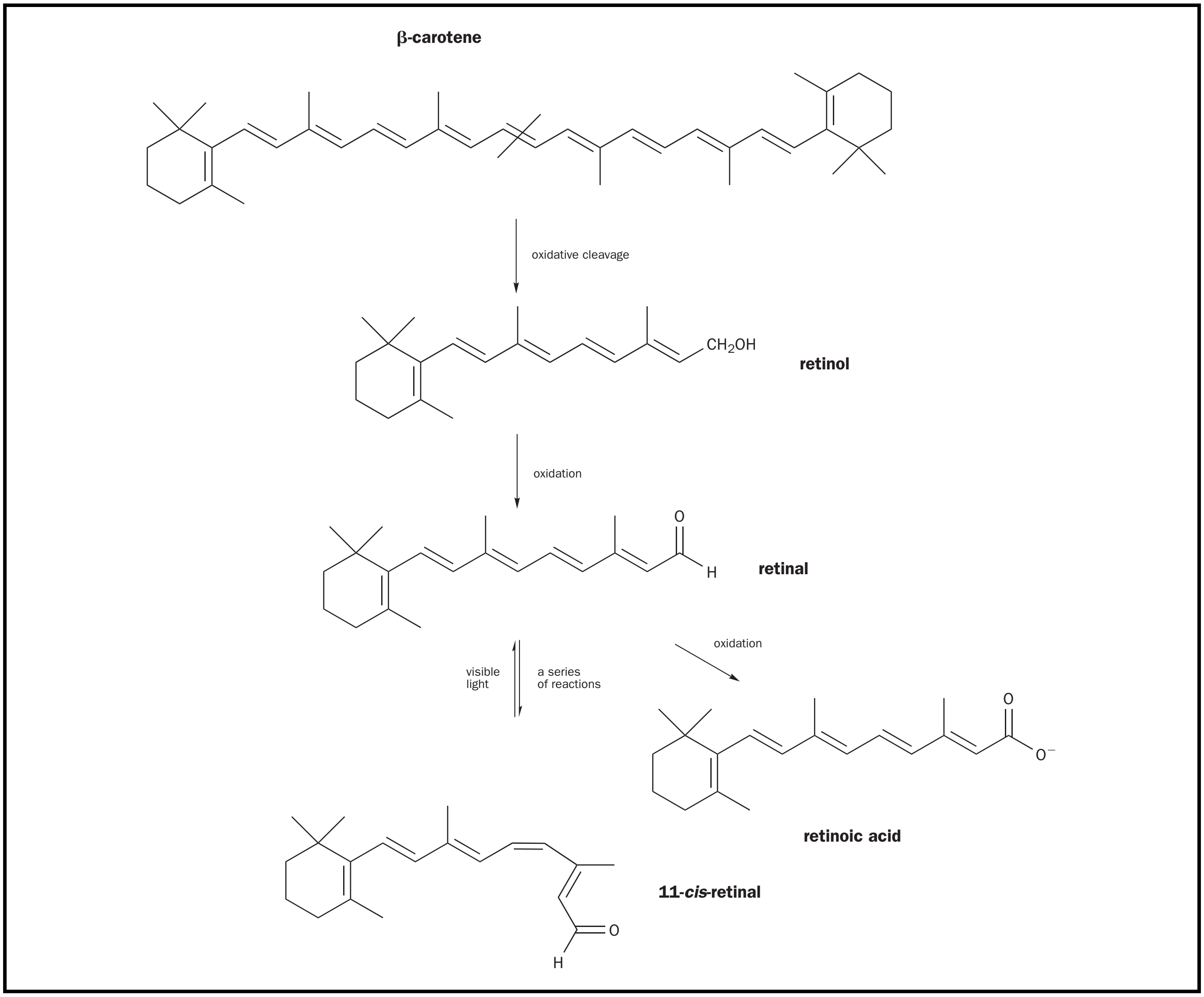

Figure 1. Vitamin A (retinol) and its derivatives.

the diet, either from organic compounds that are in animal products, such as retinyl **esters**, or from compounds in plants, most notably *β*-carotene (see Figure 1). Retinol and its derivatives are collectively called retinoids.

Chemically, retinol is an isoprenoid; isoprenoids are a group of compounds that includes vitamins E and K and cholesterol, which are synthesized from **isoprene** units. As shown in Figure 1, retinol is a hydrocarbon molecule with a single hydroxyl group at one end. This hydroxyl group can be oxidized to form an **aldehyde** group (yielding retinal), or to a **carboxylic acid** group (yielding retinoic acid). Retinal and retinoic acid are the biologically active forms of retinol. In addition to these different **oxidation** states, retinol occurs as a number of different **isomers**. The retinol structure shown in Figure 1 is all-*trans*-retinol, as all of the double bonds are in the *trans* configuration. Many *cis* isomers also occur. Two important examples are 11-*cis*-retinal, which is required for vision (see Figure 1), and 13-*cis*-retinoic acid (or isotretinoin), which is used as an anti-acne drug.

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

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

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

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

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

isomer: molecules with identical compositions but different structural formulas

One of the symptoms of vitamin A deficiency is night blindness. If the deficiency persists over time, the eyes will eventually deteriorate, and permanent blindness will result. In specialized cells of the eye, 11-*cis*-retinal is linked covalently to the enzyme opsin. Opsin is also a membrane protein; it comprises approximately 95 percent of the membrane protein of disks in the outer segments of the eye's rod cells. The disks in a rod cell are circular layers of membrane stacked on top of each other. Each cell contains hundreds to thousands of these disks. This greatly increases the membrane surface area, and thus the amount of opsin, in these light-detecting cells. The combination of 11-*cis*-retinal and opsin is called rhodopsin. Visible light is absorbed by the 11-*cis*-retinal, causing it to isomerize to all-*trans*-retinal (see Figure 1). The resulting shape change in the rhodopsin initiates a series of reactions that ultimately sends signals to the brain.

nuclear: having to do with the nucleus of a cell

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

The other active form of vitamin A is retinoic acid. Retinoic acid exerts its physiological functions via its interactions with a family of **nuclear receptors** called the retinoic acid receptors (RARs). RARs are members of a superfamily of nuclear receptors that include steroid hormone and thyroid hormone receptors. RARs are involved in regulating the **transcription** of many genes, including genes involved in the cell growth and cell differentiation of developing organisms. Because of this link between retinoic acid and development, female patients taking isotretinoin (13-*cis*-retinoic acid) must not become pregnant due to the considerable risk to offspring of severe birth defects. SEE ALSO ACNE MEDICATION.

Stephanie E. Dew

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75
Re
RHENIUM
186.207

Rhenium

MELTING POINT: 3,180°C
BOILING POINT: 5,627°C
DENSITY: 21.02 g/cm^3
MOST COMMON IONS: $[ReO_4]^-$, $[Re(Cl)_6]^{2-}$

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

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

Rhenium was discovered in a sample of gadolinite in 1925 by Walter Noddack, Ida Tacke, and Otto Berg, and was named after the Rhine River. The concentration of rhenium in Earth's crust is on the order of 7×10^{-8} percent. Rhenium crystallizes in the hexagonal close-packed arrangement and resembles platinum in appearance. It is usually obtained as a gray powder. It has the second highest melting point (3,180°C, or 5,756°F) of any **metal**. Rhenium is used in conjunction with platinum in thermocouples (thermoelectric thermometers) and as a Pt/Re reforming **catalyst** in the petroleum industry. It is used as filaments in mass spectrometry and as furnace heater windings.

IDA TACKE (1896–1979)

Working with her husband and using x rays, Ida Tacke discovered element number 75, rhenium. Her birthplace, next to the Rhine River, inspired its name. Tacke is also known for predicting nuclear fission prior to its realization, although she principally studied the chemistry of light in the human eye.

—Valerie Borek

Rhenium can be prepared by the thermal decomposition of NH_4ReO_4 or $(NH_4)_2ReCl_6$ in the presence of H_2, and by electrodeposition of $HReO_4$ from H_2SO_4 solutions. The metal is soluble in H_2O_2, concentrated HNO_3, hot H_2SO_4, and warm Br_2 water, but is not soluble in concentrated HF and

Heating elements in electric ovens are made from rhenium alloys.

HCl. It reacts in air above 400°C (752°F) to give Re_2O_7. It has the widest range of valences of any element. Dissolution of Re_2O_7 in H_2O yields Re_2O_3, ReO_2, Re_2O_5, ReO_3, and the strong acid $HReO_4$. With sulfur it forms Re_2S_7, which decomposes into ReS_2 and pure sulfur upon heating. It forms halides of stoichiometry ReX_n, where $n = 2$ to 7 for F, 3 to 6 for Cl, 3 to 5 for Br, and 2 to 4 for I. Rhenium forms coordination compounds with alkyl, aryl, carbonyl, dinitrogen, hydrido, isocyanide, nitrido, and nitrosyl **ligands**, and with other ligands containing nitrogen, phosphorus, oxygen, and sulfur donors. **Octahedral** complexes with mixed ligands are numerous; for example, $[Re(bpy)(CO)_3(py)]^{=}$, where bpy is 2,2′-bipyridine and py is pyridine.

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

D. Paul Rillema

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Rhodium

45
Rh
RHODIUM
102.9

MELTING POINT: 1,960°C
BOILING POINT: 3,700°C
DENSITY: 12.41 g/cm^3
MOST COMMON IONS: +, +2, +3

Rhodium was discovered in 1804 by the English chemist William Wollaston. Its name derives from the Greek word *rhodos*, meaning rose—the color of solutions containing rhodium salts. The abundance of rhodium in Earth's crust is approximately 0.0004 ppm. Its purification requires its separation from other platinum **metals**. Treatment of a crude platinum with metal concentrate with aqua regia leaves an insoluble portion that is then fused with bisulfate; this dissolves only the rhodium component, which is eventually converted to a solution of chloro complexes, whose treatment with H_2 precipitates the metal.

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

The extremely unreactive, silvery-white element is used in jewelry plating and is part of anodic and thermocouple materials. However, compounds containing Rh in **oxidation** states from (VI) to (−I) can be produced, the most common being those of Rh(III). Developments in Rh chemistry since the late 1960s have focused on various **catalytic** processes that use Rh(I) complexes, particularly those containing phosphines such as PR_3 (R is an aryl or alkyl group) and/or CO, because such **ligands** stabilize this oxidation state.

The catalytic processes, which operate via mechanisms that cycle between Rh(I) and Rh(III) **intermediates**, include: (1) hydrogenation (the activation of H_2 for the reduction of unsaturated organic compounds), (2) hydroformylation (the activation of H_2 and CO for their addition to olefins to generate aldehydes or alcohols); and (3) carbonylation (the activation of CO for its addition to organics). Some of the processes have been developed commercially.

1. An Rh(I) complex containing a chiral (**optically active**) phosphine ligand (i.e., one with three different substituents on the **pyramidal**

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

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

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

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

optically active: capable of rotating the plane of plane-polarized light

pyramidal: relating to a geometric arrangement of four electron-donating groups at the four vertices of a pyramid

P-atom) can catalyze a reaction such as $R(R')C{=}CHR' + H_2 \rightarrow R(R')C^*HCH_2R'$ (where *R*, *R′*, and *R′* are different substituents); the C^* atom of the product has four different substituents and is therefore chiral, and thus the use of a small amount of a chiral Rh **catalyst** generates large amounts of chiral product. Such a catalytic asymmetric hydrogenation has been used for the production of L-dopa, a drug used to treat Parkinson's disease.

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

2. An Rh(I) complex containing CO and P*R*$_3$ ligands can catalyze the formation of butan-1-al from propene ($CH_2{=}CHCH_3 + H_2 + CO \rightarrow CH_3CH_2CH_2CHO$), a commercially operated process.
3. An Rh(I) complex containing CO is used industrially to synthesize acetic acid from methanol ($CH_3OH + CO \rightarrow CH_3COOH$). SEE ALSO PLATINUM.

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Riboflavin

Riboflavin, also known as **vitamin** B$_2$, gets its name from its sugar alcohol (ribitol), and from its yellow color and its fluorescence under UV light (*flavin* comes from the Latin word for yellow). Its systematic names are 7,8-dimethyl-10-(D-ribo-2,3,4,5-tetrahydroxypentyl)isoalloxazine and 7,8-dimethyl-10-ribitylisoalloxazine; its formula is $C_{17}H_{20}N_4O_6$. Riboflavin has a molar mass of 376.37 grams (13.3 ounces). It is heat-stabile but easily degraded by light. Riboflavin was referred to as vitamin G in the early part of the twentieth century because it was recognized as a dietary factor needed for growth. Riboflavin was first isolated in 1879, and its chemical structure was determined in 1933.

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

As determined by the National Research Council of the National Academy of Sciences, the recommended daily allowance (RDA) of riboflavin for adults is about 1.5 milligrams (5.3×10^{-5} ounces). The amount required by an individual varies with factors such as age, gender, and amount of physical activity. Riboflavin is found in many foods, such as eggs, nuts, grains, dairy products, organ meats, and dark green vegetables. Overall, riboflavin content in the body can be estimated by measuring the activity of glutathione reductase (a riboflavin-containing enzyme) in red blood cells. No one has been known to ever die of riboflavin deficiency, but it can occur as a consequence of malnourishment, intake of certain medication, chronic diarrhea, or alcoholism. The first symptoms of riboflavin deficiency are often light sensitivity, blurred vision, and bloodshot eyes. Other symptoms are skin and mucous membranes lesions. Because riboflavin is water-soluble and easily **excreted**, toxicity resulting from excess intake is not considered a health problem.

excrete: to eliminate or discharge from a living entity

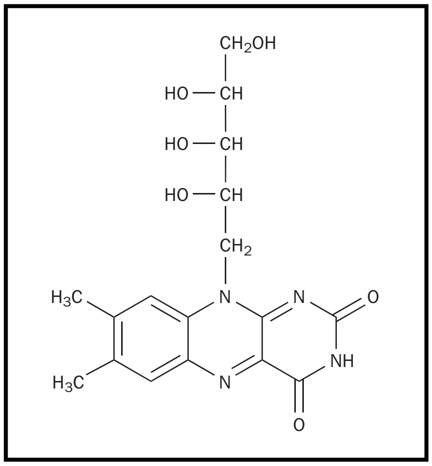

Figure 1.

Riboflavin is important biochemically because it is vital for proper utilization of carbohydrates, fats, and proteins as energy sources. It is a component

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

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

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

of two coenzymes, flavin **adenine** dinucleotide (FAD) and flavin mononucleotide (FMN). (Coenzymes are molecules that must be added to certain **polypeptides** to make them functional enzymes.) In general, FAD and FMN, when tightly bound to specific enzymes, easily lose or gain one or two electrons, or hydrogen atoms, and so drive **oxidation**/reduction reactions. In the 1930s, Warburg and Christian studied "the old yellow enzyme," a riboflavin-requiring enzyme, and laid the groundwork for our current understanding of cyclic oxidation-reduction reactions in electron transport systems vital to cell respiration. In addition to their role in electron transport chains, FAD- and FMN-requiring enzymes catalyze reactions that are part of a wide array of metabolic pathways. SEE ALSO COENZYME.

Sharron W. Smith

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Ribonucleic Acid

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

guanine: heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

uracil: heterocyclic, pyrimidine, amine base found in RNA

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

Ribonucleic acid (RNA) is a nucleic acid, like **DNA**, and is also made up of sugars, phosphates, and nitrogenous bases (or just a base). It contains a ribose sugar, whereas DNA contains a deoxyribose sugar. The four main bases found in RNA are **guanine** (G), **cytosine** (C), **uracil** (U), and **adenine** (A). DNA contains **thymine** (T) instead of uracil.

The ribose sugar of RNA gives it very different structural properties from those of DNA. RNA forms complex structures by folding a single strand upon itself. Ribose sugar makes RNA less stable than DNA, and it has to be produced often in a cell.

In most organisms RNA is made from their DNA. Some viruses, called retroviruses, contain RNA as their primary genetic material, for example, the AIDS virus and poliovirus.

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

There are many different kinds of RNA manufactured in a cell. Messenger RNA (mRNA) is produced to take the information contained in a specific segment of DNA and then use it to make proteins. Ribosomal RNA (rRNA) is part of a large RNA protein complex called the **ribosome** that binds mRNA and joins amino acids to make a protein. Transfer RNA (tRNA) brings amino acids to the ribosome and ensures that the amino acid used is in the order specified by mRNA. Many other kinds of RNA are also present in a cell. RNA plays an important role in the proper functioning of a cell. SEE ALSO DNA REPLICATION; NUCLEIC ACIDS; PROTEINS.

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Ritalin *See Methylphenidate.*

RNA *See Ribonucleic Acid.*

RNA Synthesis

Biochemists refer to RNA synthesis as **transcription**. Transcription is the process of synthesizing ribonucleic acid (RNA). Synthesis takes place within the nucleus of **eukaryotic cells** or in the cytoplasm of prokaryotes and converts the genetic **code** from a gene in deoxyribonucleic acid (**DNA**) to a strand of RNA that then directs protein synthesis.

Three types of RNA are found in cells. Transfer RNA (tRNA) carries amino acids to the site of protein synthesis. Ribosomal RNA (rRNA) along with protein makes up **ribosomes** (the mechanism that synthesizes protein). Messenger RNA (mRNA) is the code or template for protein synthesis. Special enzymes synthesize the different forms of RNA.

DNA consists of a series of regions called operons, each containing one or more genes capable of coding for an mRNA strand. An operon consists of a number of segments, principal among which are a promoter region to which **RNA polymerase**, the enzyme that synthesizes RNA, readily attaches, an operator region that acts as an on/off switch for the operon, and one or more genes that code for mRNA production. For convenience, biochemists describe locations on chains of nucleotides by speaking of the ends of the sugar-phosphate chains as having 3′ (three-prime) and 5′ ends. Both DNA and RNA are synthesized by enzymes that start at the **5′ end** of the strand being synthesized.

Transcription begins when RNA polymerase approaches the promoter gene, which often contains extended nucleotide sequences that help to match and bind the polymerase. After the polymerase binds, it is thought to move along the strand of DNA to the operator region. Protein repressor molecules that block transcription bind to operators; inducing agents may attach to the repressor molecules and pull them away from the operator, allowing the synthesis of mRNA. An example of this is the induction or turning on of the lac operon in *Escherichia coli* by the presence of lactose, producing mRNA that codes for enzymes that **metabolize** lactose.

RNA polymerase moves along the DNA molecule from the **3′ end** of the operon to the 5′ end, copying only one strand. (Copying the complementary strand would result in useless or harmful nonsense mRNA.) DNA and RNA are similar in composition, but DNA contains deoxyribose instead of ribose and the **pyrimidine base thymine** instead of **uracil**. The newly formed RNA is complementary to the DNA code; **adenine** bases on one strand pair with thymine or uracil on the other strand, and **guanine** bases

transcription:	enzyme-catalyzed assembly of an RNA molecule complementary to a strand of DNA
eukaryotic cell:	cell characterized by membrane-bound organelles, most notably the nucleus, and that possesses chromosomes whose DNA is associated with proteins
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
ribosome:	large complex of proteins used to convert amino acids into proteins
RNA polymerase:	enzyme used to make RNA using DNA as a template
5′ end:	situation in nucleic acids in which the phosphate group is attached at the fifth carbon atom from where the base is attached
metabolize:	performing metabolism—the 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)
3′ end:	situation in nucleic acids in which the phosphate group is attached at the third carbon atom from where the base is attached
pyrimidine base:	one of two types of nitrogen bases found in nucleic acids
thymine:	one of the four bases that make up a DNA molecule
uracil:	heterocyclic, pyrimidine, amine base found in RNA
adenine:	one of the purine bases found in nucleic acids, $C_5H_5N_5$
guanine:	heterocyclic, purine, amine base found in DNA

cytosine: heterocyclic, pyrimidine, amine base found in DNA

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

on one strand pair with **cytosine** on the complementary strand. The strands are said to be antiparallel; that is, the 3′ end of the DNA strand matches the 5′ end of the new mRNA strand. Since protein synthesis (translation) begins at the 5′ end of mRNA, protein synthesis in **prokaryotic** cells can begin while transcription is still under way, increasing the speed with which the organism responds to changes in its environment. SEE ALSO DEOXYRIBONUCLEIC ACID; PROTEIN SYNTHESIS; RIBONUCLEIC ACID.

Dan M. Sullivan

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Robinson, Robert

ENGLISH ORGANIC CHEMIST
1886–1975

English chemist Sir Robert Robinson, recipient of the 1947 Nobel Prize in chemistry, "for his investigations on plant products of biological importance, especially the alkaloids."

synthesis: combination of starting materials to form a desired product

An acknowledged giant of twentieth-century organic chemistry, Robert Robinson authored 700 research papers that continue to influence the way organic chemists think about **synthesis**, natural products, and reaction mechanisms. He received many awards during his sixty-year career, including the 1947 Nobel Prize in chemistry "for his investigations on plant products of biological importance, especially the alkaloids."

Robinson was born on September 13, 1886, near Chesterfield, England. His father owned a surgical dressing factory and invented many of the machines used to produce and package such dressings. In high school Robinson excelled in mathematics and physics and hoped to become a mathematician. However, his father encouraged him to study chemistry instead, so Robinson accepted the inevitable and entered the chemistry program at the University of Manchester.

Robinson received his D.Sc. from Manchester in 1910 and lectured there for two additional years. He then accepted successive academic appointments at Sydney, Liverpool, Manchester, London, and finally Oxford University.

Today chemists use computer-driven instruments to determine the structures of unknown organic compounds. In Robinson's era, however, chemists relied less on instruments and more on degrading the compound into smaller, less complex fragments and then piecing them back together again. Using these techniques, Robinson determined the structures of complex alkaloids and worked on the antibiotic penicillin during World War II. His work on the structure of strychnine (see Figure 1) is still regarded as an outstanding example of molecular puzzle solving.

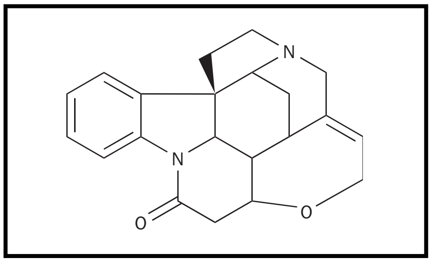

Figure 1. Strychnine.

After structure comes synthesis, and modern chemists synthesize complex medicines and other important compounds using ideas originated by Robinson. But organic synthesis was in its infancy when Robinson started out, and in his stunning synthesis of tropinone (a compound related to cocaine) in 1917, he introduced a novel strategy for preparing complex organic compounds. On paper, Robinson disconnected, or broke, certain bonds in tropinone and arrived at three simpler building blocks. He then went to the laboratory, where he combined the three building blocks using

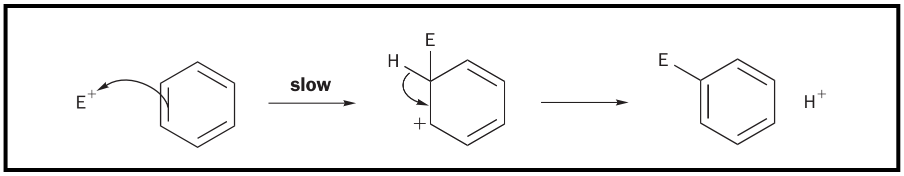

Figure 2. Curly arrows. E+ = an electrophile (a chemical compound or group that is attracted to electrons and tends to accept them).

standard procedures and produced tropinone. This process is now called retrograde synthesis.

Because Robinson wanted to take a systematic approach to organic synthesis, he developed a set of theoretical tools to predict the outcomes of organic reactions. Many important drugs and natural products contain substituted benzene rings, so Robinson began his research by trying to predict the outcomes of substitution reactions in benzene derivatives. He and his wife, Gertrude, successfully explained one class of substitution reactions in a 1917 paper but were unable to provide a general theory.

Using ideas developed in Arthur Lapworth's 1922 paper, Robinson devised a new theory in 1924 that explained the chemistry of unsaturated systems such as benzene and 1,4-butadiene (a four-carbon chain with alternating double bonds). Using his new theory, Robinson successfully predicted the outcomes of chemical reactions in these unsaturated systems. And for the first time ever, he used curly arrows to show the distribution of electrons in conjugated systems and to predict substitution reactions in benzene analogs. Hardly a day goes by when a modern organic chemist does not use curly arrows to explain a reaction mechanism or to plan a synthetic route.

Although Robinson considered the curly arrow concept his most important contribution to knowledge, few chemists know he invented it. Most chemists attribute the discovery to Christopher Ingold. Ingold embraced Robinson's ideas and over time published so many of his own related papers that chemists tended to overlook Robinson's groundbreaking work. Robinson never forgave Ingold for taking credit for his ideas.

Robinson retired from Oxford in 1955 but remained active in the field of chemistry. In his younger days he climbed the Alps, Pyrenees, and major mountains in New Zealand and Norway. Chess was another of his passions: Robinson spent three years as president of the British Chess Federation. He died on February 8, 1975. SEE ALSO ORGANIC CHEMISTRY.

Thomas M. Zydowsky

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Rocketry

The Chinese, in the second century B.C.E., were the first to make simple rockets that used gunpowder for fuel. These simple rockets were fireworks that were used for religious ceremonies. The idea of fireworks soon took on a military usage. Rocket motors were attached to arrows, to greatly extend their range. The same principles that made the rocket arrows fly has allowed people to go to the moon, launch satellites, fly the space shuttle, and even launch rockets that have bowling balls as nose cones. Rocket launches can be seen at Tripoli Rocketry Association and National Association of Rocketry launches throughout the United States. One can see small rockets as well as rockets taller than 14 feet (4.3 meters) being launched.

Rockets fly because of Newton's Third Law of Motion: for every action there is an equal and opposite reaction. Hot gases are produced from the burning of fuel in the rocket motor. The gases push against the inside of the rocket motor as they expand. The hot gas is forced out of the rocket, creating an action force. This creates a reaction force that moves the rocket in the opposite direction. The same thing happens when the end of an inflated balloon is released: the gas escapes in one direction, and the balloon moves in the opposite one.

Until the twentieth century, rockets were small. They were used for firework displays, weapons, to send life lines to ships at sea, and to send signals. Scientists such as Robert Goddard, Konstantin Eduardovich Tsiolkovsky, Hermann Oberth, and Wernher von Braun developed the science and technology that allowed large rockets to fly. In doing so, they developed the science that allowed human space travel.

Goddard realized the potential of rockets and space flight. His analysis of liquid-fuel rocket motors and rocket motors with adjustable thrust, as well as his analysis that rockets could work in space, allowed for the development of today's large rockets. Goddard holds close to seventy patents in rocketry.

In 1903 Konstantin Eduardovich Tsiolkovsky proposed using liquid propellants in rockets, and in 1929 he proposed using multistage rockets as a means of space travel. Hermann Oberth showed that liquid fuels provide a better source of energy for space flight than solid fuels. He worked with young German engineer von Braun to test liquid-fuel motors. Motors were tested in the early 1930s by tossing lit gasoline-soaked rags under a rocket motor, running for cover, and then opening the valve.

Von Braun started to develop rockets for the German army in 1932. He worked in the secret rocket laboratory in Peenemünde, in northeast Germany. He developed the V2 rocket, which served as a guide to start the space programs in the United States and the Soviet Union. This rocket was about 46 feet (14 meters) long and could carry a 2,200-pound (998-kilogram) payload of explosives at speeds of up to 3,500 miles (5,633 kilometers) per hour. Germany first launched the V2 rocket as a weapon of war at Paris on September 6, 1944, and rocket attacks on Britain followed. At the war's end, in 1945, the United States shipped home 100 V2 rockets along with many of the best rocket scientists from Peenemünde. Most of these rockets were launched for scientific research in White Sands, New Mexico. Von Braun spent fifteen years developing missiles for the United States military. He was transferred to NASA in 1960 with a mandate to develop the Saturn rocket, the rocket that went to the moon with the *Apollo* program.

The world of rocketry changed dramatically on October 4, 1957. The Soviet Union launched *Sputnik* to an orbit 340 miles (547 kilometers) high.

A captured German V2 rocket, fired from the USS *Midway,* September 6, 1947. The V2 was used in the first military attacks on a city by a ballistic missile.

The satellite circled Earth, sending back a beeping sound that amazed the world. In 1958 the United States successfully launched the 31-pound (14-kilogram) *Explorer* satellite into space for the first time.

In 1961 humans first reached outer space, when Soviet cosmonaut Yury Gagarin flew for 60 minutes in *Vostok 1*. On May 5, 1961, Alan Shepard Jr. became the first U.S. astronaut to fly in space. Shepard's Project *Mercury* flight lasted 15 minutes. John Glenn became the first American astronaut to circle Earth, on February 20, 1962.

Project *Gemini* launched a capsule for two astronauts. *Gemini's* ten flights provided experiences with space walks, docking, weightless conditions, and spacecraft recovery that made the *Apollo* missions to the moon possible.

On July 20, 1969, Neil Armstrong and Buzz Aldrin landed on the moon, where they collected soil and rock samples, took pictures, and performed experiments.

In 1973 astronauts first spent long missions in space on *Skylab*. This space station enabled experimentation and long stays in space. In 1981 *Columbia*, the first reusable spacecraft, was launched.

Fuels used in the solid-fuel rockets are a mixture of aluminum **metal** and ammonium perchlorate. This fuel is used to power the space shuttle boosters. It also powers amateur rockets flown at Tripoli Rocketry Association and National Association of Rocketry launches.

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

Engines on the space shuttle also burn a mixture of hydrogen and oxygen. The hydrogen and oxygen are compressed and cooled to a liquid in the main fuel tank. When they burn to form water, the **combustion** is so complete that it often does not look like the motor is burning. Liquid-fuel motors may also burn combinations of kerosene and liquid oxygen. Hybrid motors, using a liquid and solid fuel, are used in amateur rocketry. The fuel

combustion: burning, the reaction with oxygen

A full-scale operational model of the Mars *Viking* Lander, with its mechanical soil-collecting arm extended.

is solid cellulose, and the liquid oxidizer is nitrous oxide (N_2O). The hybrid motors are advantageous, as they have a lower cost per flight than does a solid fuel motor.

NASA's Lewis Research Center is applying new battery technology with space flights. Lithium-ion batteries are flat batteries that are connected in series to obtain the required **voltage**. They are more efficient and weigh much less than the rechargeable NiCd batteries. They do not use lithium metal and do not require liquid; instead, they use a solid polymer electrode. Even when subjected to high pressure or shorts, the batteries do not explode. Possible spin-off uses include powering cell phones, laptop computers, and electric vehicles. SEE ALSO New Battery Technology.

voltage: potential difference expressed in volts

Bill Bertoldi

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Röntgen, Wilhelm

GERMAN PHYSICIST
1845–1923

In 1901 Wilhelm Conrad Röntgen (or Roentgen) was the recipient of the first Nobel Prize in physics, awarded to him "in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him." The "remarkable rays" Röntgen called x rays (for want of a better name), but in Germany they very quickly came to be called Röntgen rays. A very shy man, Röntgen declined to give the customary acceptance speech at the awards ceremony.

Röntgen's critical discovery was made in 1895 when he happened to observe that, as a cathode-ray tube was being operated in a darkened room, paper covered with barium platinocyanide lying some distance from the tube "lit up with brilliant fluorescence." The fluorescence of barium platinocyanide was used at that time to establish the presence of invisible rays of the solar spectrum (such as ultraviolet). However, on this occasion, the tube had been surrounded by a close-fitting shield of black cardboard, quite opaque to ultraviolet light or sunlight.

With further experimentation Röntgen learned that the fluorescent screen lit up when it was placed "behind a book of a thousand pages" or "behind two packs of cards." Similarly, tinfoil, blocks of wood, and glass (as long as it contained no lead) offered little resistance to the enigmatic radiation. Moreover, "if a hand be held before the fluorescent screen, the shadow shows the bones darkly, with only faint outlines of the surrounding tissues." Röntgen soon found that his x rays darkened a photographic plate. One of his first x-ray photographs revealed the bone structure of his wife's hand.

When Röntgen first published his results, the macabre revelation of living bone structures created a sensation, and within a month articles on the value of x rays within medicine appeared in major medical journals. x rays have been an invaluable tool in medicine, dentistry, and industry ever since. A roentgen, abbreviated as R, is the international unit of quantity or dose for both x rays and gamma rays. It is equal to the amount of x or gamma radiation that produces as a result of **ionization** one electrostatic unit of charge in one cubic centimeter (0.034 ounces) of dry air.

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

Röntgen was born in Lennap, Germany, in 1845, but his family shortly thereafter moved to Holland. At age sixteen, he entered the Utrecht Technical School, where he remained for three years. He then moved to the Polytechnic Institute in Zurich, where he earned a diploma as a mechanical engineer in 1868 and a Ph.D. degree a year later. He became an assistant to the physicist August Kundt, whom he accompanied to the University of Würzburg in 1871, and then to the University of Strasbourg. The volume of his research output at this time resulted in his being offered the chair of physics at the University of Giessen in Hesse, where he resided from 1879 until 1888. In 1888 he returned to the University of Würzburg as professor of physics and director of its Physical Institute. It was here that he made his momentous discovery of x rays. In 1900 he moved to the University of Munich, from which he retired in 1920. He died in 1923, aged seventy-seven. SEE ALSO RADIATION.

Keith L. Manchester

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Rubber

Rubber is an elastomer—that is, a polymer that has the ability to regain its original shape after being deformed. Rubber is also tough and resistant to weathering and chemical attack. Elastomers can be naturally occurring polymers, such as natural rubber, or they can be synthetically produced substances, such as butyl rubber, Thiokol, or neoprene. For a substance to be a useful elastomer it must possess a high molecular weight and a flexible polymer chain.

Natural Rubber

Natural rubber is one of nature's unique materials. The Native Americans of tropical South America's Amazon basin knew of rubber and its uses long before Christopher Columbus's explorations brought it to the attention of Europeans. The Indians made balls of rubber by smoking the milky, white latex of trees of the genus *Hevea* that had been placed on a wooden paddle, to promote water evaporation and to cure the substance.

Spanish navigator and historian Gonzalo Fernández de Oviedo y Valdes (1478–1557) was the first European to describe these balls to a European audience. In 1615 a Spanish writer enumerated the practical uses of rubber. He reported that the Indians waterproofed their cloaks by brushing them with this latex and made waterproof shoes by coating earthen molds with it and allowing these coatings to dry.

In 1735 interest was revived in this unusual substance when French mathematical geographer and explorer Charles-Marie de La Condamine (1701–1774) sent several rolls of crude rubber to France with an accompanying description of products made from it by the South American natives. Although it met with some use in waterproofing boots, shoes, and garments, it largely remained a museum curiosity. Crude rubber possessed the valuable properties of elasticity, plasticity, strength, durability, electrical nonconductivity, and resistance to water; however, products made from it hardened in winter, softened and became sticky in summer, were attacked by solvents, and smelled bad.

Early Uses

Rubber, sometimes called "gum-elastic," was known to the Indians by the name of *caoutchouc* (from *caa*, "wood," and *o-chu*, "to flow or to weep"). In 1770 English chemist and Unitarian clergyman Joseph Priestley (1733–1804), the discoverer of oxygen, proposed the name "rubber" for the substance because it could be used to erase pencil marks by its rubbing on paper in lieu of previously used bread crumbs.

In 1791 rubber was first used commercially when English manufacturer Samuel Peal patented a method for waterproofing cloth by treating it with a solution of rubber in turpentine. In 1820 the modern rubber industry began when English coachmaker and inventor Thomas Hancock (1786–1865) established the first rubber factory. He was the first to compound rubber with other materials to be shaped into molds, a common modern industrial practice.

In 1823 Scottish chemist and inventor Charles Macintosh (1766–1843) began to manufacture double-textured rainproof garments known as "mackintoshes." He made these by introducing a coal tar naphtha solution of rubber between two pieces of fabric, thus circumventing the sticky (when warm) and brittle (when cold) surfaces associated with single-textured rubber-containing garments.

Composition and Structure

Crude rubber is primarily hydrocarbon in nature. In 1826 English chemist Michael Faraday (1791–1867) analyzed natural rubber and found it to have the empirical (simplest) formula C5H8, along with 2 to 4 percent protein and 1 to 4 percent acetone-soluble materials (resins, fatty acids, and sterols). In 1860 English chemist Charles Hanson Greville Williams (1829–1910) confirmed Faraday's analysis and in 1862 distilled natural rubber to obtain the pure monomer, which he named **isoprene**. He determined isoprene's vapor density and molecular formula, and he showed that it polymerizes to a rubbery product—an observation that led to the notion that rubber is a linear polymer of isoprene, proposed in 1910 by English chemist Samuel Shrowder Pickles (1878–1962).

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

The molecular weights of rubber molecules range from 50,000 to 3,000,000. Sixty percent of the molecules have molecular weights of greater than 1,300,000. The repeating unit in natural rubber has the *cis* configuration (with chain extensions on the same side of the ethylene double bond), which is essential for elasticity. If the configuration is *trans* (with chain extensions on opposite sides of the ethylene double bond), the polymer is either a hard plastic (naturally occurring gutta-percha, obtained from the leaves of *Palaquium*, a species of sapotaceous Malaysian and East Indies trees) that was used for wire and cable coating during the nineteenth century; or a substance like gutta-percha (balata, obtained from *Mimusops globosa*, trees native to Panama and South America), used for modern golf ball covers.

Vulcanization

Because there are few (if any) cross-links in the chains of rubber molecules, natural rubber is thermoplastic; that is, it becomes soft and sticky in summer and hard and brittle in winter. It is also malodorous and softened or dissolved by various solvents, as noted. These undesirable properties of natural rubber were not overcome until 1839, when American inventor Charles Goodyear (1800–1860), at the end of five years of constant experimentation, accidentally placed a sample of rubber mixed with sulfur and litharge (lead oxide, PbO) on a hot stove in Woburn, Massachusetts. The operation converted rubber into a heavily cross-linked, and therefore insoluble and infusible, thermosetting polymer or "thermoset." William Brockedon, a friend of Hancock's, named Goodyear's curing process "vulcanization" (after Vulcan, the ancient Roman god of fire and metalworking). Goodyear later used the term, but only reluctantly.

In practice, vulcanization was so simple that many persons used it without paying royalties, and Goodyear spent much of his time contesting approximately sixty infringements of his patent. He died a pauper and left behind debts estimated at between $200,000 and $600,000. His name lives on in Goodyear tires and Goodyear blimps.

Paradoxically, neither Goodyear nor any of his family members or descendents were involved with the Goodyear Tire and Rubber Company, whose founder, Frank A. Seiberling, named it to honor one of America's most famous inventors and the founder of an industry that is indispensable to modern life. In 1851 Goodyear's brother Nelson used sulfur to convert natural rubber into ebonite, the first thermosetting plastic.

The Modern Rubber Industry

Vulcanization marked the birth of the modern rubber industry, and although later discoveries have somewhat modified Goodyear's original procedure, today it remains essentially the same as his process of 1839. Vulcanization is still an imperfectly understood chemical reaction between rubber and sulfur. It results in cross-linking between linear chains of rubber molecules and prevents slippage of the chains as the material retains the desired elasticity.

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

Temperatures of 140–180°C (184–356°F) are used for modern vulcanization, and additives other than sulfur are often used. Accelerators permit the reaction to occur at lower temperatures and in less time, and antioxidants prolong the life of rubber products by reducing the deterioration that is caused by atmospheric oxygen (or ozone), which breaks **covalent bonds** and lowers the molecular weight. Reinforcing agents (e.g., carbon black) increase stiffness, tensile strength, and resistance to abrasion. Coloring agents and fillers are sometimes added.

The Search for Substitutes

The earliest synthetic polymers were synthetic rubbers. Before 1920 natural rubber was the only available elastomer, but constant attempts, with varying degrees of success, to develop commercial rubber substitutes had been made previously, especially by English and German chemists, who competed with each other in the search.

As mentioned, natural rubber is a polymer consisting of repeating units of isoprene, its "mother substance." Scientists at first sought an exact chemical equivalent. But they attained their first success in preparing a suitable substitute only when they abandoned their attempts to synthesize rubber from isoprene, butadiene, or other dienes (hydrocarbons with two double bonds) and tried to synthesize an original polymer that possessed the physical properties of natural rubber.

The development of a synthetic rubber was a slow process, because it was almost impossible for the early synthetic products to compete economically with cheap natural rubber and because they were not as good as natural rubber for most uses. The driving force in the search for synthetic rubber was the shortages created by wartime needs.

CARL "SPEED" MARVEL (1894–1988)

During World War II, the United States was almost entirely blockaded from its rubber suppliers. Carl Marvel became a part of the successful effort to meet the demand for synthetics. Along with others, he worked to increase the efficiency and production of existing rubber syntheses.

—Valerie Borek

During World War I German chemists, whose country was cut off from its sources of natural rubber by the British blockade, polymerized 3-methylisoprene (2,3-dimethyl-1,3-butadiene) units, ($CH_2{=}C(CH_3)C(CH_3){=}CH_2$), obtained from acetone, to form an inferior substitute called methyl rubber. By the end of the war Germany was producing 15 tons (13.6 metric tons) of this rubber per month. The USSR (Union of Soviet Socialist Republics), which built a **pilot plant** at Leningrad (now St. Petersburg) in 1930 and three factories in 1932 and 1933, was the first country to institute a full-scale synthetic rubber industry.

pilot plant: intermediate stage of testing for chemical process, between bench-top and production scale

Two Serendipitous Discoveries

During World War II the United States, cut off from India, Ceylon (now Sri Lanka), Malaysia, and the Dutch East Indies (areas which, since the late nineteenth century, had replaced South America as the main suppliers of natural rubber), developed several superior synthetic rubbers. The U.S. synthetic rubber industry originated from two discoveries that were serendipitous; that is, they occurred while the researchers were searching for something else.

In 1922 independent inventor and physician Joseph C. Patrick (1892–1965) was trying to make ethylene glycol ($HOCH_2CH_2OH$) to be used as antifreeze. Instead he discovered Thiokol (a trade name that has become generic), a rubbery polysulfide condensation product of ethylene dichloride and sodium tetrasulfide. This early product is still used for gaskets, sealants, sealer adhesives, and hoses because it is resistant to oil and organic solvents.

In 1931 Arnold Collins, a chemist in the Du Pont research group of Wallace Hume Carothers (1896–1937), the discoverer of nylon, discovered neoprene accidentally while studying the by-products of divinylacetylene ($H_2C{=}CH\text{-}C{\equiv}CH$). There are several types of neoprenes. They have high tensile strength, high resilience, and excellent resistance to oxygen, ozone, other chemicals, and oil. They also resist heat, flame, and tearing. They are good general-purpose rubbers, but they are limited to uses requiring rubbers with special properties because of their high cost.

Other Synthetic Rubbers

In 1937 Robert McKee Thomas (1908–1986) and William Joseph Sparks (1904–1976) at the Standard Oil Development Company (now Exxon) synthesized butyl rubber via the copolymerization (polymerization of a mixture of monomers) of isobutylene (2-methylpropene $(CH_3)_2C{=}CH_2$) with a small amount of isoprene.

By 1929 the German firm I. G. Farben developed a series of synthetic rubbers similar to those produced in the USSR. They were called Buna rubbers ("Bu" for butadiene, one of the copolymers, and "na" for sodium, the polymerization **catalyst**). They included the oil-resistant Buna S (S for styrene) and Buna N (N for nitrate). Buna S, styrene butadiene rubber, is currently called SBR, and it is produced at about twice the volume of natural rubber, making it the most common synthetic rubber. Buna N, acrylonitrile-butadiene rubber, is now called NBR. During World War II the United States produced these rubbers for the American war effort.

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

stereospecific: yielding one product when reacted with a given compound but the opposite product with its stereoisomer

While earlier attempts to produce satisfactory synthetic rubber from isoprene were unsuccessful, in 1955 American chemist Samuel Emmett Horne Jr. (b. 1924) prepared 98 percent *cis*-1,4-polyisoprene via the **stereospecific** polymerization of isoprene. Horne's product differs from natural rubber only in that it contains a small amount of *cis*-1,2-polyisoprene, but it is indistinguishable from natural rubber in physical properties. First produced in 1961, BR (for butadiene rubber), a rubberlike polymer that is almost exclusively *cis*-1,4-polybutadiene, when blended with natural or SBR rubber, has been used for tire treads.

Polyurethane (PU) was first synthesized in the 1930s by German chemist Otto Bayer (1902–1982), who was trying to prepare a nylonlike fiber. PU is a versatile polymer that is used for rigid and flexible foams, bristles, coatings, fibers, and automobile parts, such as bumpers. Other synthetics are used in products such as stretchable fabrics and binders for paints.

After the end of World War II the American synthetic rubber industry declined sharply. However, by the early 1950s, as better and more uniform synthetic rubbers became available, it underwent a renaissance. By the early 1960s the amount of synthetic rubber produced worldwide equaled that of natural rubber, and it has increased steadily ever since. Although natural rubber performs well for most uses, some of the newer synthetics are superior to it for specialized purposes. Today rubber is indispensable for a variety of products and industries, and our modern world, with its many necessities and luxuries, would be unthinkable without it. SEE ALSO POLYMERS, NATURAL; POLYMERS, SYNTHETIC.

George B. Kauffman

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

37
Rb
RUBIDIUM
85.4678

Rubidium

MELTING POINT: **39.5°C**
BOILING POINT: **688°C**
DENSITY: **1.532 g/cm^3**
MOST COMMON IONS: **Rb^+**

Rubidium is a soft, silvery alkali **metal** that reacts explosively with water. The word *rubidium* is derived from "rubidus" (Latin for "deepest red"), due

Rubidium is the sixteenth most abundant element in the earth's crust. Among its compounds' uses are as batteries.

to the deep red lines observed by Robert Bunsen and Gustav Kirchoff during their analysis of lepidolite ore using a spectroscope in 1861. Currently, rubidium metal is obtained via the electrolysis of molten RbCl or by treating molten RbCl with calcium and distilling the mixture. Rubidium is usually obtained as a by-product of lithium processing because it is found in low concentrations in the minerals lepidolite, carnallite, and pollucite, as well as in the brines at Searles Lake, California. It is the sixteenth most abundant element in Earth's crust (about 78 ppm). Rubidium is never found in its elemental state in nature. It is the second most electropositive element and will ignite in air (unlike Na and K). Rubidium burns yellow-violet in the flame test.

The demand for rubidium metal and its compounds is quite small. The metal is used as a getter to remove oxygen in vacuum tubes. The crystalline compound $RbAg_4I_5$ has a conductivity similar to dilute sulfuric acid, which may make it useful in batteries and other electrochemical applications. Rubidium carbonate, Rb_2CO_3, is used in the manufacture of specialized glasses. SEE ALSO Alkali Metals.

Nathan J. Barrows

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Rust *See Corrosion.*

44
Ru
RUTHENIUM
101.07

Ruthenium

MELTING POINT: 2,310°C
BOILING POINT: 3,900°C
DENSITY: 12.2 g/cm^3
MOST COMMON IONS: Ru^{2+}, Ru^{3+}, $RuO_4{}^{2-}$, $RuO_4{}^{-}$

Ruthenium was discovered in 1844 in ores extracted from the Ural Mountains in Russia by Karl Klaus, who named it after *Ruthenia*, the Latin name for Russia. Its abundance in Earth's crust is about 0.0001 ppm. Ruthenium crystallizes in the hexagonal close-packed arrangement, is lustrous, and is silvery in color. It is used primarily to harden platinum and palladium in **alloys**. It is extracted from platinum **metal** ore concentrates and isolated as a gray powder or a sponge using chemical techniques. Ruthenium will dissolve in fused KOH to give $K_2[RuO_4]$. It will react with F_2 to give RuF_5, and with Cl_2, Br_2, or I_2 to yield RuX_3, where X = Cl, Br, or I. It also combines with the elements As, P, Si, and B at high temperatures to form binary compounds of various stoichiometries, and with air upon heating to yield RuO_2. RuO_4 (mp 25.5°C, or 77.9°F), a powerful oxidizing agent, is obtained by reaction of ruthenium in acidic solution with oxidizing agents such as MnO_{4-} and has found use as a **catalyst** in the **oxidation** of various substrates. In the +2 and +3 oxidation states, ruthenium forms numerous coordination complexes with **ligands** containing carbon, nitrogen, phosphorus, oxygen, and sulfur donors. It also forms oxo- and ligand-bridged binuclear and trinuclear metal complexes, such as $[(NH_3)_5Ru–N–N–Ru(NH_3)_5]^{4+}$ and $[(NH_3)_5Ru–O–Ru(NH_3)_4–O–Ru(NH_3)_5]^{6+}$, and dioxo-compounds such as *cis*- or *trans*- $[Ru(bpy)_2(O)_2]$, where bpy is 2,2′-bipyridine. In the lower oxidation states, ruthenium together with carbonyl, phosphine, and/or hydrido ligands form alkene, diene, alkyne, and allyl complexes. SEE ALSO PALLADIUM; PLATINUM.

D. Paul Rillema

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

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

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

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

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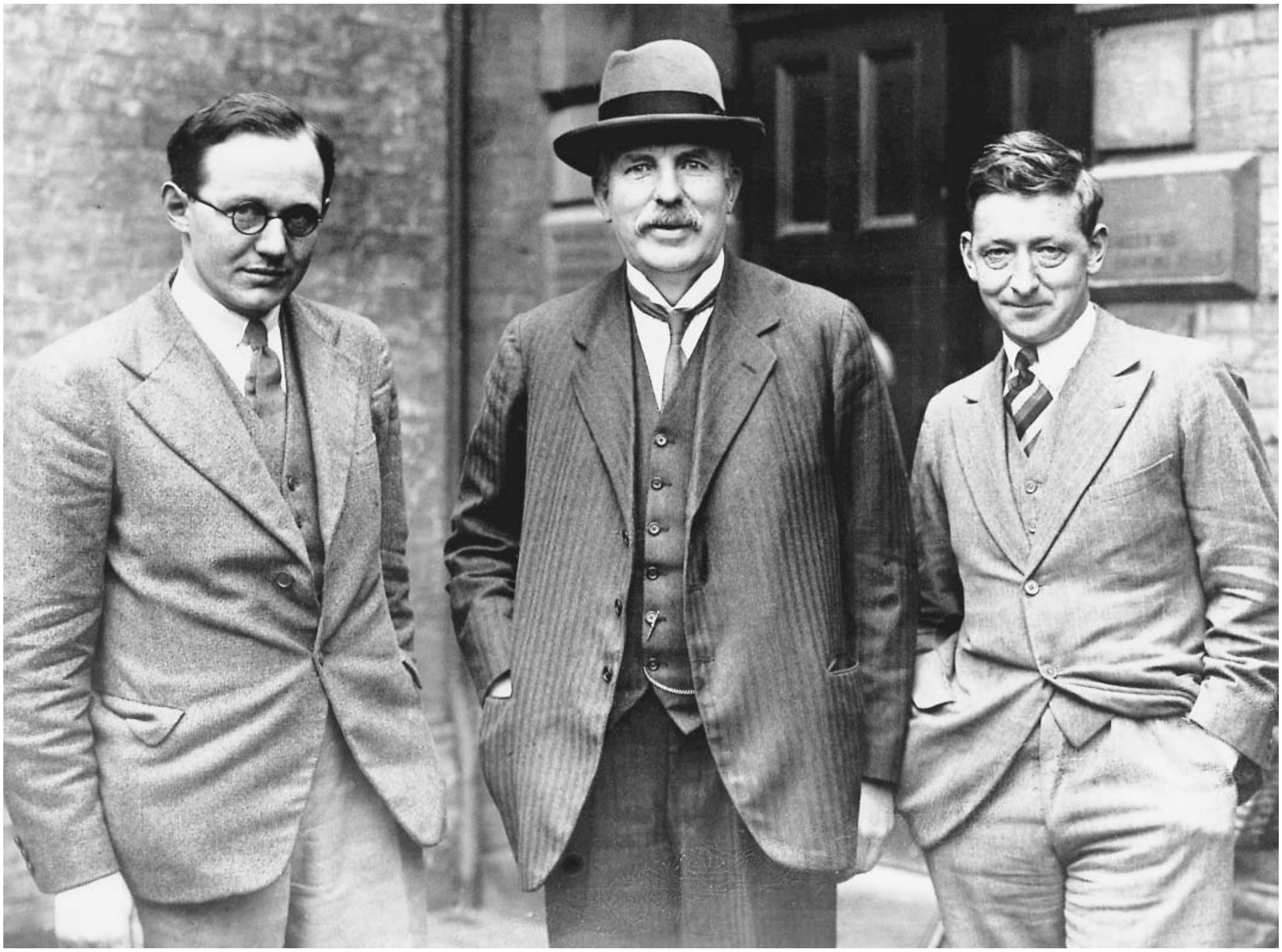
Rutherford, Ernest

BRITISH PHYSICIST
1871–1937

Ernest Rutherford was born on August 30, 1871, near Nelson, New Zealand. He was a very good student, excelling at science and mathematics. In 1889 Rutherford won a scholarship to study at Canterbury College, Christchurch, New Zealand, and it was at college that he began his work as a scientist. He conducted experiments on the speed of induction in iron placed in rapidly alternating magnetic fields. In 1894, in part because of his original work, he was awarded a scholarship to study at Trinity College, Cambridge, with famed physicist J. J. Thomson. At first he continued his research on magnetism, but by 1896 Rutherford and Thomson were working together on the conductivity of electricity in gases using x rays.

Rutherford's skill and experience in conceiving and building delicate experimental apparatus were crucial to another project that would prove to be



British physicist Ernest Rutherford (middle), recipient of the 1908 Nobel Prize in chemistry, "for his investigations into the disintegration of the elements, and the chemistry of radioactive substances."

his most important contribution to science. Following his research on x rays, Rutherford began to study the effect of radiation from uranium on the conductivity of gases. During this work, he determined that there were two kinds of radiation, which he called α and β rays. These could be distinguished by their ability to penetrate materials: α rays would not pass through a thin piece of paper; β radiation was more powerful and could penetrate thin sheets of **metal** foil.

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

In 1903, with the scientist Frederick Soddy, Rutherford concluded that radiation was caused by atoms of radioactive material breaking apart. The tiny bits that broke off were the α and β rays. This was a revolutionary idea, since it had been a basic principle of physics and chemistry that atoms were the smallest possible particles of matter and therefore indivisible. Rutherford went on to demonstrate that **α-particles** were, in fact, a form of the helium atom. He did this by placing a delicate glass bulb containing radon gas, which emitted α-particles, in an evacuated tube. The particles would penetrate the glass of the bulb but not escape the tube, and could then be analyzed.

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

As part of these studies, Rutherford and his assistant Hans Geiger created an α-particle detector (known today as the Geiger counter) in 1908. In 1909 Rutherford gave his student Ernest Marsden the task of studying whether metal would deflect the path of an α-particle. This was the well-known gold foil experiment, in which it was observed that one particle in about 8,000 bounced off a thin foil of gold rather than passing through it. This surprised everyone, and as Rutherford stated, "It was about as credible as if you had fired a 15-inch shell at a piece of tissue paper and it came back and hit you" (Glasstone, p. 93). Rutherford showed that the collision had to occur with something that was small and very massive (compared to the α-particle) and that carried an electrical charge.

These experiments led to Rutherford's 1911 hypothesis that the atom consisted of a hard core (named the *nucleus* in 1912) that contained almost all the mass of the atom and had a positive charge, and that the electrons, which had little mass and a negative charge, orbited the core at a distance. Rutherford's work transformed the concept of the atom from that of a solid body into one of mostly empty space. Although the new model explained the experimental results, it was not compatible with classical physics. If the electrons orbited the nucleus like planets orbit the Sun, they would slow down and collapse into the center. In 1912 the Danish physicist Niels Bohr arrived in England to work with Rutherford, and he applied the quantum theory of the German physicist Max Planck to the model. According to this theory, electrons could only gain or lose energy in fixed amounts called **quanta**. So long as an electron did not change its orbit, it would never collapse into the nucleus. Although there have been further refinements to the Bohr-Rutherford model of the atom—for example, electrons do not actually orbit—it is an important model of atomic structure.

quantum: smallest amount of a physical quantity that can exist independently, especially a discrete amount of electromagnetic energy

Rutherford won many awards for his work as a scientist and teacher. He won the Nobel Prize for chemistry in 1908 and was knighted in 1914. In 1919 he became the Cavendish Professor of Physics at Cambridge. He was made Lord Rutherford of Nelson in 1931. Rutherford died at Cambridge on October 19, 1937. SEE ALSO Bohr, Niels; Marsden, Ernest; Soddy, Frederick; Thomson, Joseph John.

Andrew Ede

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104
Rf
RUTHERFORDIUM
261

Rutherfordium

MELTING POINT: **Unknown**
BOILING POINT: **Unknown**
DENSITY: **Unknown**
MOST COMMON IONS: **Unknown**

Rutherfordium is the first transactinide element. It was discovered in 1969 by Albert Ghiorso and his coworkers, who carried out the reactions ^{249}Cf

(^{12}C, 4n) → ^{257}Rf (half-life of approximately 3.8 seconds) and ^{249}Cf (^{13}C, 3n) [→] ^{259}Rf (half-life of approximately 3.4 seconds). There are ten known **isotopes** of rutherfordium, having mass numbers that range from 253 to 262, the isotope with the longest measured half-life being ^{261}Rf (half-life of approximately 1.1 minutes). After its discovery, it was postulated that rutherfordium, as the first transactinide element, should be a member of a new, fourth transition series, extending from Z=104 to Z=112, and an atom in which the *6d* electronic shell is filled. The outer orbital electronic configuration of Rf should be $[Rn]5f^{14}6d^{2}7s^{2}$. As such, it should behave similarly to its analogs titanium and hafnium and should form **volatile** tetrachlorides that are *less* volatile than $HfCl_4$. The first gas **chromatographic** studies showed that rutherfordium forms *more* volatile chlorides than hafnium—a deviation from Periodic Table trends that was predicted from **relativistic calculations**. The first aqueous chemistry studies showed the neutral and anionic complexes of Rf to behave like the corresponding complexes of the Group IVB elements, rather than of the trivalent actinides, demonstrating that Rf is indeed a transactinide. Detailed studies of the extraction chromatography of Rf complexes have shown chemical behavior similar to that observed of Rf complexes in gas chromatographic experiments—that is, Rf does not behave as expected according to a simple extrapolation of Periodic Table trends, but in a more complicated manner. For example, in the extraction of substances with tributylphosphate, the extraction sequence Zr > Rf > Hf is observed. These and other experiments show that the aqueous chemistry of rutherfordium is a challenge to current relativistic molecular theories. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Thorium; Uranium.

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

volatile: low boiling, readily vaporized

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

relativistic calculation: quantum mechanical model that includes the effects of relativity, particularly for core electrons

Walter Loveland

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Rydberg, Johannes

SWEDISH MATHEMATICIAN AND PHYSICIST
1854–1919

Johannes Robert Rydberg was born in Halmstad, Sweden, on November 8, 1854. His father, Sven, was a local merchant and minor shipowner who died when Rydberg was young. Rydberg attended the local gymnasium (or high school) in Halmstad and studied languages, religion and philosophy, history and geography, and natural history, along with mathematics and physics. Although a good all-around student, Rydberg chose to pursue mathematics at the university.

He entered the University of Lund in the autumn of 1873, and it is fair to say that he never left. He received his doctorate in mathematics from that institute in 1879 and was appointed a teacher of mathematics there in 1881. But in 1876 Rydberg was also appointed as a teaching assistant at Lund's physics institute. His experimental study on friction electricity led to a position as a teacher of physics in 1882.

As a physicist and mathematician, Rydberg was driven by a desire to understand the basic physical laws behind the Periodic Table. He set out to

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

find order in the mass of **spectroscopic** data that was then available. Atomic spectra had been used to characterize minerals and to ascertain the chemical composition of distant stars, but the underlying order was not apparent. While various spectroscopists had noted that line spectra could be discriminated into "sharp," "principal," and "diffuse" patterns, a guiding relationship between the lines had not yet emerged.

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

Rydberg decided to use the wave number as a measure of frequency in his calculations. A wave number is the reciprocal of the wavelength, and, although Rydberg did not know this at the time, it is directly related to energy, unlike the more common wavelength that bears an inverse relationship. Having made this change, patterns began to emerge in the data with a particular series of lines for any atom leading to a **hyperbolic relationship**. Indeed, the same relationship was observed for all the different spectroscopic series and for different elements.

Rydberg devised the formula

$$n = n_0 - N_0/(m + m')^2$$

and was testing it against the data when the Swiss mathematician and physicist Johann Balmer published his result for hydrogen atoms, wavelength = $hm^2/(m^2 - 4)$. Rydberg quickly realized that this was just a special case of his formula with $m' = 0$ and $N_0 = 4n_0$ and that N_0 must be a universal constant. Using this information, Rydberg was able to show that his equation was more general and published it in 1890, well before the spectroscopic series discovered by Balmer, the American Theodore Lyman, or the German Friedrich Paschen provided experimental confirmation.

The formula is now written as

$$1/\lambda = \mathrm{R_H}(1/\mathrm{n_1}^2 - 1/\mathrm{n_2}^2)$$

nuclear: having to do with the nucleus of an atom

where both values of n are integers, but n_2 n_1. The term N_0 has been replaced by R_H, the so-called Rydberg constant. It is a fundamental constant of nature and a measure of the strength of the **nuclear**-electron interaction in atoms. SEE ALSO BALMER, JOHANN JAKOB; SPECTROSCOPY.

Todd W. Whitcombe

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S

Saccharides ***See Carbohydrates.***

Saccharine ***See Artificial Sweeteners.***

Salt

The word "salt" is a general chemical term that refers to ionic compounds formed when an acid reacts with a base. They may be simple salts such as

A large pile of salt at an Uppington, South Africa, salt mine.

NaCl, KCl, and Na_2SO_4; acid salts like $NaHCO_3$ and NaH_2PO_4; or double salts like $KAl(SO_4)_2$. Table salt is sodium chloride, a chemical compound with the formula NaCl. Sodium chloride has been used to flavor and preserve food for thousands of years. As a result, salt became an essential part of commercial transactions and was often used as money or barter. Exchange of salt for slaves in ancient Greece gave rise to the expression "not worth his salt." The Romans gave a *salarium* (salary) to those who were "worth their salt," and Roman soldiers were given salt rations known as *salaria argenta*. Today, salt continues to be of major economic importance, with thousands of uses in addition to flavoring and preserving food.

Sodium chloride forms colorless, cubic crystals that are made up of large numbers of NaCl formula units, to give a three-dimensional crystalline **lattice** in which each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. The strong electrostatic attractions between the positive and negative ions, known as ionic bonds, hold the solid sodium chloride together.

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

Sodium chloride occurs naturally as the mineral halite, commonly called rock salt, in large underground deposits on every continent. Seawater contains about 3.5 percent dissolved minerals, of which 2.8 percent is sodium chloride and the other 0.7 percent is primarily calcium, magnesium, and sulfate ions. Natural brines, or salty waters other than seawater, are found in wells and lakes, such as the Great Salt Lake of Utah and the Dead Sea. Salt is also found in surface deposits in regions subject to arid climates.

The manufacture and use of salt is one of the oldest chemical industries. The three main methods for recovering salt are: (1) underground salt mining, which uses techniques similar to those for mining coal; (2) solar evaporation of seawater or natural **brine** in lakes or large lagoons; and (3) evaporation of brines obtained by pumping water into a rock salt deposit, dissolving the salt, and bringing the brine to the surface. If the salt is going to be used for food flavoring or preservation, additional purification is required, usually by methods that use multi-stage evaporation of brine solutions. The annual world salt production is about 200 million tons (181,436,948 metric

brine: water containing a large amount of salts, especially sodium chloride (NaCl) tons). The top producers are the United States and China with 45 million and 30 million tons (40,823,313 and 27,215,542 metric tons), respectively.

Uses

Table salt is pure salt that has been ground into fine particles. Because salt tends to cake in humid climates, an anti-caking agent such as magnesium carbonate or calcium silicate is often added. Table salt is also available as iodized salt with 0.1 percent potassium iodide by weight. Because iodide ion is essential to thyroid gland function, the routine use of iodized salt ensures adequate iodine in the diet.

Salt is used to cure meat and fish by soaking them in brine, rubbing salt onto them, or injecting them with a salt solution. Bacon and cured ham are examples of meats preserved by the use of salt. Salt is also used to make pickles by soaking cucumbers in brine.

Rock salt is sprinkled on highways to melt ice. The lowest temperature at which salt can melt ice is −21°C (−6°F), at a concentration of 23 percent salt, and it works best when temperatures are at or slightly below freezing, 0°C (32°F).

Nearly half of the 45 million tons (40,823,313 metric tons) of salt produced each year in the United States is used in the chemical manufacture of chlorine and sodium hydroxide (caustic soda) by electrolysis of brine solution

$$2\ \mathrm{NaCl}\ (aq) + 2\ \mathrm{H_2O}\ (l) \rightarrow 2\ \mathrm{NaOH}\ (aq) + \mathrm{H_2}\ (g) + \mathrm{Cl_2}\ (g)$$

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

Electrolysis of molten sodium chloride produces sodium **metal** and chlorine gas

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

Salt is also one of the raw materials used in the Solvay process for manufacturing sodium carbonate (soda ash).

Both sodium chloride and potassium chloride are essential to the electrolyte balance in body fluids. Good health depends on the proper ratio of potassium ions to sodium ions. Typical values are greater than one. Natural, unprocessed foods have high K^+/Na^+ weight ratios. Fresh, leafy vegetables average a K^+/Na^+ ratio of 35, and fresh, non-leafy vegetables and fruits average a ratio of 360, with extreme values of 3 for beets and 840 for bananas. After such foods are eaten, the body achieves K^+/Na^+ ratios of greater than 12. However, during processing (and cooking, if foods are boiled), both potassium and sodium compounds are dissolved by the water used, which is then discarded. The sodium ions are replenished by the salting of the food, which gives it a lower K^+/Na^+ weight ratio. One solution is to eat unprocessed, natural foods and to salt foods with a commercial product that contains both potassium and sodium chlorides called "Lite Salt." SEE ALSO ALKALI METALS; CHLORINE; HALOGENS; SODIUM.

Melvin D. Joesten

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Samarium

MELTING POINT: 1,072°C
BOILING POINT: 1,900°C
DENSITY: 7.536 g/cm^3
MOST COMMON IONS: Sm^{2+}, Sm^{3+}

62
Sm
SAMARIUM
150.36

In 1886, French chemist P. E. Lecoq de Boisbaudran, working with the mixture of oxides known as didymia, isolated the element gadolinium and, three years later, a mixture known as samaria. Working with this mixture, Eugene-Anatole Demarçay (1901) discovered the elements europium and samarium (getting its name from the mineral samarskite). The element comprises 6.47 $\times 10^{-4}$ percent of the igneous rocks of Earth's crust. The important minerals are bastnasite (in which are found fluorocarbonates of the cerium group), and monazite and xenotime (in which are found phosphates of the cerium and yttrium group, respectively). Two crystal structures exist: α-Sm (at room temperature to 917°C) and β-Sm (at >917°C, body-centered cubic).

The chemistry of samarium(III) is essentially that of all the **lanthanide** (III) ions. Sm(III) can be reduced to Sm(II) under special conditions, but in solution it is rapidly oxidized to the +3 state. With respect to the solid state, the halides (SmX_2) and some chalogenides(II) (oxide, sulfide, selenide, and telluride compounds) have been obtained. SmF_3, together with the oxide, hydroxide, carbonate, oxalate, and phosphate compounds are insoluble in **aqueous solution**. The halide, perchlorate, nitrate, and acetate compounds are water-soluble.

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

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

The commercially important samarium-containing minerals are treated with concentrated sulfuric acid or, in the case of monazite, with a solution of sodium hydroxide (73%) at approximately 40°C (104°F) and under pressure. The element is separated from the solutions via solvent extraction or ion exchange. Sm^{3+} salts are weakly yellow and may exhibit ion emission. Sm^{2+} ions show luminescence and are sometimes used to generate lasers. Samarium is used in the manufacture of headphones and tape drivers. SEE ALSO CERIUM; DYSPROSIUM; ERBIUM; EUROPIUM; GADOLINIUM; HOLMIUM; LANTHANUM; LUTETIUM; NEODYMIUM; PRASEODYMIUM; PROMETHIUM; TERBIUM; YTTERBIUM.

Lea B. Zinner

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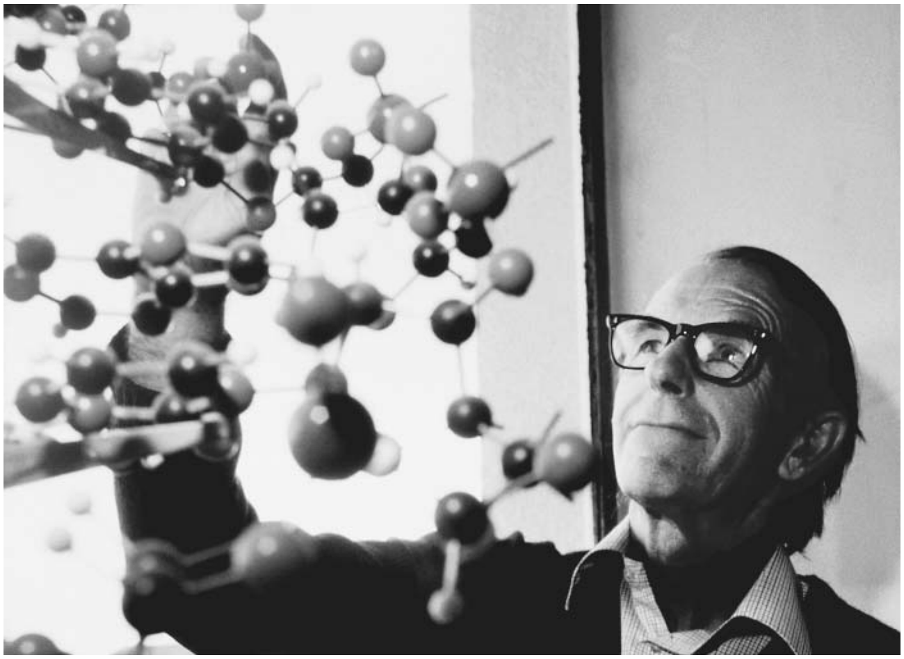
Sanger, Frederick

BRITISH CHEMIST
1918–

Frederick Sanger is surely one of the most outstanding biochemists of modern times. His methods for determining the exact sequence of amino acids in proteins and of nucleotides in deoxyribonucleic acid (**DNA**) have won him numerous awards, including two Nobel Prizes in chemistry.

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

Sanger was born on August 13, 1918, in the village of Rendcombe in Gloucestershire, England. He attended St. John's College, Cambridge Uni-



British biochemist Frederick Sanger, recipient of the 1958 Nobel Prize in chemistry, "for his work on the structure of proteins, especially that of insulin," and co-recipient, with Walter Gilbert and Paul Berg, of the 1980 Nobel Prize in chemistry, "for their contributions concerning the determination of base sequences in nucleic acids."

versity, from which he received a B.A. in biochemistry in 1939. He remained at Cambridge as a conscientious objector during World War II and earned his Ph.D. in biochemistry for work on amino acid **metabolism** and the nitrogen of potatoes with Albert Neuberger in 1943. Later that year he joined Antony C. Chibnall's group at Cambridge and began research on proteins and, in particular, insulin.

The basic principles of protein chemistry were firmly established when Sanger started his work on insulin. It was known that proteins were composed of amino acids linked through amide bonds to form long **polypeptide** chains. Although the relative number of each of the twenty amino acids could be obtained for a given protein, the particular order, or sequence, of those amino acids in the protein had never been determined. Sanger saw sequence as the key to understanding living matter and set out to determine the exact sequence of amino acids in insulin.

Sanger first needed to characterize the free amino groups in insulin. For this he developed a **reagent**, dinitrofluorobenzene (FDNB), that reacted with amino groups present in proteins to form an acid-stable dinitrophrenyl (DNP) derivative. The DNP protein was treated with acid to break the polypeptide backbone, and the free DNP amino acid derivatives were isolated and compared to standards prepared from known amino acids. In this way, Sanger determined that insulin was made up of two peptide chains: one (chain A) with an amino-terminal glycine residue and another (chain B) with an amino-terminal phenylalanine. Subsequent work revealed that chain A was composed of twenty amino acids and chain B thirty-one.

The individual chains were then broken down into smaller components: Acid was used to **cleave** the polypeptide backbone, performic acid was used to break the cysteine **disulfide bonds**, and proteolytic enzymes were used to **hydrolyze** the polypeptide at specific sites on the chain. The reaction products were separated from each other and their sequence determined.

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)

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

reagent: chemical used to cause a specific chemical reaction

cleave: split

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

hydrolyze: to react with water

Sanger was able to deduce the complete sequence of insulin after twelve years of painstaking research and molecular puzzle solving. The Nobel committee was quick to recognize Sanger's accomplishment and awarded him the 1958 Nobel Prize in chemistry for "his work on the structure of proteins, especially that of insulin."

In 1962 Sanger moved to the Medical Research Council Laboratory of Molecular Biology in Cambridge, where he became interested in nucleic acid sequencing. He and his colleagues developed a cleave-and-sequence method for small ribonucleic acid (RNA) molecules, but they soon realized that a different method was needed to sequence the much larger DNA molecules. For DNA sequencing, he chose to investigate copying procedures.

Sanger eventually settled on a procedure that uses DNA polymerase to copy short fragments (200 nucleotides) of single-stranded DNA obtained from enzyme-catalyzed cleavage of the parent DNA. In addition to the usual radiolabeled deoxyribonucleotide triphosphates, the DNA **synthesis** cocktail contains a $2'$, $3'$-dideoxy analog that is incorporated into the growing DNA strand and blocks further DNA synthesis. After repeating the reaction using each of the remaining dideoxy nucleotides, the various chain-terminated fragments are separated by gel **electrophoresis** and the DNA sequence read directly from the gel. Sanger used this method to sequence a DNA containing more than 5,000 nucleotides and shared the 1980 Nobel Prize in chemistry for "contributions concerning the determination of base sequences in nucleic acids."

synthesis: combination of starting materials to form a desired product

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

Sanger retired in 1983 after forty years of service at the Medical Research Council and after helping to usher in a new era in biology and medicine. SEE ALSO DNA REPLICATION; INSULIN; PROTEINS.

Thomas M. Zydowsky

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Scandium

MELTING POINT: 1,539°C
BOILING POINT: 2,832°C
DENSITY: 2.989 g/cm^3
MOST COMMON IONS: Sc^{3+}

21
Sc
SCANDIUM
44.9559

Drawing on his periodic law and his categorization of the elements, Russian chemist Dimitri Mendeleev predicted the existence of element 21 in 1871. However, it was not until 1879 that Swedish chemist Lars Frederick Nilson identified the element scandium as part of a novel compound he had isolated. Working with 10 kilograms (22 pounds) of euxenite, a mineral found only in Scandinavia at that time, Nilson eventually succeeded in purifying 2 grams (0.07 ounces) of what later became known as scandium oxide.

Since its discovery, scandium has been found only in several rare minerals. It is found in highest concentration in the Norwegian mineral thortveitite (35–40% scandium). Its abundance in Earth's crust is a point of conjecture; it is generally agreed that scandium occurs in greater abundance in the Sun and certain stars.

In addition to forming an oxide (scandium oxide, Sc_2O_3), scandium is capable of forming a number of colorless salts. For instance, scandium reacts with **halogens** to form halides that have the formula ScX_3 (where X = F, Cl, Br, or I). Additionally it occurs as an aqua ion, $[Sc(H_2O)_6]^{3+}$, which undergoes hydrolysis to form hydroxide-bridged **metal** clusters. A wide range of organic compounds may also react with scandium.

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

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

Because of its scarce distribution and difficulties associated with its extraction, scandium is very expensive. As a result and despite more than 100 years of research, it still has only a limited number of applications. It is added to aluminum **alloys** to increase the strength, thermal resistance, and durability of the materials (without adding much weight). Such alloys have been used to make everything from missiles to premium bicycle frames. Scandium is as light as aluminum but has a much higher melting point, thus its appeal to space missile designers. SEE ALSO ALUMINUM; HALOGENS; HYDROLYSIS.

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

Helen R. Webb

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Scheele, Carl

SWEDISH CHEMIST
1742–1786

Carl Wilhelm Scheele was born in Pomerania (on the Baltic coast of northeastern Europe, then under Swedish control). As a young man Scheele worked as an apothecary and studied chemistry under the famous chemist Torbern Bergman. Bergman once called Scheele one of his greatest discoveries. Scheele's laboratory techniques in chemistry were so exacting that his work fostered advances in several areas of chemistry. Scheele's achievements in organic chemistry included the isolation of glycerin and twelve organic acids—among them tartaric, citric, oxalic, mucic, malic, lactic, uric, gallic, and tannic acids. Among the **metals** Scheele was the first to identify were barium, molybdenum, and tungsten. He was the first to isolate elemental phosphorus from bone. Scheele was the first to characterize plumbago (graphite) as a form of carbon. He was one of the discoverers of the adsorption of gases by "activated charcoal." In 1777 Scheele was the first to describe the reduction of silver salts to metallic silver via the action of sunlight (the basis of photography).

Swedish chemist Carl Wilhelm Scheele, who discovered oxygen with Joseph Priestley and Antoine-Laurent Lavoisier.

Scheele developed a general method for investigating organic acid. His first step was to precipitate the acid as a crystalline calcium salt. He would purify the salt and then decompose it using sulfuric acid. (Calcium sulfate precipitates out, leaving the free organic acid for characterization.) Another of Scheele's separation techniques was the precipitation of the lead salts of acids, which were generally less soluble than the calcium salts. The lead salts were also decomposed with sulfuric acid to produce the free organic acids.

His investigations of reactive gases and corrosive liquids included such compounds as ammonia, hydrogen chloride (the gaseous form of hydrochloric acid), hydrogen fluoride (which can dissolve glass), silicon fluoride (highly corrosive), hydrogen sulfide (the active ingredient of a stink bomb), hydrocyanic acid, and **arsenic** acid. He was the first to isolate chlorine gas, which became the basis of the bleaching industry.

arsenic: toxic element of the phosphorus group

Scheele is most often remembered as one of the discoverers of oxygen, along with Joseph Priestley and Antoine Lavoisier. Scheele's work on the gas he called "fire-air" was completed between 1770 and 1773. This predated the work of Lavoisier or Priestley. Scheele's *Chemical Observations and Experiments on Air and Fire* was not published until 1777, after the comparable findings of Lavoisier and Priestley had been reported. Like Priestley, Scheele retained use of the phlogiston theory in most of his chemical work. Unlike Priestley, Scheele died at a young age. He died at forty-three, at a time when Lavoisier was consolidating the chemical revolution. SEE ALSO Chlorine.

David A. Bassett

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Schrödinger, Erwin

AUSTRIAN THEORETICAL PHYSICIST
1887–1961

Erwin Schrödinger was born in Vienna, Austria, in 1887. In 1906 he entered the University of Vienna with the intention of studying statistical thermodynamics with the mathematician and physicist Ludwig Boltzmann. Unfortunately it was the year Boltzmann committed suicide, and Schrödinger studied under Boltzmann's successor, Fritz Hasenöhrl. Schrödinger received his doctorate in 1910 for a dissertation on electrical conduction. The next four years were spent as an assistant instructor in experimental physics at the University of Vienna. In 1914 he was drafted to serve in the Austro-Hungarian army and fought on the side of Germany during World War I. In 1917 he returned to his former position in Vienna. In the aftermath of several research successes, Schrödinger found himself to be in great demand, and he accepted, one right after the other, faculty positions at the Universities of Jena, Stuttgart, and Breslau. Finally, in late 1921 he accepted the chair in **theoretical physics** at the University of Zurich (in Switzerland). Although his stay there was relatively short (six years), it was there that he published his most significant work—in quantum statistics, the dynamics of crystal lattices, the theory of color vision, and quantum theory.

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

Schrödinger's work in quantum theory resulted in the creation of a new scientific discipline—wave mechanics, which has as its centerpiece the Schrödinger wave equation, explained in a series of four papers published in 1926. This equation and the later relativistic versions are considered by many scientists to have the same central importance to molecular quantum mechanics as Newton's laws of motion have to large-scale classical mechanics.

Austrian physicist Erwin Schrödinger, co-recipient, with Paul Adrien Maurice Dirac, of the 1933 Nobel Prize in physics, "for the discovery of new productive forms of atomic theory."

Schrödinger began to search for a wave equation in 1925 after reading a paper by Albert Einstein about Louis de Broglie's ideas that matter could possess both wave and particle properties simultaneously, as expressed in the de Broglie equation relating the wavelength of a matter wave to its momentum. Schrödinger demonstrated that the de Broglie equation could be generalized so as to apply to particles such as electrons in atoms. The Schrödinger equation is a wave equation that explains the properties and behavior of all types of submicroscopic particles with small masses and that are in the presence of electric and magnetic fields. Schrödinger's work was immediately accepted worldwide, and he received a call to accept the challenge of succeeding Max Planck in the department of theoretical physics at the University of Berlin. He stayed until 1933, but by that time he had become so outraged by the German government's treatment of Jewish scientists that he accepted a position at Oxford University in England, just before he was informed that he had been awarded the 1933 Nobel Prize in physics for his development of wave mechanics. For the next seven years (during which time a return to Vienna would have been most difficult), he accepted several temporary appointments. In 1941 he became director of the School of Theoretical Physics at the Dublin Institute for Advanced Studies (in Ireland). There he worked mainly on unified field theory.

He also published a number of books. Of these, *What Is Life? The Physical Aspect of the Living Cell* is credited with having persuaded physicists to take an interest in the problems of biology. It is also credited with having attracted many young people to the new field of molecular biology. For instance, James Watson, one of the discoverers of the structure and function of **DNA**, stated that, from the moment he read the book, he "became polarized toward finding out the secret of the gene."

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

In 1955 Austria became free of Soviet occupation, and Schrödinger returned to the University of Vienna, where he received many honors as Austria's greatest living scientist. Schrödinger retired in 1958 and died in 1961. SEE ALSO DE BROGLIE, LOUIS; QUANTUM CHEMISTRY; WATSON, JAMES DEWEY.

John E. Bloor

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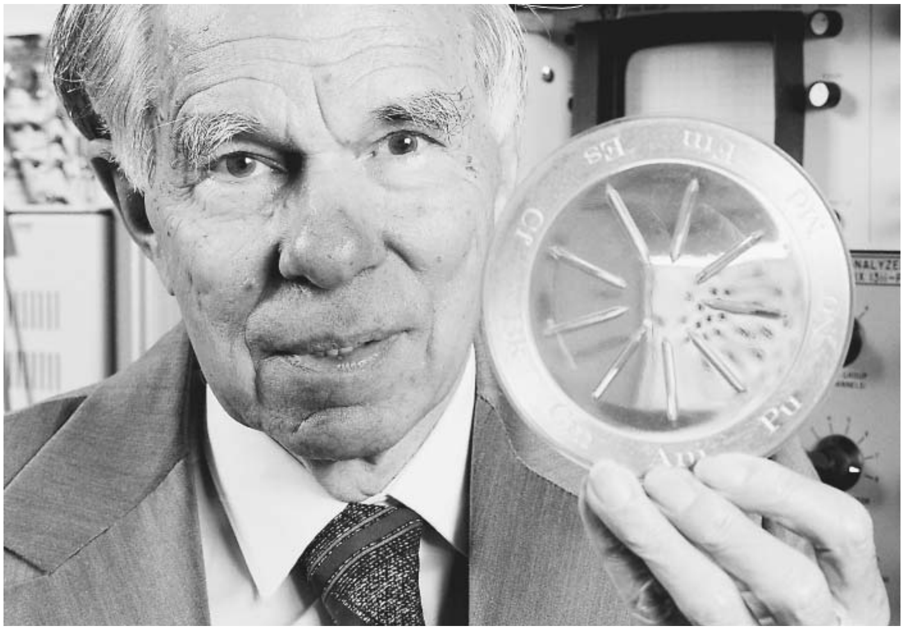
Scurvy ***See Ascorbic Acid.***

Seaborg, Glenn Theodore

AMERICAN NUCLEAR CHEMIST
1912–1999

Elder statesman, chemist, and codiscoverer of more elements than any other scientist, Glenn Theodore Seaborg started life in Ishpeming, Michigan, in



American chemist Glenn Theodore Seaborg, corecipient with Edwin Mattison McMillan of the 1951 Nobel Prize in chemistry, "for their discoveries in the chemistry of the transuranium elements." Here, Seaborg holds a container of samples of the radioactive elements 94 through 102.

1912. In an autobiographical account Seaborg divided his life into eight periods—a notion that perhaps sprang from his consideration of the eight periods of the present Periodic Table. In that account the first two periods correspond to his childhood and youth and conclude with his graduation from UCLA in 1934.

Seaborg went on to the University of California at Berkeley for graduate work, obtaining his Ph.D. in 1937. It was around this time that his interest in transuranium elements (elements of higher **atomic number** than uranium) took shape. His research interest was in **nuclear** physics but, as he once said, "one could get a chemistry Ph.D. in those days doing nuclear physics."

atomic number: the number assigned to an atom of an element that indicates the number of protons in the nucleus of that atom

nuclear: having to do with the nucleus of an atom

Upon finishing his doctoral dissertation, Seaborg went to work as personal research assistant to the chemist Gilbert Newton Lewis. His work with Lewis dealt with the concepts of primary and secondary acids (part of traditional chemistry). However, during his tenure as instructor (1939–1941) and assistant professor (1941) at Berkeley, his research in transuranic elements and **isotope** production reemerged. During the period 1934 to 1942, Seaborg participated in the discovery of plutonium and its **fissionable** isotopes (which were essential to the construction of a nuclear bomb). During this period he was also deeply involved in the **synthesis** of radioactive isotopes from nonradioactive elements ^{131}I, ^{60}Co, and ^{99m}Tc, which have found important applications in the diagnosis and treatment of diseases.

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

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

synthesis: combination of starting materials to form a desired product

From 1942 to 1946, Seaborg, on leave from Berkeley, was employed by the Metallurgical Laboratory, at the University of Chicago. It was during this period that he devised chemical processes for the separation and purification of plutonium. Plutonium, critical to the success of the **Manhattan Project**, was given the code name "copper." When actual copper was required in the project, the resulting confusion was eliminated by the use

Manhattan Project: government project dedicated to creation of an atomic weapon; directed by General Leslie Groves of "honest-to-God copper." Also at this time, Seaborg maintained his research on transuranium elements; he took part in the discoveries of both americium (element 95) and curium (element 96). But it was upon his return to Berkeley in 1946 that his transuranium research program gained momentum, whereupon it generated a string of discoveries: berkelium (element 97), californium (98), einsteinium (99), fermium (100), mendelevium (101), and nobelium (102). In 1951 Seaborg and Edwin Mattison McMillan received the Nobel Prize in chemistry "for their discoveries in the chemistry of the transuranium elements."

Between 1953 and 1958 Seaborg served as the faculty athletic representative at the University of California at Berkeley and helped to redesign the Intercollegiate Athletic Union, giving it new rules and regulations that would govern athletic scholarships. From 1958 to 1961, Seaborg served as chancellor at the University of California at Berkeley, during which time he oversaw notable successes in athletics, new building construction, and the establishment of research centers.

From 1961 to 1971, Seaborg was chairman of the United States Atomic Energy Commission. Solicited for the job by President Kennedy, Seaborg at first had doubts about taking on the position. (Seaborg disliked the idea of quitting research.) Kennedy gave him one day to decide. (Seaborg accepted.) His ten years as chairman, during which he served under three presidents and through some of the most turbulent times in U.S. history, established his credentials as an elder statesman.

Seaborg returned to the University of California at Berkeley in 1971. There, in 1974, he discovered with his colleagues one more element. Although it was a controversial discovery due to competing claims, the element was eventually named "seaborgium" (with the result that prior to his death in 1999, Glenn Seaborg was the only living person after whom an element had been named).

In his career he was president of both the American Chemical Society and the American Association for the Advancement of Science. Because of his belief in the importance of education, he undertook to reform the chemistry and science curricula of high schools. CHEM Study, a project designed to improve the teaching of chemistry at the high school level, became an internationally recognized educational resource under his direction. He was a founder of GEMS (Great Explorations in Math and Science) and many other science education projects.

Seaborg worked hard to ensure that science education was not slighted and that science would be seen as a tremendous boon to humanity. Along these lines, it was his leadership that helped to bring into existence the Lawrence Hall of Science at Berkeley as a tribute to Ernest Orlando Lawrence. SEE ALSO AMERICIUM; CURIUM; LAWRENCE, ERNEST; PLUTONIUM.

Todd W. Whitcombe

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Secondary Structure

The secondary structure refers to the conformation present at a local region of a **polypeptide**. A few types of secondary structure are particularly stable and occur widely in proteins. These include the α-helix and β-sheet conformations, which are both stabilized by **hydrogen bonds**. The α-helix is a rigid, rod-like structure that forms when a polypeptide chain twists into a helical conformation. Hydrogen bonds form between the amino (N–H) group of one amino acid and the carbonyl (C=O) group of the amino acid four residues away. The amino acid side chains extend outward from the helix. In the β-sheet, two or more polypeptide chains (or two or more portions of the same chain) are arranged side by side to form a sheet. Hydrogen bonds form between the backbone amino groups and the carbonyl groups of adjacent chains. The sheets are pleated, not flat, and the amino acid side chains of adjacent amino acids extend from the pleat structure in opposite directions. In a protein, loops or bends can connect the secondary structures. SEE ALSO PRIMARY STRUCTURE; TERTIARY STRUCTURE.

Elizabeth S. Roberts-Kirchhoff

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

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

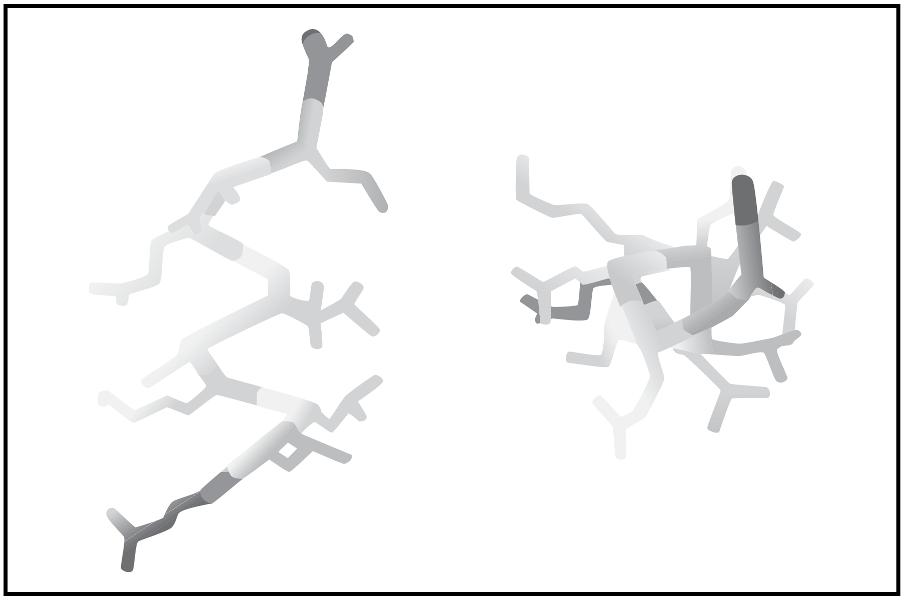

Figure 1. Alpha helix.

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Seibert, Florence

AMERICAN BIOCHEMIST
1897–1991

Florence Seibert made several important contributions to medicine during her long career. Most notably, she purified a protein from tuberculosis bacteria that became the international standard for tuberculosis testing. She also greatly improved the safety of intravenous injections by inventing a method to make distilled water free of contaminants that had caused serious problems in many patients.

Seibert was born in Easton, Pennsylvania. As a girl she contracted polio; although the disease left her with a lifelong limp, it did not affect her academic skills. She graduated as high school valedictorian, earning a scholarship to Goucher College in Maryland. After graduating in 1918, Seibert briefly worked as a chemist at a paper mill. She then attended Yale University to earn a doctoral degree in biochemistry, graduating in 1923. During her graduate work at Yale, Seibert devised an improved method for making distilled water that eliminated bacterial contaminants that had caused fevers in some patients receiving injections with substances dissolved in distilled water.

In 1924, following additional studies at the University of Chicago, Seibert became an instructor, then an assistant professor, at the Sprague Memorial Institute in Chicago. In 1932 she moved to the University of Pennsylvania, where she remained until retiring in 1958 as a full professor.

It was at the University of Pennsylvania that Seibert began her important work in tuberculosis research. Robert Koch had reported as early as 1891 that animals previously infected with tuberculosis had a unique reaction when tuberculosis bacteria fragments or dead bacteria were injected under the skin. The culture extract used by Koch and others was called tuberculin, and the appearance of welts in response to the injection was called the tuberculin reaction. The reaction is due to an immune response known as delayed hypersensitivity and appears in humans who have either active tuberculosis infections or who have had active infections in the past. It is thus valuable to public health officials for identifying potential tuberculosis carriers. The preparations of tuberculin prepared by Koch and others, however, were complex mixtures of many substances, including the presumed active protein component, and the contents were not consistent from batch to batch. Thus the ability to induce the tuberculin reaction varied enormously from preparation to preparation.

Seibert devised a way to purify a protein causing the tuberculin reaction, which allowed standardization of strength from one preparation to another. She published her first work on purification of tuberculin in 1934. The

American biochemist Florence Seibert, who developed the procedure that isolated the crystalline tuberculin derivative, which is used in the standard TB test.

protein she isolated was much improved over old tuberculin and was called Purified Protein Derivative (PPD). By 1940 Seibert had improved her protein purification procedure sufficiently for it to become the international standard for use in tuberculin tests, contributing enormously to public health campaigns. For this work she was awarded the Trudeau Medal by the National Tuberculosis Association in 1938 and the Garvan Medal by the American Chemical Society in 1941.

Over the years Seibert's research interests evolved from tuberculosis to cancer research. Following her retirement from the University of Pennsylvania she became director of the cancer research laboratory at a hospital in St. Petersburg, Florida. In 1968 she published an autobiography entitled *Pebbles on the Hill of a Scientist*. Seibert continued publishing scientific research papers until 1977, when declining health forced her to give up research. She was inducted into the National Women's Hall of Fame in 1990, one year before her death.

Robert K. Griffith

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34
Se
SELENIUM
78.96

Selenium

MELTING POINT: 217°C
BOILING POINT: 685°C
DENSITY: 4,819 kg/m^3
MOST COMMON IONS: SeO_3^{2-}, SeO_4^{2-}, Se^{2-}

Selenium (from the Greek word *selēnē*—the Moon), discovered by Swedish chemist Jöns Jakob Berzelius in 1817, ranks thirty-fourth among elements in Earth's crust. It has six naturally occurring **isotopes**, a large number of allotropes (elemental forms), and in compounds has **oxidation** states −2, +4, and +6. The gray elemental form has the unique photoelectric property of exhibiting lowered electrical resistance when struck by light, and it is used in photovoltaic cells and photocells (e.g., light meters) and in xerography. It conducts electricity in a "unipolar" manner, hence it is commonly used in electrical rectifiers. It is also used to tint glass red and to decolorize green glass.

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)

Selenium substitutes for sulfur in amino acids to form seleno-cysteine, cystine, and methionine. The selenium-containing antioxidant glutathione peroxidase is biologically important, and selenium is a necessary trace nutrient in warm-blooded animals. Grazing animals develop a form of **muscular dystrophy** and other disorders when grazing in areas in which the selenium has been depleted; with selenium-depleted diets, people develop

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

The element selenium contains important antioxidants and nutrients but is also harmful to some life-forms.

Keshan disease, a form of cardiomyopathy. When its intake is too high, selenium disrupts enzyme function, causing poor health in mammals and birth defects and reproductive failure in birds and fish. Good sources of selenium in human diets include wheat, garlic, Brazil nuts, and walnuts. SEE ALSO CHALCOGENS.

John Harwood

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Semiconductors

The development of semiconductors is clearly among the most significant technological achievements to evolve from the study of solid-state chemistry and physics. Aside from their well-known applications in computers and electronics, semiconductors are also used in a wide variety of optical devices such as lasers, light-emitting diodes, and solar panels. The diversity of applications can be readily understood with only a basic understanding of the theory behind these materials.

Theory

The operation of semiconductors is best understood using band theory. At its most fundamental level, band theory can be extremely complex, requiring relatively advanced mathematics and physics. When a large number of atoms combine to form a solid, the electrons e^- in the solid are distributed into energy bands among all the atoms in the solid. Each band has a different energy, and the electrons fill these bands from the lowest energy to the highest, similar to the way electrons occupy the orbitals in a single atom. The variation in properties between electrical insulators, conductors (**metals**), and semiconductors stems from differences in the band structures of these materials (see Figure 1). For this discussion, three terms must be defined. The highest energy band that contains electrons is called the **valence** band, whereas the lowest energy empty band is called the conduction band. The band gap is the difference in energy between the valence and conduction bands. The laws of quantum mechanics forbid electrons from being in the band gap; thus, an electron must always be in one of the bands.

In a metal (e.g., copper or silver), the valence band is only partially filled with electrons (Figure 1a). This means that the electrons can access empty areas within the valence band, and move freely across all atoms that make up the solid. A current can therefore be generated when a **voltage** is applied. In general, for electrons to flow in a solid, they must be in a partially filled band or have access to a nearby empty band. In an electrical insulator, there is no possibility for electron flow (Figure 1b), because the valence band is completely filled with electrons, and the conduction band is too far away in energy to be accessed by these electrons (the band gap is too large). A semiconductor (Figure 1c) is a special case in which the band gap is small enough that electrons in the valence band can jump into the conduction band using thermal energy. That is, heat in the material

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

valence: combining capacity

voltage: potential difference expressed in volts

A conventional tube amplifier, at left, and a solid-state memory cell, at right. The size of such semiconductors allows for the manufacturing of smaller devices.

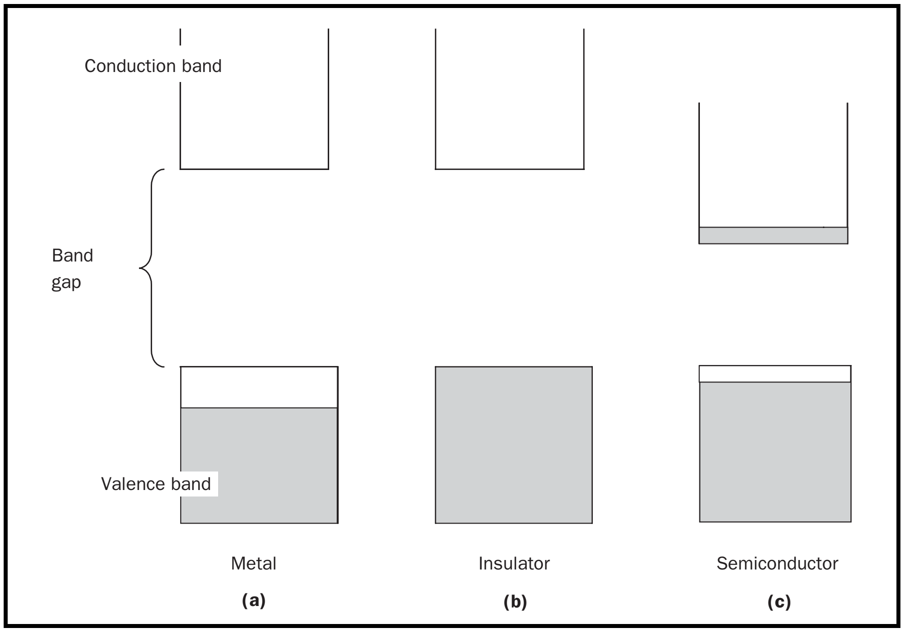


Figure 1. Schematic of the electronic band structures of different types of solids. Electrons are represented by shaded areas.

(even at room temperature) gives some of the electrons enough energy to travel across the band gap. Thus, an important property of semiconductors is that their conductivity increases as they are heated up and more electrons fill the conduction band. The most well-known semiconductor is silicon (Si), although germanium (Ge) and gallium arsenide (GaAs) are also common.

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of the substance

To complete the development of semiconductor theory, the concept of **doping** must be described (see Figure 2). In principle, the idea is to introduce a different kind of atom into a semiconductor in order to modify its electronic structure. Consider, for example, adding a small amount of phosphorus, P, into a silicon host. Phosphorus is one column to the right of silicon in the Periodic Table, so it contains one additional electron. This means that doping P into Si has the effect of introducing additional electrons to the material, such that some e^- must go into the conduction band. Because extra negatively charged electrons are added to the system, phosphorus-doped Si is called an *n*-type semiconductor, and phosphorus is described as a donor (of electrons). Similarly, a *p*-type semiconductor can be fabricated by adding an element to the left of Si in the Periodic Table. Boron, B, is a common dopant for a *p*-type. In this case, the valence band will be missing electrons. These empty locations in a *p*-type semiconductor are also referred to as holes. Since holes represent the absence of an electron, they carry a positive charge. In *p*-type semiconductors, boron is referred to as an acceptor (of electrons). From Figure 2, it can be seen that both *n*- and *p*-type materials create partially filled bands, allowing for electrical conduction. Dopant concentrations are fairly small, around 10^{16} atoms/cm^3, constituting only about ten-billionths of the total mass of the material.

If *p*- and *n*-type materials are layered together, a *p-n* junction results (Figure 2c). Right at the interface, some of the excess electrons from the *n*-type combine with holes from the *p*-type. The resulting charge separation creates an energy barrier that impedes any further movement of electrons. In most technological applications, the important properties of semiconductors are the result of the band structure of the *p-n* junction. A single

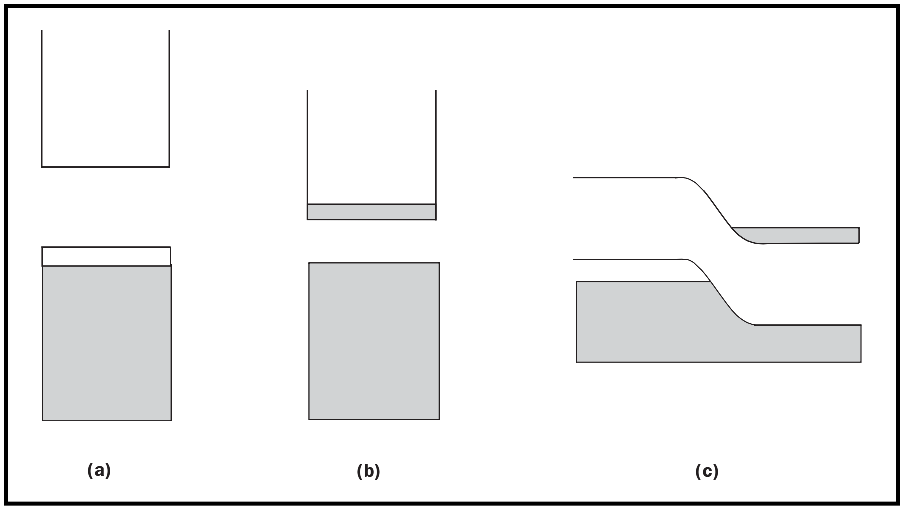


Figure 2. Schematic diagrams of the band structures of (a) *p*-type semiconductors, (b) *n*-type semiconductors, and (c) a *p-n* junction.

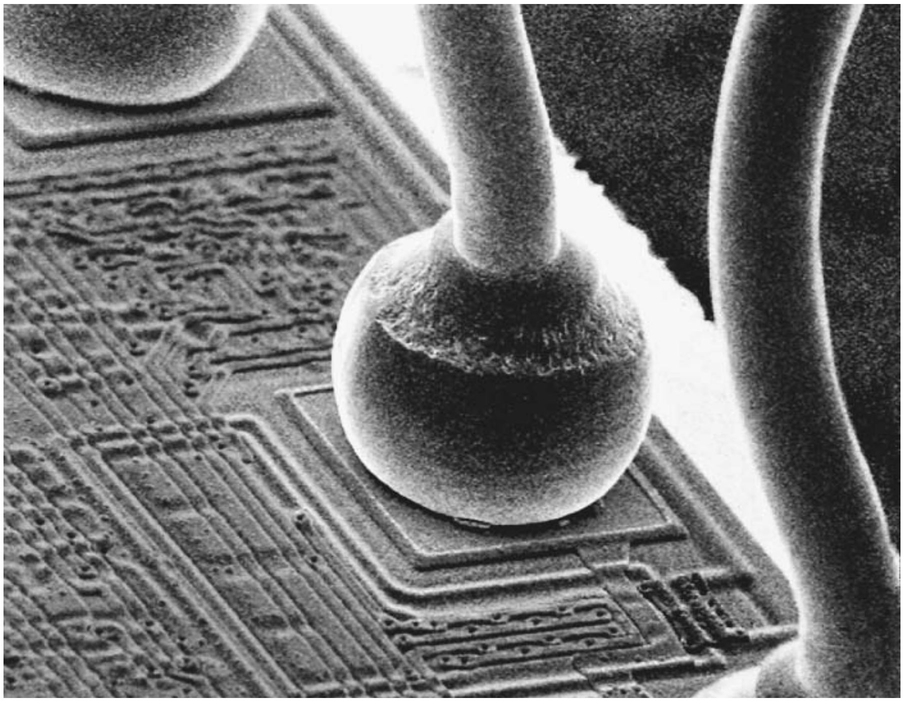
junction based on the same host material (e.g., one interface of *p*- and *n*-doped silicon) is called a homojunction. The homojunction model is used here to describe the properties of many devices that are based on semiconductors. However, it should be noted that real systems are typically composed of multiple *p-p*, *n-n*, and *p-n* junctions, called heterojunctions. Such configurations greatly improve the performance of these materials; in fact, the development of heterojunction devices was critical to the widespread practical application of this technology.

Semiconductors in Electronics

Semiconductors are used extensively in solid-state electronic devices and computers. The majority of materials for these applications are based on doped silicon. An important property of *p-n* junctions is that they allow electron flow only from the *n* side to the *p* side. Such one-way devices are called diodes. Consider Figure 2c again. If a positive voltage (also called a forward bias) is applied that lowers the energy barrier between *n* and *p*, then the electrons in the conduction band on the *n* side can flow across the junction (and holes can flow from *p* to *n*). A reverse bias, however, raises the height of the barrier and increases the charge separation at the junction, impeding any flow of electrons from *p* to *n*.

Diodes have several important applications in electronics. The power supplied by most electrical utilities is typically alternating current (AC); that is, the direction of current flow switches back and forth with a frequency of sixty cycles per second. However, many electronic devices require a steady flow of current in one direction (direct current or DC). Since a diode only allows current to flow through it in one direction, it can be combined with a capacitor to convert AC input to DC output. For half the AC cycle, the diode passes current and the capacitor is charged up. During the other half of the cycle, the diode blocks any current from the line, but current is provided to the circuit by the capacitor. Diodes applied in this way are referred to as rectifiers.

The by far most important application of semiconductors is as logic gates and transistors in computers. Logic gates, such as OR and AND gates, take advantage of the one-way nature of diodes to compare the presence or



Micro-wires bonded on a silicon chip.

absence of current at different locations in a circuit. More complex solid-state transistors are composed of *npn* or *pnp* junctions. The device geometry is slightly more complicated than that observed in a diode, but the result is materials that allow for the generation of the zeros and ones required for the binary logic used by computers.

Optoelectronic Devices

Optoelectronic materials are a special class of semiconductors that can either convert electrical energy into light or absorb light and convert it into electrical energy. Light-emitting diodes (LEDs), for example, are commonly used for information display and in automotive interior lighting applications. In an LED, a forward bias applied across the junction moves electrons in the conduction band over holes in the valence band. The electron and hole combine at the junction, and the energy created by this process is conserved via the emission of light (Figure 3a). The wavelength of emitted light will depend on the band gap of the material; larger band gaps lead to shorter wavelengths of light. Only certain kinds of semiconductors, called direct gap semiconductors, exhibit this behavior. GaAs is an example of a direct gap semiconductor used in these applications. Silicon is an indirect gap material, and electrons and holes combine with the generation of heat instead of light.

A diode laser operates in essentially the same fashion as an LED. Two additional requirements must be met for a direct gap semiconductor to be an efficient laser. The first is that larger forward bias currents are needed for a laser than for an LED, because lasers require a higher degree of population inversion—a large number of electrons in the conduction band above empty levels in the valence band. Lasers also require an optical cavity; light bounces back and forth within the cavity, building up intensity. In a diode

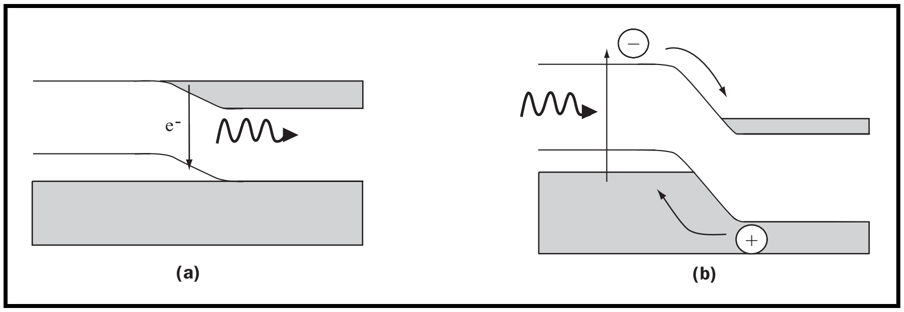


Figure 3. Principle of operation of (a) a light-emitting diode or diode laser and (b) a photodetector or solar cell.

laser, this can be achieved by cleaving and polishing opposite faces of the diode. The smooth faces act like partially reflecting mirrors. This kind of laser is used to read information on compact disks and is also used in laser pointers.

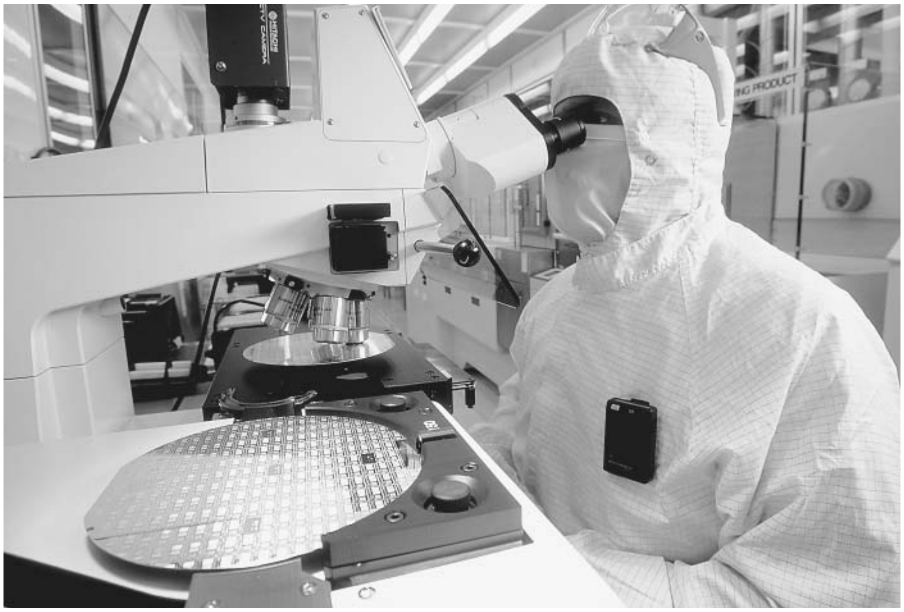
The most common materials for lasers and LEDs are heterojunctions based on GaAs. More complex systems containing Ga, As, P, Al, and N are also used. The band gap of these materials can be tailored to create emission from infrared to yellow. In optical data storage systems, such as compact disks, the amount of information that can be stored is dependent in part on the wavelength of light being used to read the disk—shorter wavelengths allow for denser information storage. Thus, there has been considerable interest in developing larger band gap LEDs and lasers that emit in the blue. This has been achieved in semiconductors based on GaN (gallium nitride). Further refinement of these materials will no doubt lead to significant advances in optoelectronic technology in the coming years.

A final important class of optoelectronic devices based on semiconductors is photovoltaics, such as photodetectors and solar cells. In some respects, these can be regarded as LEDs operating in reverse. Light energy incident on the *p-n* junction is absorbed by an electron, which then jumps to the conduction band (Figure 3b). Once in the conduction band, the electron travels downhill (energetically) to the *n* side of the junction, with a hole migrating to the *p* side. This creates a flow of current that is the reverse of what is seen in a forward biased diode. The result is the conversion of light energy to electrical energy. These devices can therefore be used to detect light, as in digital imaging systems or miniature cameras; or the electrical energy can be stored, as in solar cells. Commercial photovoltaics are based on a variety of host materials, including Si, AlGaAs, and InAlAs.

Fabrication

The industrial fabrication of semiconductors can be extremely complex, involving high-purity materials, sophisticated equipment, and hundreds of steps. Most processes begin with the growth of a large single crystal of *n*-type Si, called a wafer. A dopant (e.g., phosphorus) is added to high-purity molten silicon, and a crystal is then slowly extracted from this melt. The polished wafer is 20 to 30 centimeters (7.9–11.8 inches) in diameter.

The rest of the processing will depend on the nature of the device being produced. A simple *p-n* junction is usually fabricated via photolithography and etching processes. In this method, a layer of silicon dioxide, SiO_2, is created on the surface of the wafer by heating it in the presence of



A worker is testing silicon wafers at the Matsushita Semiconductor plant in Puyallup, Washington. Semiconductors are used in many different electronic products, such as computers, lasers, and solar panels.

oxygen. Some of the SiO_2 is then chemically stripped away, or etched, exposing only a portion of the Si wafer. This exposed part of the wafer is made into *p*-type material by bombarding it with boron ions. As these ions diffuse into the Si wafer, *p*-type Si is formed. Since the original wafer was *n*-type, a *p-n* junction forms where the diffusion of boron stops. Metal contacts can then be added to each side of the junction to create a simple homojunction device.

Fabrication of more complicated devices is achieved via combinations of etching, deposition, and ion implantation steps. In the production of integrated circuits for computers, about 400 chips can be synthesized on a single 30-centimeter (11.8-inch) wafer. Each chip may contain as many as 50 million transistors in a space barely more than 1 centimeter (0.39 inches) on a side—a truly remarkable technological achievement. As faster and faster systems are developed, the demand for smaller and smaller features increases. Such miniaturization is the most significant challenge facing the semiconductor industry today.

Semiconductors are used in a wide variety of electronic and optoelectronic applications. The useful properties of semiconductors arise from the unique behavior of doped materials, the special control of electron flow provided by *p-n* junctions, and the interaction of light energy with electrons at these junctions. The industry continues to grow, and research in this and related areas (i.e., organic semiconductors and molecular transistors) is occurring at academic institutions around the world. SEE ALSO GERMANIUM; SILICON.

Anthony Diaz

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Silicon

MELTING POINT: 1,410°C
BOILING POINT: 2,355°C
DENSITY: 2.329 g/cm^3
MOST COMMON IONS: Si^{4+}, $H_3SiO_4^{-}$, $H_2SiO_4^{2-}$, $HSiO_4^{3-}$, SiO_4^{4-}

14
Si
SILICON
28.086

Silicon is the second most abundant element in Earth's crust and mantle, after oxygen. It is the seventh most abundant element in the universe. It was first obtained in elemental form by Jöns Jakob Berzelius in 1823, from reduction of a complex fluoride, K_2SiF_6, by potassium. It has a strong chemical affinity for **electronegative** elements such as oxygen and fluorine. It is always found in nature in bound form, as the oxide, SiO_2, or in silicate minerals such as olivine, $(Mg,Fe)_2SiO_4$. The principal hydride is silane (SiH_4), a pyrophoric gas, and the halides (e.g., SiF_4, $SiCl_4$) are gases or liquids. Silicate minerals form in a wide variety of crystallographic structures, i.e., a mineral's internal (repeating) structure; many of these minerals are important ceramics (e.g., heated mica produces clays used in pottery; calcium silicates are the primary components of cement). Amorphous (noncrystalline) silicates form glasses used in windows and containers. Silicon nitride, Si_3N_4, is an important ceramic used in turbine engines. Silicon carbide, SiC, is an ultrahard solid used in abrasives.

electronegative: capable of attracting electrons

Silicon is extracted from quartz (SiO_2) sand by high temperature reduction with carbon. The crystalline element is a shiny gray semiconducting solid with the tetrahedral diamond structure. Usually **doped** with boron, **arsenic**, or phosphorus, it conducts electricity via the diffusion of electrons or positive "holes" (electron vacancies). Polymorphs of silicon formed under high pressure conditions are metallic and contain **octahedral** silicon; the liquid is metallic also. Amorphous silicon formed by vapor **phase** decomposition of silane is used to transform light into electricity in solar cells. Silicones (organic silicon compounds containing Si-O-Si linkages) are prepared from silane, silicon halides, or **metal**-Si **alloys** by hydrolysis of the silicone material to give oils, greases, synthetic rubbers, and adhesives. SEE ALSO SEMICONDUCTORS; SOLAR CELLS.

Paul F. McMillan

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of the substance

arsenic: toxic element of the phosphorus group

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

phase: homogeneous state of matter

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

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Silicone

The term “silica” denotes the compound silicon dioxide, SiO_2. It is a ubiquitous chemical substance with rich chemical, geological, and commercial importance. Commercially, it has many uses, and it is the only source of elemental silicon.

The Evolution of Silicones

Silicon is a member of the Group IV elements in the Periodic Table. However, little of the chemistry of silicon can be inferred from carbon, one of its closest neighbors. Although silicon is the second most abundant element in Earth’s crust (approximately 26%), it does not exist in nature as a free element. Silicon must be freed from its oxides through a chemical process known as carbothermic reduction. In this reaction, silica and a carbon source (generally wood) are heated together at extremely high temperatures to yield silicon in its elemental form. The Swedish chemist Jöns Jakob Berzelius (1824) was the first to isolate silicon from its natural matrix. Silicon is widely used in the electronics and chemical industries.

Silanes, siloxanes, and silicones are commercially produced from silicon and methyl chloride in a process known as the “direct reaction” or the “Rochow-Muller direct process.”

$$\mathrm{Si + (excess)\ CH_3Cl \rightarrow (CH_3)_xSiCl_{(4-x)}}$$

This reaction yields methylchlorosilanes (silicon compounds containing both methyl groups and chlorine). They are distilled (purified), and the isolated dimethyldichlorosilane is hydrolyzed to give siloxanes and silicones. This product can be formulated or finished into thousands of different products, which are sold to every major industrial segment. Although the direct reaction is used to commercially produce silicon-based materials today, the first example of an organosilicon compound (a material containing a silicon-carbon bond) was described in 1863 (as the U.S. Civil War raged and author Mark Twain was just beginning his literary career). French chemist Charles Friedel and U.S. chemist James Mason Crafts are credited for not only making the first compound that contained a silicon-carbon bond, but also determining the molecular weight of silicon during their years of research in this area of chemistry. By the turn of the twentieth century English chemist Frederic Stanley Kipping began to investigate this new area of science, publishing fifty-four papers on the subject between 1899 and 1937, but he failed to foresee the potential commercial value of his work. In one publication, he actually referred to the products from his work as “uninviting oils and glues.”

In 1930 chemist J. Franklin Hyde, called the “father of silicone chemistry,” met with Eugene Sullivan, vice president and director of research at Corning Glass Works. Sullivan was worried about the emerging plastics industry and its potential for competitive advantage over glass. Sullivan believed that it might be possible to combine the advantages of glass with some of the superior properties of organic plastics to produce a hybrid material. The idea was radical, but Hyde took Sullivan’s idea for an inorganic-organic hybrid and used it as the foundation for what is now an $8 billion global industry, organosiloxanes. Hyde recognized the commercial importance of some of Kipping’s observations and applied them to forge his

PUTTY WARS

Bouncing Putty, later sold as Silly Putty®, is an example of a silicon-based material with very unusual properties. It is a liquid that behaves as a solid or a solid that acts like a liquid. The material is a mixture of silicone polymers and boric acid. The polymers are terminated (end group) at both ends with an alcohol group (-OH) in contrast to the typical methyl group (-CH_3). The polymer ends (-OH) and the boric acid react with each other in a reversible fashion. This reversible reaction allows Silly Putty® to be a very thick viscous liquid because bonds between the polymers and the boric acid are constantly being formed and broken. Stress (pulling the material sharply or striking it against the table) interferes with the reverse reaction, and the material behaves as a solid until the stress has been removed. The identity of the person who really invented bouncing putty is still debated today. R. R. McGregor and E. L. Warrick hold the U.S. Patent (2,431,878) that was issued in 1947 to Dow Corning Corporation. However, James Wright, an engineer for General Electric, has claimed that he conducted the initial experiments in 1943 that led to Silly Putty®'s discovery. The truth is that neither company could find a good use for the interesting material. Silly Putty® was brought to commercial success by Ruth Fallgatter (owner of the Block Shop toy store in New Haven, Connecticut) and her marketing consultant (Peter Hodgson of Marketing, Inc.) around 1950, with General Electric being the sole supplier of the material until 1959. Silly Putty® remains a wonderful curiosity to all who handle the "liquid solid." It has been to the Moon (aboard *Apollo 8*) and was commemorated in a Smithsonian exhibit devoted to significant objects from the 1950s that shaped American culture.

hybrid technology. The Dow Corning Corporation was thus formed; at Dow the first commercial "silicones" were produced.

Silicones

Silicones (or silicon-based materials) are an integral part of daily life. These materials make our denim clothing feel softer; they help our hair to shine and our skin to feel silky. Silicon-based materials are used in our food and drink to control foam. They lubricate and protect critical surfaces. They can be found in automobiles, buildings, and homes. These materials allow for the construction of skyscrapers as well as seal our aquariums and bathtubs. Have you ever wondered why you can peel a name tag from its paper backing and it still remains sticky enough to adhere to your clothing? The answer is silicones. Each day, we unknowingly come into contact with scores of products that contain silicones for the very special properties that they possess.

The German chemist Friedrich Wöhler first coined the term "silicone" in 1857. However, his strategy to name silicon-containing materials based on a nomenclature system derived from organic chemistry was lost when the silicon analog to a **ketone** could not be isolated. Today the term is often used as a generic for nearly all substances that contain a silicon atom. However, it is more properly described as an entirely synthetic polymer containing a Si-O backbone. To this backbone, organic groups are attached.

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

This general description defines the broad class of polymers known as silicones or silicon-based materials. The most common example is poly(dimethylsiloxane) or PDMS. This polymer has a repeating $(CH_3)_2SiO$ unit.

These materials are the basic building blocks of the silicone industry. Depending on the number of repeat units in the polymer chain and the degree of cross-linking (how the polymer chains are tied together), at least six classes of commercially important families of products can be produced: fluids, emulsions, compounds, lubricants, resins, and elastomers or rubbers.

How Are Silicones Used?

Silicones are highly valued materials because they have a combination of physical properties not found in other polymers. They have outstanding heat stability and can be used in applications where organic materials would melt or decompose. Many silicones seem to be impervious to the effects of aging, weather, sunlight, moisture, heat, cold, and some chemical assaults. Numerous silicones are used to stick, bond, or couple things together.

Unique surface properties further distinguish silicones from other materials. The low surface tension of silicone fluids makes them ideal for applications such as paper release agents, fiber lubricants, textile hand modifiers, mold release agents, antifouling materials, and water repellents. In fact, silicones have been used in foam control and as anticaking aids, corrosion inhibitors, emulsifiers, lubricants, conditioners, and gloss enhancers—all because of their special surface properties. SEE ALSO Polymers, Synthetic.

Thomas H. Lane

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Silver

47
Ag
SILVER
107.868

MELTING POINT: 961°C
BOILING POINT: 2,212°C
DENSITY: 10.53 g/cm^3
MOST COMMON IONS: Ag^+, Ag^{2+}

Silver is a precious **metal** and (like gold and copper) is classified as a coinage metal. The date of its discovery is not known, but it has been identified in jewelry, coins, and religious ornaments dating to more than 2,000 years ago from ancient civilizations in South America, Egypt, Mesopotamia, and China.

Silver exists as two **isotopes**, ^{107}Ag and ^{109}Ag, occurring in similar proportions. It exhibits three valance/**oxidation** states: Ag(I), Ag(II), and Ag(III). The chemistry of silver was not well-known before 1980, although silver nitrate was used medicinally in the 1800s. Recent research has recognized the highly reactive nature of the silver ion and its ability to form numerous inorganic and organic complexes (halide, sulfide, nitrate, oxide, and acetylide

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

oxidation: process that involves the loss of electrons (or the addition of an oxygen atom) compounds, cyano-derivatives, olefin complexes, etc.). Ag(II) complexes are less stable than those of Ag(I) and Ag(III), but unlike many other silver compounds are brightly colored red or blue. Silver ion binds readily to proteins in the human body (including albumins and **metallothioneins**) and interacts with trace metals in metabolic pathways.

Silver is the sixty-third most abundant metal in Earth's crust; the average concentration of silver in water is 0.5 ppb, in soil it is 10 ppb. It is found naturally as native metal or in ores in which it is complexed with lead, copper, tellurium, mercury, **arsenic**, or antimony. Silver is found mainly throughout the Americas, Japan, Australia, and central Europe. Extraction is by **amalgamation** and displacement (using mercury), solution, or **smelting** methods.

Silver is used in the manufacture of photographic film chemicals such as silver nitrate, as an analytic **reagent** in organic chemistry, as a **catalyst** in photo-oxidation reactions, in electrochemical reactions, in **nuclear** magnetic resonance and analyses, and in silver plating.

Medically, silver is used in the manufacture of bone prostheses, cardiac implants and replacement valves, needles used in ocular surgery, peritoneal catheters, and wound sutures. It is an antiseptic ingredient used in wound management (silver nitrate, siler sulfadiazine, and cerium nitrate). A new generation of sustained silver release products is showing promise in the treatment of skin wounds, skin ulcers, and burns; silver ion is released from the dressings (Acticoat™, Actisorb™, etc.) in the presence of wound fluids, exudates, and is "activated." Activated silver ion is toxic to bacteria and yeasts. Silver is used in the making of dental amalgam fillings. Silver exhibits wide-spectrum antibacterial activity; it is toxic to bacteria at low concentrations (10^{-5} to 10^{-7} Ag ions per cell), the so-called oligodynamic effect.

Silver is toxic. Silver nitrate used in antiseptic mouthwashes leads to deposits of silver sulfide in the skin and a slate-gray skin discoloration (known as argyria); argyria is also caused by the colloidal silver used in antiseptics and mouthwashes. Silver absorbed through the skin is deposited in the liver and kidney and complexes with albumin and cellular proteins. Another silver hazard is allergy to silver, occurring as a result of the silver that is used in jewelry, medicinal products, coins, and antiseptics.

Alan B. G. Lansdown

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

arsenic: toxic element of the phosphorus group

amalgam: metallic alloy of mercury and one or more metals

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

reagent: chemical used to cause a specific chemical reaction

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

nuclear: having to do with the nucleus of an atom

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Soap

Soaps are cleaning agents that are usually made by reacting alkali (e.g., sodium hydroxide) with naturally occurring fat or fatty acids. The reaction produces sodium salts of these fatty acids, which improve the cleaning process by making water better able to lift away greasy stains from skin, hair, clothes, and just about anything else. As a substance that has helped clean bodies as well as possessions, soap has been remarkably useful.

History of Soap

The discovery of soap predates recorded history, going back perhaps as far as six thousand years. Excavations of ancient Babylon uncovered cylinders with inscriptions for making soap around 2800 B.C.E. Later records from ancient Egypt (c. 1500 B.C.E.) describe how animal and vegetable oils were combined with alkaline salts to make soap.

According to Roman legend, soap got its name from Mount Sapo, where animals were sacrificed. Rain would wash the fat from the sacrificed animals along with alkaline wooden ashes from the sacrificial fires into the Tiber River, where people found the mixture helped clean clothes. This recipe for making soap was relatively unchanged for centuries, with American colonists collecting and cooking down animal tallow (rendered fat) and then mixing it with an alkali **potash** solution obtained from the accumulated hardwood ashes of their winter fires. Similarly, Europeans made something known as castile soap using olive oil. Only since the mid-nineteenth century has the process become commercialized and soap become widely available at the local market.

potash: the compound potassium oxide, K_2O

Chemistry of Soap

The basic structure of all soaps is essentially the same, consisting of a long hydrophobic (water-fearing) hydrocarbon “tail” and a hydrophilic (water-loving) anionic “head”:

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2COO^-$$
$$\text{or } CH_3(CH_2)_nCOO^-$$

carboxylate: structure incorporating the –COO– group

The length of the hydrocarbon chain (“n”) varies with the type of fat or oil but is usually quite long. The anionic charge on the **carboxylate** head is usually balanced by either a positively charged potassium (K^+) or sodium (Na^+) cation. In making soap, triglycerides in fat or oils are heated in the presence of a strong alkali base such as sodium hydroxide, producing three molecules of soap for every molecule of glycerol. This process is called saponification and is illustrated in Figure 1.

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

Like synthetic detergents, soaps are “surface active” substances (**surfactants**) and as such make water better at cleaning surfaces. Water, although a good general solvent, is unfortunately also a substance with a very high surface tension. Because of this, water molecules generally prefer to stay together rather than to wet other surfaces. Surfactants work by reducing the surface tension of water, allowing the water molecules to better wet the surface and thus increase water’s ability to dissolve dirty, oily stains.

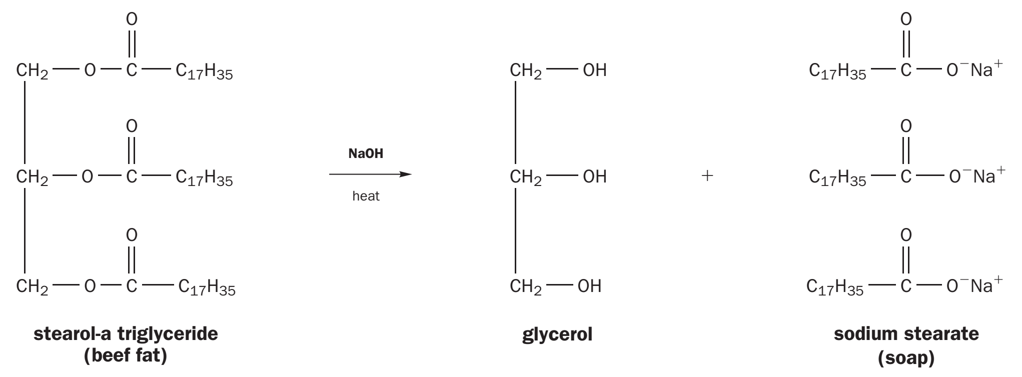

Figure 1.

In studying how soap works, it is useful to consider a general rule of nature: "like dissolves like." The **nonpolar** hydrophobic tails of soap are **lipophilic** ("oil-loving") and so will embed into the grease and oils that help dirt and stains adhere to surfaces. The hydrophilic heads, however, remain surrounded by the water molecules to which they are attracted. As more and more soap molecules embed into a greasy stain, they eventually surround and isolate little particles of the grease and form structures called micelles that are lifted into solution. In a micelle, the tails of the soap molecules are oriented toward and into the grease, while the heads face outward into the water, resulting in an **emulsion** of soapy grease particles suspended in the water.

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

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

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

With agitation, the micelles are dispersed into the water and removed from the previously dirty surface. In essence, soap molecules partially dissolve the greasy stain to form the emulsion that is kept suspended in water until it can be rinsed away (see Figure 2).

As good as soaps are, they are not perfect. For example, they do not work well in hard water containing calcium and magnesium ions, because the calcium and magnesium salts of soap are insoluble; they tend to bind to the calcium and magnesium ions, eventually precipitating and falling out of solution. In doing so, soaps actually dirty the surfaces they were designed to clean. Thus soaps have been largely replaced in modern cleaning solutions by synthetic detergents that have a sulfonate ($R\text{-}SO_3^-$) group instead of the carboxylate head ($R\text{-}COO^-$). Sulfonate detergents tend not to precipitate with calcium or magnesium ions and are generally more soluble in water.

Uses of Soap

Although the popularity of soap has declined due to superior detergents, one of the major uses of animal tallow is still for making soap, just as it was in years past. Beyond its cleaning ability, soap has been used in other applications. For example, certain soaps can be mixed with gasoline to produce gelatinous napalm, a substance that combusts more slowly than pure gasoline when ignited or exploded in warfare. Soaps are also used in "canned heat," a commercialized mixture of soap and alcohol that can be ignited and used to cook foods or provide warmth. Overall, soap is a remarkably useful substance, just as it has been for thousands of years.

David A. Dobberpuhl

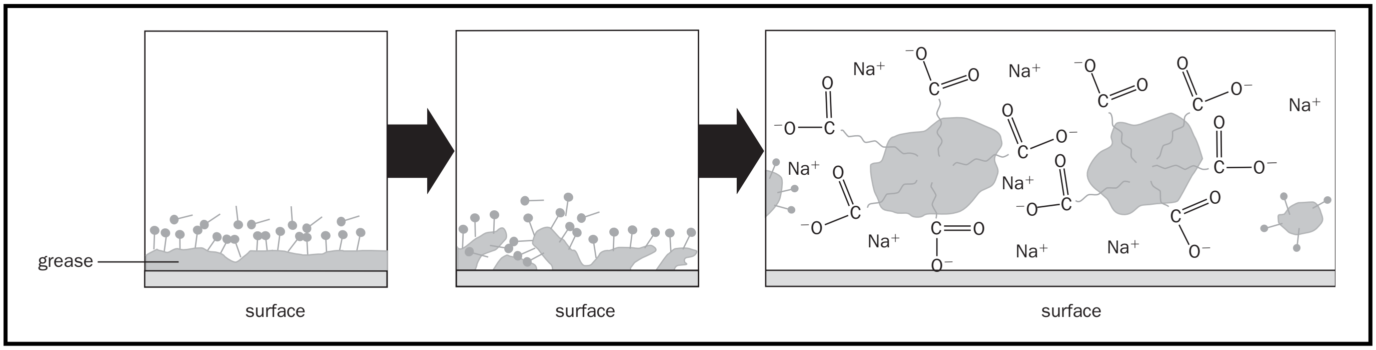

Figure 2. How soap works: The hydrophobic tails of soap molecules embed in grease and oil, breaking it up into particles called micelles that lift off the surface and disperse into water.

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Soddy, Frederick

ENGLISH RADIOCHEMIST
1877–1956

Frederick Soddy, the youngest of seven sons of a London corn merchant, was born on September 2, 1877, in Eastbourne, England. Raised by his half-sister, this precocious scientist attended Eastbourne College (1892–1894) and the University College of Wales, Aberystwyth (1895). In 1895 he won a scholarship to Merton College, Oxford University, from which he graduated with the highest honors in chemistry (1898).

After two years of research at Oxford, Soddy served as a demonstrator (laboratory instructor) at McGill University in Montreal, Canada (1900–1902), where he worked with Ernest Rutherford, studying the gaseous emanation of radium and showing that radioactivity involved the disintegration of radioactive atoms to form new elements. He called the process "transmutation," a term that he borrowed from **alchemy**.

alchemy: medieval chemical philosophy having among its asserted aims the transmutation of base metals into gold

The two proved the existence of two **radioactive decay** series: one starting with uranium and the other with thorium. The final product of both series was lead. They predicted that helium should be the decay product of radium, and they were the first to calculate the tremendous amount of energy that could be evolved during radioactive reactions.

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

Soddy then worked with William Ramsay at University College, London (1903–1904), where they used **spectroscopy** to show that helium was formed during the radioactive decay of radium and that it was also evolved in the decay of radium emanation. From 1904 to 1914 he served as a lecturer in physical chemistry and radioactivity at the University of Glasgow.

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

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

At Glasgow, Soddy posited his "group displacement law," which stated that the emission of an ***α*-particle** (a doubly charged particle consisting of two protons and two neutrons, identical to the helium nucleus, He^{2+}) from a radioactive element causes that element to move back two places in the

Periodic Table. In a short letter to the editor of *Nature*, published on December 4, 1913, he first proposed the term ***isotope*** to designate chemically identical elements with different atomic weights (in modern terms, elements with the same atomic numbers but different mass numbers). Isotopes occupy the same place in the Periodic Table.

English chemist Frederick Soddy, recipient of the 1921 Nobel Prize in chemistry, "for his contributions to our knowledge of the chemistry of radioactive substances, and his investigations into the origin and nature of isotopes."

Soddy wrote and spoke about the practical applications of radioactivity and envisioned **nuclear** energy as the basis for an advanced civilization and as a solution to the increasing depletion of natural resources. His book *The Interpretation of Radium* (1914) inspired H. G. Wells to write his science fiction novel *The World Set Free* (published the same year).

After he left Glasgow, Soddy abandoned his work on radioactivity and no longer followed recent advancements in the field. He developed an interest in financial, economic, social, and political theories, which found no general acceptance, as well as unusual mechanical and mathematical problems.

In 1914 Soddy assumed the chair of chemistry at Aberdeen University, Scotland, but his teaching and research were largely interrupted by World War I. In 1919 he was appointed to the Lee Chair of Chemistry at Oxford University, a post he held until his retirement in 1937. In 1921 Soddy received the Nobel Prize in chemistry "for his contributions to our knowledge of the chemistry of radioactive substances, and his investigations into the origin and nature of isotopes." He died in Brighton, England, on September 22, 1956. SEE ALSO RAMSAY, WILLIAM; RUTHERFORD, ERNEST.

George B. Kauffman

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

nuclear: having to do with the nucleus of an atom

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Sodium

MELTING POINT: 97.8°C
BOILING POINT: 883°C
DENSITY: 0.971 g/cm^3
MOST COMMON IONS: Na$^+$

11
Na
SODIUM
22.989770

Sodium is a soft, silvery alkali **metal** and reacts vigorously with water to generate hydrogen gas. The word *sodium* is derived from "sodanum" (a Medieval Latin name for a headache remedy), and "natrium" (Latin for "soda") is the origin of the element's symbol. Humphry Davy isolated the element in 1807 via the electrolysis of caustic soda, NaOH. Currently, sodium metal is obtained from the electrolysis of a molten mixture of sodium chloride and

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

Water and sodium acetate mixing causes a hot pack to release heat. Hot packs are used to relieve stiffness and pain.

calcium chloride (in an electrochemical cell called the Downs cell). In nature it is never found in its elemental form, but sodium compounds are quite common. Sodium is the most abundant alkali metal and the seventh most abundant element in Earth's crust (22,700 ppm). Sodium burns yellow-orange in the flame test.

The demand for metallic sodium is declining. Its primary use had been as a substance used in the production of tetraethyl lead, an antiknocking gasoline additive; however, because of its damaging effects on the environment, tetraethyl lead is being phased out. Sodium is used to produce sodamide from reaction with ammonia and to reduce $TiCl_4$, $ZrCl_4$, and KCl to Ti, Zr, and K, respectively. An **alloy** of Na and K is used in **nuclear** reactors as a heat transfer agent.

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

nuclear: having to do with the nucleus of an atom

Several sodium compounds are economically important. NaCl (ordinary salt) is a de-icing compound, a condiment, and a food preservative. NaOH finds use in the manufacture of soaps, detergents, and cleansers. Na_2CO_3 (washing soda) is used to make glass, soaps, fire extinguishers, and "scrubbers" that remove SO_2 from gases generated in power plants before it escapes into the atmosphere. The paper industry uses Na_2SO_4 (salt cake) to make brown wrapping paper and corrugated boxes.

Appropriate sodium ion levels (along with potassium levels) are essential for proper cell function in biological systems. SEE ALSO ALKALI METALS.

Nathan J. Barrows

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Solar Cells

A solar cell is, in principle, a simple semiconductor✷ device that converts light into electric energy. The conversion is accomplished by absorbing light and ionizing crystal atoms, thereby creating free, negatively charged electrons and positively charged ions. If these ions are created from the basic crystal atoms, then their ionized state can be exchanged readily to a neighbor from which it can be exchanged to another neighbor and so forth; that is, this ionized state is mobile; it behaves like an electron, and it is called a hole. It has properties similar to a free electron except that it has the opposite charge.

✷Solar cells can be made from single crystals, crystalline and amorphous semiconductors. For simplicity this article begins with a description of crystalline material.

Each photon of the light that has a high enough energy to be absorbed by the crystal's atoms will set free an electron hole pair. The electron and hole are free to move through the **lattice** in a **Brownian motion**; however, on average they will never move too far from each other. When the electron comes too close to a hole during their Brownian motion, they will recombine. On the other hand, when they experience an electric field, this will tend to separate the electrons from the holes; the electrons will drift toward the positive pole (the anode), and the positively charged holes will drift toward the cathode. Recombination will then take place in the external circuit (within the electric wires). Consequently a current will flow. Since it is generated by photons, one speaks of a photo current. And the semiconductor that performs this effect is called a photo conductor. Photo conductors are passive devices. They react to light by changing their electric conductivity. In order to activate them an external electric power source, such as a battery, needs to be supplied to draw a current that increases with increasing light intensity. There are many photo conductor devices in our surroundings; as for example, in cameras, in streetlight controls to switch the lights off at dawn and on at dusk, or for light barriers in garage door safety controls.

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

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

However, if an electric field is incorporated into the semiconductor, it will separate the electrons and holes. The part of the crystal that accumulates the electrons will be negatively charged; the part that accumulates the holes will be positively charged. The resulting potential difference, referred to as an open circuit, can be picked up by an electrometer. When electrodes are provided at both sides, a current can flow between them. The crystal, when exposed to sunlight, acts as a battery and becomes a solar cell (see Figure 1).

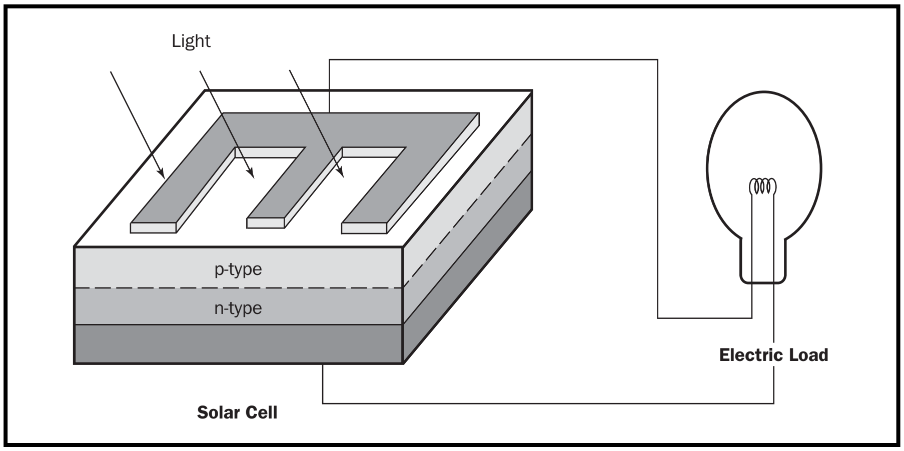

Figure 1. Schematics of a typical solar cell with light falling through an electrode grid onto a semiconductor sheet containing a *pn* junction that separates electrons and holes that flow to the respective electrodes and create a current through an external circuit.

Such a built-in field is easily created in certain semiconductors that can dissolve a *small quantity* of different impurities; can donate a free electron, called a donor; and can also accept an additional electron, called an acceptor. When dissolving these impurities (called doping) separately in different parts of the crystal, the region that contains donors is called the *n*-type region, the region with acceptors is called the *p*-type region. Between these two regions lies an *np* junction. This region represents the built-in field, since the *n*-type region is negatively charged compared to the *p*-type region. Here electrons that are created by light can be separated from the accompanying holes, with the electrons moving into the attracting *p*-type region and the holes moving preferably into the *n*-type region.

This, in principle, describes the essentials of a solar cell. The following portions of the article deal with each part of the solar cell in more detail, present a quantitative description of its performance, indicate performance limitations (called the "efficiency" of the solar cell), and give a variety of solar cell materials with comparative performance.

The *pn* Junction

The *pn*-junction can be easily understood in the band model with the conduction band populated by free electrons and the valence band populated by free holes. Without light, these carriers are created in thermodynamic equilibrium by donors and acceptors respectively. Mathematically their concentration is given by the Fermi-function (Eq.1)

$$n \approx N_C \exp -\left(\frac{E_C - E_F}{kT}\right) \tag{1}$$

with the determining Fermi level E_F , in the *n*-type region lying essentially in the middle between the donor level and the lower edge of the conduction band, E_c. N_c is the effective density of states at the lower edge of the conduction band and is on the order of 10^{19} cm^{-3}. A similar equation holds for the density of holes; here the Fermi level lies between the acceptor level and the upper edge of the valence band (see Figure 2a).

In thermodynamic equilibrium the Fermi level is horizontal throughout the crystal, thereby forcing both conduction and valence bands to bend, creating the *pn*-junction (see Figure 2b). Electrons from the *p*-type region will thereby "roll down" the hill and holes from the *n*-type region will "bubble up" the slope; hence both will be separated until their charge will force a reduction potential barrier so that the thermal motion across the junction will become equal from the left and from the right.

With light, additional carriers are created, hence equation 1 needs to be modified, replacing E_F with E_{Fn} or E_{Fp}, the two quasi-Fermi levels in the *n*-type or *p*-type region respectively. These quasi-Fermi levels are now split; the higher the light intensity the more they split. Close to the electrode both quasi-Fermi levels collapse toward the majority quasi-Fermi level, where they are connected to the metal Fermi level (Figure 3). This shift of the Fermi levels in the electrodes represents the open circuit voltage that can be approximated by the shift of the minority quasi-Fermi levels (Figure 3):

$$V_{oc} \approx E_{Fn}(p) - E_{Fp}(n) \tag{2}$$

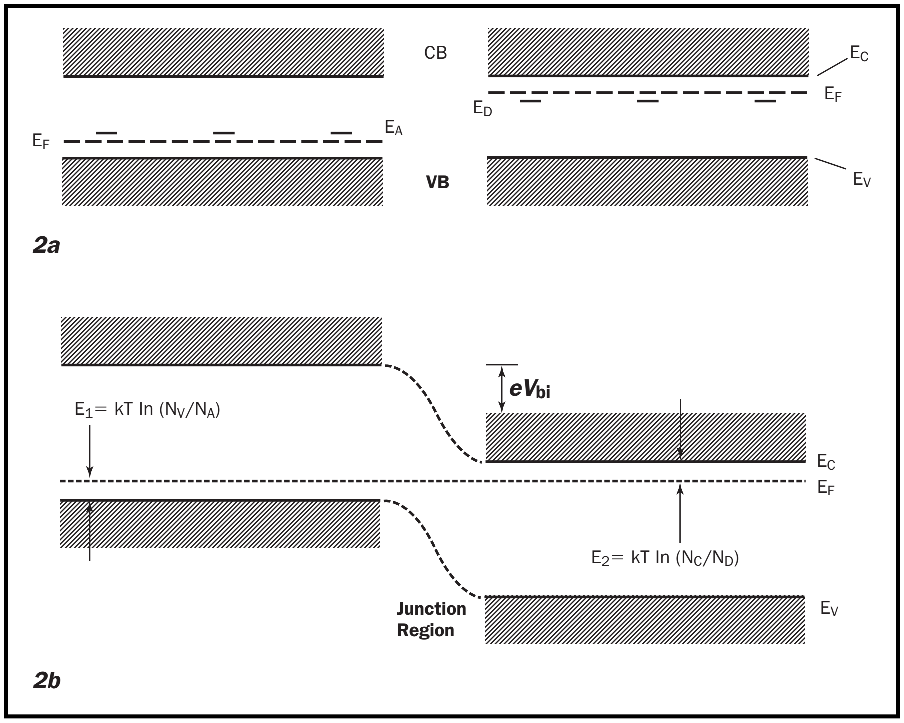

Figure 2a. Band picture with conduction band (CB) and valence band (VB) in an *n*- and a *p*-type region with the Fermi level E_F identified, which usually lies close to the donor-(E_D) or acceptor level (E_A) respectively. Figure 2b. A *pn* junction when both regions are joined resulting in the junction region with a barrier height of eV_b; of the built-in electric field.

Current-Voltage Characteristics

Materials with a *pn*-junction show a nonlinear, rectifying characteristic, since it is much easier to move electrons from the electrode through the *p*-type region and through the junction than from the *n*-type region over the junction barrier into the *p*-type region. The current-voltage characteristic through a *pn*-junction is given by the typical diode equation:

$$j = j_o\,[\exp\left(\frac{eV}{kT}\right) - 1] \tag{3}$$

as shown as the dark current curve in Figure 4.

When the device is exposed to light, the additional carriers cause an increased current, recognized by an essentially parallel shift of the characteristic downward by j_L, shown in Figure 4. (For a more precise discussion see Böer, 2002.)

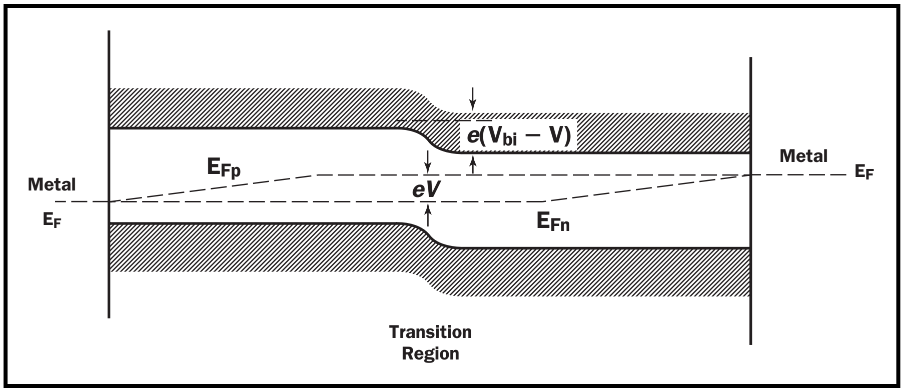

Figure 3. A *pn* junction with light, showing the quasi-Fermi levels and their connection to the electrodes, with V the applied voltage and V_{bi} the built-in voltage. Close to the metal surface enhanced surface recombination will cause both quasi-Fermi levels to collapse.

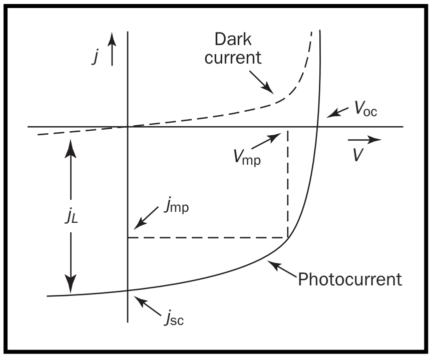

Figure 4. Current-voltage characteristics. Dark current (dashed) and photo current (solid); (the shift from the dark current is shown j_L) indicating open circuit voltage and short circuit current. The inscribed maximum rectangle represents the maximum power point voltage and current.

The photovoltaic characteristic is consequently given by (see, e.g., Fahrenbruch and Bube 1983):

$$j = j_o\,[\exp\left(\frac{eV}{kT}\right) - 1] - j_L \tag{4}$$

j_L is the maximum current obtained in short-circuiting the device. With $j_0 << j_L \sim j_{SC}$ one obtains for the open circuit voltage (when j = 0) from Eq. 4:

$$V_{oc} \approx \frac{kT}{e}\ \ln\left(\frac{j_L}{j_o}\right) \tag{5}$$

Whenever the current-voltage characteristic extends into the fourth quadrant, electric power can be extracted. Its maximum value is given by the largest rectangle that can be inscribed in the characteristic (Figure 4). This identifies the maximum power current, j_{mp} and the maximum power voltage $V_{mp.}$ The ratio of the products of these maximum power points to the products of the short circuit current and open circuit voltage is called the fill factor, which can be approximated for ideal solar cells by (see, e.g., Green 2001):

$$FF = \frac{V_{mp}\, j_{mp}}{V_{oc}\, j_{sc}} \approx \frac{\nu_{oc} - 1\mathrm{n}(\nu_{oc} + 0.72)}{\nu_{oc} + 1} \tag{6}$$

with $v_{oc} = V_{oc}/(kT/e)$. The actual fill factor is usually somewhat smaller and is a measure of the quality of the solar cell. It is a function of the diode doping and of solar cell materials.

The net carrier transport in a solar cell can be pictured as shown in figure 5, with light (*hv*) coming from the left and generating (g_0) electron hole pairs in the *p*-type front layer (of thickness *d*). The electrons move towards and through the junction, the holes in opposite direction. When both are shown as electron current (the arrow head is inverted for holes) one visualizes the continuity of the carrier flow and its building up with increasing depth of the front layer.

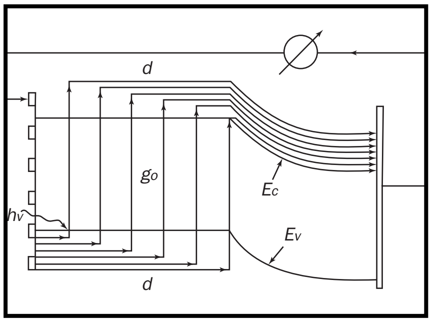

Figure 5. Generation of electron hole pairs and their motion to the respective electrodes.

Solar Cell Materials

A wide variety of materials have the potential of yielding solar cells; several are considered attractive candidates for reasons of high conversion efficiency and ease of fabrication.

For a solar cell one can select a single semiconductor having a junction, usually referred to as homojunction, or a combination of two materials, with the junction at the interface referred to as heterojunction. The selected material needs to match the solar spectrum; i.e., it has to absorb most of the spectrum for maximizing the short circuit output, therefore it has to have a low band gap. However, this is counteracted by the desire to also have a large open circuit voltage, requiring a larger band gap and forcing a compromise. Consequently, for homojunction materials a band gap between 1 and 1.5 eV is preferred.

Typical representatives of this class of homojunction semiconductors are Si; several III-V compounds, most prominently GaAs; and from the class of II-VI compounds CdTe, since it can be doped *p*- and *n*-type, while others cannot. Several ternary compounds are also used, most prominently $CuInSe_2$ and similar ternaries. An example for a heterojunction cell is the CdS/CdTe combination (Meyers and Birkmire, 1995). For more details see Green (2001).

These materials can be employed as single crystals (Si and GaAs), as polycrystals (Si), other thin-film materials (CdTe and all ternaries), and as amorphous material (a-Si:H). Single crystals have the advantage of having high crystal quality and a minimum density of recombination centers; therefore they have a high carrier lifetime that is essential for the carriers to reach the junction after generation, in order to be separated and to contribute to the current.

Other factors that influence the output of solar cells are degradation of surfaces and of electrodes; the first causes a reduction of carrier lifetime, the second causes a reduction in solar cell life expectancies. An example of the first is the beneficial effect of a natural oxide layer that reduces surface recombination of Si solar cells, while special efforts need to be made for GaAs cells to passivate the surface. An example for the second effect is the CdTe solar cell, which has difficulties maintaining stable electrodes on the *p*-type side.

Optimization of Photon Absorption

In order to make maximum use of the impinging photons and obtain maximum solar cell output, one has to maximize surface penetration, minimize reflection, and reduce obstacles, such as electrodes.

A typical example for such optimization is the structure (shown in Figure 6) developed by Martin Green and his group in order to produce highly-efficient Si solar cells. In addition to an anti-reflecting coating, it contains an etched pyramidical surface that permits light capture (velvet effect) by multiple reflections downward. It also reduces the surface cover of electrodes that are of sufficient thickness to carry the current by depositing it vertically into narrow grooves. It also minimizes the probability of both types of carriers reaching the same electrode by providing a repulsive field through strong doping of a thin surface layer.

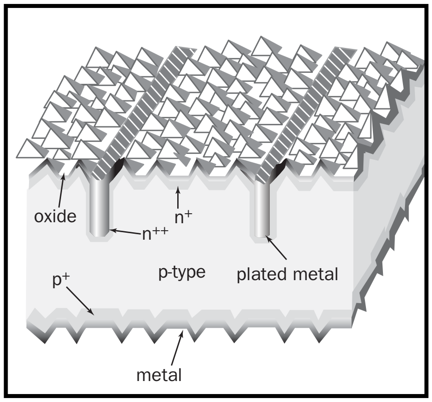

Figure 6. Solar cell that optimizes light penetrations through the surface by anti-reflecting coating and pyramidal surface shaping, as well as using buried contacts that minimize surface obstruction while still providing sufficient electrode cross section to carry the current. (See Green, 2001.)

Solar Cell Efficiency

Solar cell efficiency is a most valuable measure of its performance. With sunlight impinging from the zenith on a sunny day, a surface perpendicular to the light receives about 1 kW/m^2. When converted by a solar cell of 10 percent efficiency (presently reached or exceeded by most commercially available solar panels), this means that 100 W/m^2 in electrical energy can be harvested. This is sufficient if surface areas are ample and the panels are relatively inexpensive. However, where surface areas are at a premium—e.g., on top of a solar car or in some satellites—it is essential to use more efficient solar cells. These are available from carefully engineered Si cells or from GaAs, reaching efficiencies close to 25 percent.

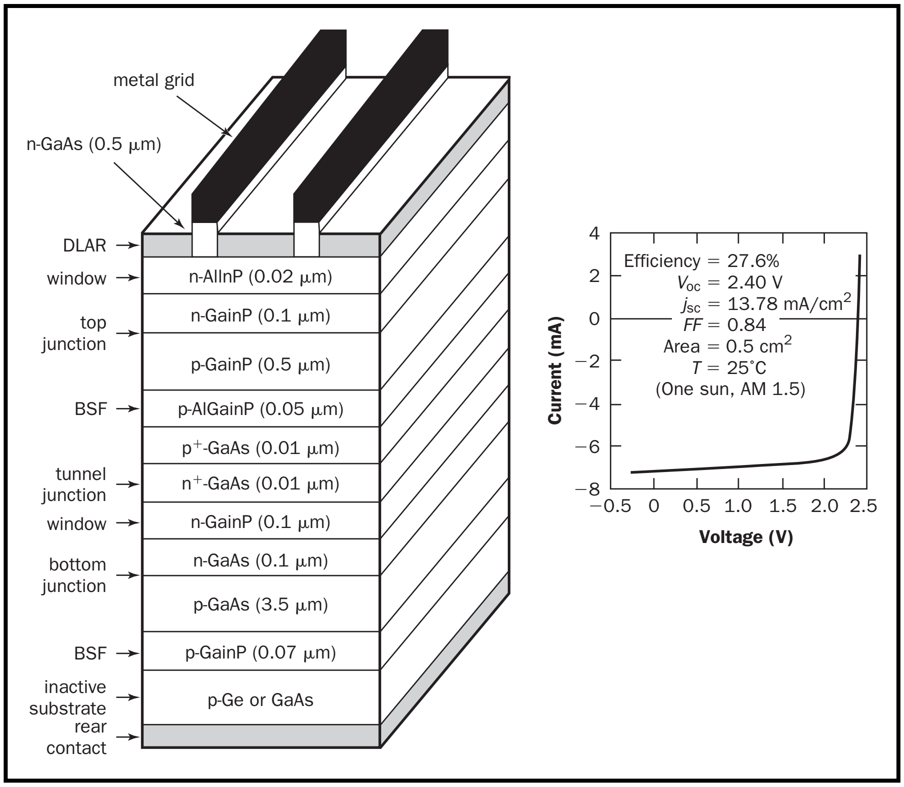

Figure 7. Monolytic GaInP/GaAs solar space cell (panel a) and a similar AlGaAs/GaAs solar cell have reached 27.6% efficiency at AM 1.5 insolation (after Chung et al., 1990). [AM refers to the airmass, and AM 1.5 indicates a solar angle at which the light penetrates through 1.5 times the vertical thickness of the air, that is at a zenith angle of 48.19°.]

When still higher efficiencies are desired, one can resort to tandem solar cells made by adding a semiconductor of a lower band gap on the bottom, so that photons of lower energy that were not absorbed in the top cell have a second chance to be absorbed and produce additional electric power. Adding a third layer to such a tandem can be beneficial. An example is shown in Figure 7 for a monolytic cell (with matched current and only two electrodes). AlGaAs/GaAs tandem cells reach 27.8 percent efficiency. Mechanically stacked cells (with four electrodes) between GaAs and Si have reached 31 percent (Gee and Virshup, 1988). For more on a large variety of solar cell materials and their best efficiencies, see Green (2001) or Bube (1998). Comprehensive solar cell efficiency tables are provided in Green et al. (2000). SEE ALSO Solid-State Devices.

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Solid State

Matter is commonly encountered in one of three states—solid, liquid, or gas. Air is an example of a gas and water an example of a liquid. Objects such as rocks, concrete buildings, or pages in a book can be classified as solids. But what exactly is a solid?

Defining the solid state is difficult because while many things are described as solids, they may be heterogeneous (i.e., they may contain molecules of liquids or gases). Consider, for example, the pages of a book, which are made from paper and are primarily cellulose. Even though there is no question that they are solid, they do contain a quantity of water within the cellulose structure—typically about 5 percent. Paper is not described as a liquid, however, because it would not be a useful way to describe its properties.

The defining characteristics of a solid are a question of molecular motion. Atoms and molecules in a gaseous state move rapidly and independently, with little interaction. A gas therefore occupies the shape of the container that holds it as the gas molecules bounce off the walls. Particles in the liquid state do not move as rapidly or as independently as molecules in a gas, but they do move past one another, forming only loose and temporary associations. Liquids also lack definable shape, adopting the shape of the container that holds them. Conversely, particles in a solid do not change position and can interact strongly with their neighbors. They may vibrate in place and oscillate about their average position, but they do not shift from one location to another. It is incorrect to say that particles in a solid do not move, as they do "jiggle" in place, but they do not move from their fixed position. In the case of paper, the molecules of cellulose and water are, in the absence of an external force, fixed in place. An external force is required to allow the atoms of a solid to shift, such as when a piece of paper is ripped or a strip of metal is bent.

An analogy for the three states of matter is students in a classroom. Sitting at their desks, they represent a solid. Moving around the classroom, they are like a liquid. Once the bell rings, they are like a gas that is spread throughout the neighborhood. The arrangement of the components of a solid—in this analogy, how the students' desks would be arranged—allows for solids to be classified in one of two broad categories: amorphous or crystalline.

Glass is a classic example of an amorphous material and diamond of a crystal material. Both are transparent solids with molecules and atoms that are held together with strong covalent bonds. Yet it would be hard to mistake one for the other, as diamonds are the hardest known natural substance while glass breaks fairly easily. To use the classroom analogy, the difference between glass and diamonds is that in glass, the desks are arranged completely at random, whereas in diamonds, the desks are lined up in neat and orderly rows.

Amorphous Solids

Glass is a heterogeneous material formed from silicon, oxygen, sodium, and a variety of other elements, depending upon the type of glass. It lacks long-range structure: Short units of silicon dioxide are bound together, but there is no overall order. At an atomic level, glass looks like a frozen liquid. Individual clusters exist, but they are not connected to each other and are held together only by van der Waals interactions. This is why when glass breaks it forms curved or jagged edges and why it shatters if struck with a hard blow.

Glass is only one example of an amorphous material. Another is paper, composed of randomly oriented cellulose molecules. Many familiar objects are made up of amorphous solid materials, all lacking long-range structure or order. They are aperiodic substances—substances that do not display periodicity. Consequently, it is hard to analyze the structure of amorphous materials as each sample is unique.

Crystalline Solids

Crystalline solids make up a much smaller percentage of everyday objects, but they are easier to understand. A subdiscipline of chemistry called crystallography is devoted to analyzing crystalline material. The defining characteristic of a crystalline material is that it is periodic with an underlying structure that is regular and repeating. A crystal displays long-range structure made up of the same building block used over and over.

Consider a crystal of gold, composed of endless planes of gold atoms. Within each plane, gold atoms adopt a regular pattern, with each atom occupying the center of a hexagon and surrounded by its closest neighbors. Each gold atom looks just like the one next to it—the pattern is repeated countless times. Also consider the diamond, which is like glass in appearance but is a covalent network solid with a three-dimensional lattice of tetrahedrally bound carbon atoms. Each carbon is attached to four neighbors in endless repetition. The three-dimensional structure and covalent bonds ensure that diamonds are incredibly hard.

The critical feature of crystalline material is that it is periodic. Although it may not be intuitively obvious, there are only seven shapes in nature that can be packed in a long-range periodic three-dimensional pattern. Packing a collection of spheres leaves a hollow shape between one sphere and the next, so a sphere is not one of the basic shapes for packing crystals. A cube, on the other hand, gives a three-dimensional, repeating structure with no voids. Considering the difference between a stack of boxes and a stack of bowling balls, it is easy to see that the boxes make a much more solid structure.

This is not to say that atoms and molecules are little boxes but rather that particles are arranged in a solid as if they were contained in molecular-size boxes. Each of these boxes is called a unit cell, and the overall arrangement of the unit cells is called a lattice. There are seven unit cell types possible for crystal growth, and all crystals belong to one of these seven crystal systems (see Table 1).

The spatial arrangement of atoms and molecules in any crystalline solid can be assigned to one of these seven geometric systems, even though the atoms themselves are spherical in shape. For example, the lattice of tetrahedrally bonded carbon atoms in a diamond can be described using a repeating cube. Another example is the cube that is described by sodium chloride (NaCl), or common table salt. In this instance, a sodium atom can be found at the center of the cube, surrounded by six chloride ions, each

System	Edges	Angles
cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$
tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$
orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$
hexagonal	$a=b\neq c$	$\alpha=\beta=90°$; $\gamma=120°$
monoclinic	$a=b\neq c$	$\alpha=\gamma=90°$; $\beta=90°$
trigonal	$a=b=c$	$\alpha=\beta=\gamma\neq 90°$
triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$

Table 1. Crystals belong to one of these seven crystal systems.

occupying one of the faces. Twelve more sodium atoms occupy the edges and eight more chlorides occupy the corners. Considering that each chloride at each corner resides in eight different cubes, that each sodium along an edge resides in four different cubes, and that each chloride on a face resides in two different cubes, only one ion—the central sodium—is contained entirely within the unit cell. However, one-eighth of the eight chlorides at the corners and two of the six chlorides on the faces result in a total of four chlorides in the unit cell. Similarly, one-fourth of the twelve sodium atoms along the edges and the one in the middle results in a total of four sodium ions. The net result is that each repeating unit—each cube of sodium and chloride—has four of each atom and, overall, the formula for table salt can be written as NaCl.

This idea of repetition—of using unit cells to build up a crystalline solid—allows crystallographers to use x-ray diffraction and neutron diffraction to map out electron density within a unit cell. Using mathematics and a knowledge of where the electrons are located, it is possible to determine the exact position of each and every atom within the cell. From this, it is possible to determine which atoms are in close contact. Physically, two atoms are said to be bonded together by a covalent interaction when the distance between them is less than the sum of their respective van der Waals radii. Chemists and physicists have been able to use the concept of bonding and the techniques of crystallography to determine the structure of a great many substances. Indeed, approximately 100,000 crystal structures have been determined and registered in the Cambridge Crystallographic Database.

Diamonds represent a class of compounds called network crystals because they extend the full length of the crystal. Every carbon in a diamond is connected, via covalent bonding, with every other carbon atom. Sodium chloride, or table salt, represents a class of compounds called ionic crystals because it is composed of oppositely charged ions held in place by electrostatic attraction. These interactions can be incredibly strong and give rise to minerals and gemstones, such as magnetite and rubies. Ionic interactions are the binding force in all salts, regardless of whether they are crystalline. In the crystalline state, however, they give rise to almost all minerals and gems.

Two other classes of crystalline solids are molecular crystals and metallic crystals. Molecular crystals are assembled through the interaction of molecules to form a regular and repeating lattice. The most familiar example would be solid water (ice). Each water molecule in a crystal of ice is independent and internally bonded through covalent interactions. In the gaseous state, water molecules move independently and do not interact. In the solid state, the amount of energy present is insufficient to overcome hydrogen bonding interactions, and the molecules link one to the other to form an extended hexagonal lattice. Each molecule is held tightly in place by its neighbors. The interactions between molecules tend to be weaker than in either a network or ionic crystal, with the result that these crystals are easily broken—think of trying to crush an ice cube versus a diamond.

In a metallic crystal, the latticework of the atoms is bound together by a sea of electrons. Each atom—or, more accurately, each nucleus—occupies a position within a crystalline lattice. The electrons, on the other hand, move among all of the available atoms in a series of conduction bands. The net result is that even in an amorphous state metals readily conduct electricity and heat, they are ductile and malleable, and they exhibit the luster seen on metallic surfaces. In the crystalline form, metals can do all of the above and exhibit other properties such as magnetism (which requires ordered crystalline domains). SEE ALSO Glass; Salt.

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Solid-State Devices

Solid-state devices are the controlling components of both high-tech and very ordinary devices. Their widespread usage is related to the fact that they can be utilized to interface with all human senses. Light emitting diodes (LEDs) and solid-state lasers produce light used in all kinds of displays that interface with sight. The first applications of solid-state devices were the use of transistors in radios and amplifiers that interface with our sense of hearing. Thermoelectrics are solid-state devices that can be used for heating or cooling—an interface with the sense of touch. While solid-state devices do not emit odor or flavor, they can be utilized as sensors to monitor odiferous or toxic substances, interfacing with the senses of smell and taste. To a degree, the modern sense of time, driven by the information revolution, points back to solid-state devices.

At the beginning of the twenty-first century, there were more solid-state devices produced than any other manufactured thing. More than ten billion components are fabricated onto a single eight-inch silicon wafer. During the 1940s the jobs of simple solid-state devices were performed with vacuum tubes and mechanical relays. (If a vacuum tube covered one square inch of area, the same ten billion devices that fit on an eight-inch wafer would cover 6.5 square kilometers [2.5 square miles].) The invention of the transistor in 1947 at Bell Laboratories ushered in an electronic age, beginning with telephones and radios and eventually providing ever smaller and faster computers, more efficient lighting, a means to harvest electrical energy from the Sun, and much more.

The Materials of Solid-State Devices

Solid-state devices consist of intricate organizations of crystalline materials that exhibit insulating, semiconducting, or conducting properties. Insulators, typically composed of SiO_2, block the flow of current from one part of the device to another. Semiconductors, typically silicon or materials related to silicon, are the principal materials of solid-state devices, controlling the number and rate of flow of charged carriers (electrons or holes). Holes are formed when an electron is removed and thus carry a positive charge. Conductors, typically **metals** such as aluminum or copper, are used for electrical connections to the devices. The design, operation, and fabrication of solid-state devices are generally the subject of physics and engineering. The properties of the materials used to make the devices, however, are determined by chemistry.

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

The difference between conductors, semiconductors, and insulators is determined by how easily electrons (or holes) can move through the crystalline material. The movement (delocalization) of electrons, or their localization on or between particular atoms, is determined by the chemical bonding. In a crystal, it is necessary to consider the repeating bonding interactions between the many atoms rather than just the bonding interactions between two atoms in an isolated molecule.

Consider the bonding analogy between the dihydrogen molecule, H_2, and a hypothetical one-dimensional hydrogen crystal, H_n, symbolically represented in Figure 1. Each hydrogen atom has one electron in one **atomic orbital**. When two such atoms are brought together, the electrons are shared between them in a bonding molecular orbital, σ, where the orbitals are in **phase** with each other. An antibonding orbital, σ^*, is also created at higher energy with the two orbitals out of phase with respect to each other. A stable bonding situation is created when the electron configuration fills bonding molecular orbitals and leaves antibonding molecular orbitals empty.

atomic orbital: mathematical description of the probability of finding an electron around an atom

phase: homogeneous state of matter

When an approximately infinite number of atoms are brought together to form a crystal, they bring along an infinite number of orbitals and corresponding electrons. When all these orbitals are in phase, the lowest energy crystal orbital is obtained. When they are all out of phase, the highest energy crystal orbital is obtained. But with the near infinite number of atoms, and thus a near infinite number of atomic orbitals, there must be a near infinite number of crystal orbitals formed with energies intermediate between the most bonding and most anti-bonding levels. This collection of crystal orbitals is referred to as an energy band.

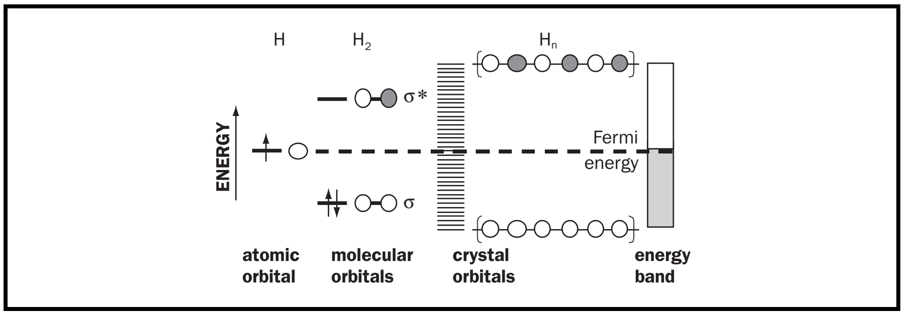


Figure 1. Evolution of an energy band.

Each band can be filled with electrons in a similar fashion to filling a plastic bottle with sand. If that bottle of sand is completely full, it is possible to tilt it or even turn it upside down and the grains of sand will not move. If the plastic bottle is not completely full (i.e., a partially filled band), then the grains of sand can easily move when the bottle is tilted. They are not localized in one position but **delocalized** across the top surface. In a similar way, electrons of a partially filled band are delocalized across the crystal and can conduct electricity. The energy of the highest filled levels is called the Fermi energy.

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

Understanding Conductivity

A metallic conductor is a substance that has a partially filled band. It takes very little energy to move electrons from a filled level to an empty level in a band; this results in high conductivity because there is no energy gap at the Fermi level. When the temperature of a metallic conductor is lowered, the conductivity increases because the thermal motion of the atoms in the crystal is slowed, allowing the electrons to move more easily.

In contrast, both semiconductors and insulators have band structures in which all of their electronic bands are either completely full or completely empty. Because real crystals have more than one orbital, unlike the hydrogen example, there will be several bands giving rise to the electronic band structure. Bands filled with electrons occur below the Fermi energy and bands at higher energy are empty. The difference in energy between the highest part of the filled band and the lowest part of the empty band is the band gap. The difference between an insulator and a semiconductor is the size of the band gap. A material with a band gap of less than about 3.5 eV is considered a semiconductor, whereas materials with larger band gaps are insulators. In a semiconductor, the filled band below the Fermi level is called the **valence** band and the empty band above the Fermi level is called the conduction band.

valence: combining capacity

If sufficient energy is supplied to a semiconductor, an electron can be promoted from the valence band to the conduction band; this also creates a hole in the valence band. The electron promoted to the conduction band and/or the hole left in the valence band can be delocalized across the crystal, resulting in electronic conductivity. The magnitude of the conductivity is strongly determined by the energy supplied to the semiconductor. For this reason, the conductivity of a semiconductor will increase with increasing temperature.

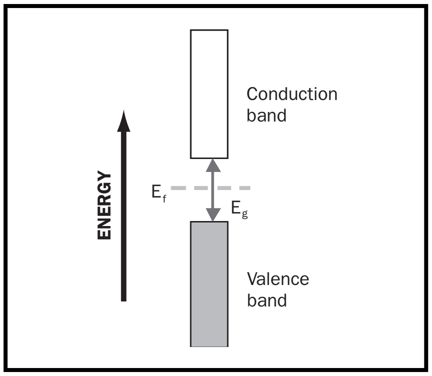


Figure 2. Band structure of a semiconductor. E_f is the Fermi energy and E_g is the band gap.

The Chemistry of Semiconductors

The properties of a semiconductor are determined by the elemental composition of the material, its structure, and the presence of any impurities. Impurities, commonly referred to as dopants, add extrinsic properties to the semiconductor, compared with the properties intrinsic to the pure material itself.

Intrinsic semiconductors. The group fourteen elements carbon, silicon, germanium, and tin can be found to adopt the diamond-type crystal structure shown in Figure 3a. Other crystalline structures are also found; for example, graphite and diamond are different crystal structures of the same element, carbon. Because of its size and orbital energies, carbon forms very strong bonds, so there is large energy separation between the bonding and antibonding bands in diamond. This results in a large band gap of 6.0 eV, making diamond an insulator. In contrast, bonding between the heavier elements (silicon, germanium, and tin) is not as strong, so the band gap decreases going down the column of the Periodic Table: silicon, 1.1 eV; germanium, 0.7 eV; and grey tin, 0.1 eV. In addition, at temperatures below 13°C (55°F), tin undergoes a crystal rearrangement to the structure of white tin that has no band gap because it is metallic.

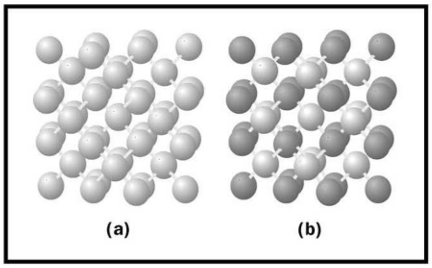


Figure 3. Crystal structure of (a) diamond and (b) a diamond-type compound semiconductor.

Compound semiconductors are made up of more than one element and give the ability to chemically tune the size of the band gap. Typical compound semiconductors will combine elements from group thirteen and group fifteen on the Periodic Table. These compound semiconductors also adopt a diamond-type crystal structure but with alternation of the atom types in the crystal network (Figure 3b). By combining elements with three and five valence electrons (such as aluminum and phosphorus, respectively)—an average of four electrons per atom—a material with properties similar to silicon with four valence electrons is obtained. However, because the orbitals of phosphorus are lower in energy and the orbitals of aluminum are higher in energy than silicon, a larger band gap is observed for the compound semiconductor AlP (3.0 eV). Combination of the heavier elements gallium and arsenic will form gallium arsenide (GaAs), with a band gap of 1.4 eV. A similar chemistry is possible by combining elements of groups twelve and sixteen, which, for example, yield the semiconductors zinc sulfide (ZnS) and cadmium selenide (CdSe), with band gaps of 3.8 eV and 1.8 eV, respectively.

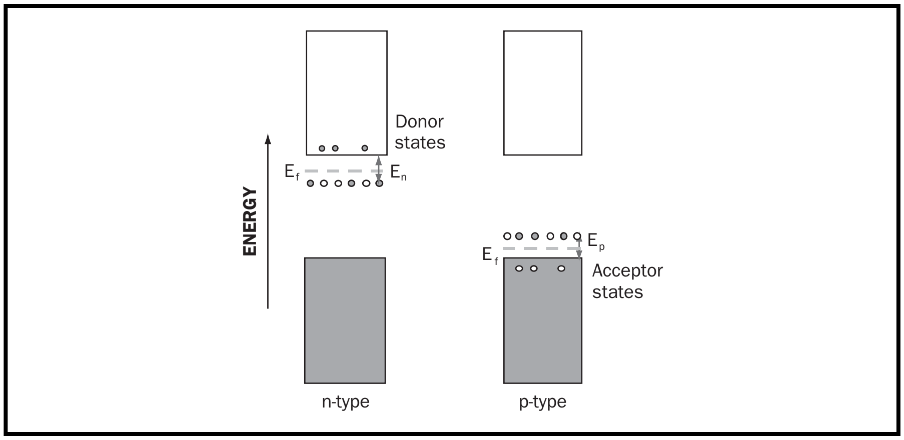
Dopants in semiconductors. Purity for an electronic grade semiconductor must be greater than 99.999 percent. Controlling the amount and type of impurity, however, can fine-tune the properties of the semiconductor. For example, adding a phosphorus impurity (with five valence electrons) to silicon (with four valence electrons) effectively adds one extra electron for each phosphorus atom added to the crystal. Thus the phosphorus is a donor to silicon. The dopant phosphorus atoms will displace silicon atoms in the crystal, but the overall crystal structure does not change, nor does the band structure. The extra electron must go into the conduction band, however, since the valence band was already full. This yields an *n*-type semiconductor. Conversely, **doping** silicon with aluminum provides one too few electrons, leaving one hole in the valence band for each aluminum atom added. Thus aluminum is an acceptor from silicon. Having lost electrons, the holes bear a positive charge, forming a *p*-type semiconductor. Because the gap in energy between the donor levels and the conduction band (E_n) or between the acceptor levels and the valence band (E_p) is very small, these doped semiconductors will exhibit a greater conductivity and much less temperature dependence than is observed for an intrinsic semiconductor.

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

The *P–N* junction. The Fermi level of a *p*-type semiconductor is lower in energy than that of an *n*-type semiconductor. When *p*- and *n*-type semiconductors are joined, a common Fermi level is created by the combination of holes and electrons at the interface. No carriers are present in this depletion zone at the junction. When a positive **voltage** is applied to the *p*-type side of the *p-n* junction and a negative voltage to the *n*-type side, current can flow since the positive voltage pushes the holes toward the

voltage: potential difference expressed in volts

Figure 4. *N*- and *p*-type doping of a semiconductor.



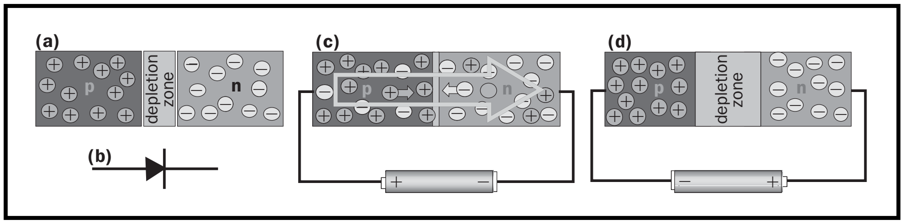
negative cathode and the negative voltage pushes the free electrons toward the positive anode. By contrast, hooking the battery up in reverse will increase the size of the depletion zone, because the negative voltage attached to the *p*-side of the junction will pull more holes toward that electrode and the positive voltage attached to the *n*-type semiconductor will pull electrons toward the electrode and away from the junction, leaving a larger depletion zone. As a result there are no free carriers and no current can flow. Thus this *p-n* junction forms the simplest solid-state device, known as a diode.

Diodes. Diodes are essentially one-way valves for electronic conductivity. Such a device is very important in a power supply that converts AC to DC current, necessary for many electronic devices. Connecting a single diode to an AC electrical circuit will block either the positive or negative voltage swings, described as half rectification. The connection of four diodes (as shown in Figure 6) will give full wave rectification, converting AC to DC current. The addition of capacitors to this circuit will smooth the voltage oscillations for actual device operation.

When electrical current is passed through any *p-n* junction, electrons traveling through the conduction band or holes traveling through the valence band can recombine with holes or electrons, respectively, across the band gap. This recombination primarily occurs to electrons that have been pushed into the *p*-type region of the diode and to holes that have been pushed into the *n*-type region of the diode by the external voltage. As electrons and holes are recombined across the band gap, energy is released, often as a **photon** with an energy equal to that of the band gap. Semiconductors with band gaps between 1.8 eV and 3.1 eV will emit photons of visible light (red [700 nanometers; 2.76 × 10^{-5} inches] to violet [400 nanometers; 1.58 × 10^{-5} inches]). These are known as LEDs. In fact, all diodes emit light, but most have a band gap that is smaller than the energy of a visible pho-

photon: particle of light as defined by Max Planck

Figure 5 a) Schematic of a *p-n* junction, b) symbol for a diode with arrowhead indicating the direction of current flow, c) a forward biased *p-n* junction indicating the direction of current flow from + to - with the arrow (center), and d) a reverse biased *p-n* junction, which does not allow current to flow.



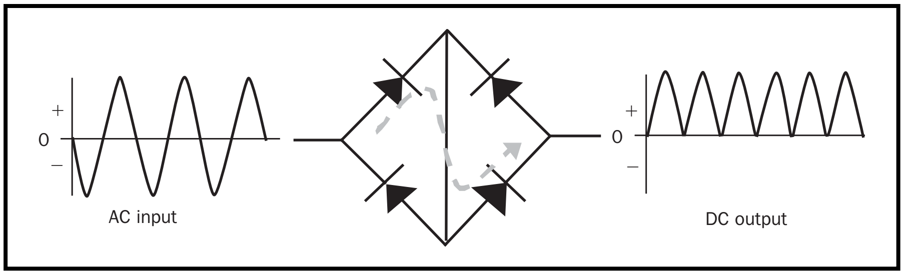


Figure 6. Four diodes linked to form a full wave rectifier. The dotted-line arrow indicates the direction of current flow under the positive AC oscillations.

ton. As a result, most diodes emit infrared photons. Such infrared emission is used for signaling in many remote control devices.

Transistors. Transistors are solid-state switching and amplifying devices, and it was their invention in 1947 that truly began the electronics revolution of the late twentieth century. An *n-p-n* bipolar transistor is formed by connecting *n*-type semiconductors on either side of a thin *p*-type semiconductor. As shown in Figure 7, the transistor acts as a switch for the circuit connected to the 10 V power supply. If a small negative voltage is applied to the base (contact B), the holes are removed from the *p*-type semiconductor, creating an insulating barrier. This is the same process as trying to force current the wrong way through two *p-n* junctions. As a result, no current will flow between any of the contacts. If a small positive voltage is applied to the base contact, however, some current will flow through the control loop (electrons going from the emitter to the base). Because the voltage supplied between the emitter (contact E) and the collector (contact C) is much larger than the base voltage, a much greater fraction of the electrons will cross the thin *p*-type layer, giving the much larger collector current.

As described above, the transistor functions as a simple on/off device, depending on the sign of the voltage applied to across the base and emitter. Because the base current is small and the collector current is large, this same solid-state device can also be used as a signal amplifier. The ratio of the collector current to the base current is essentially constant for a given device. Since the base current is proportional to the base-emitter voltage (voltage between B and E) and the collector current is proportional to the emitter-collector voltage (voltage between E and C), a small oscillation in the voltage input from a microphone, for example, into the BE loop will be

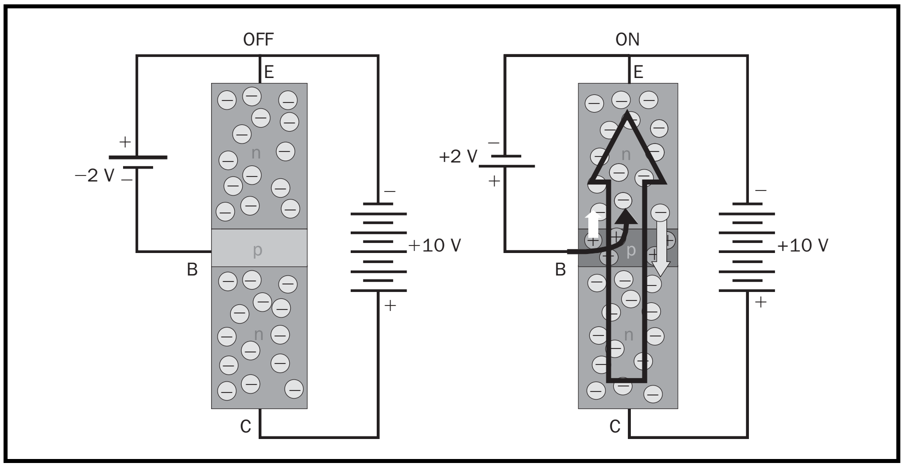


Figure 7. An *n-p-n* bipolar transistor. B, base; E, emitter; and C, collector. The direction of flow for the electrons and holes in the on state is described with grey and white arrows, respectively. The primary current, defined as flow from + to -, is shown in the large black block arrow, and the current through the control loop is represented by the smaller black arrow.

amplified to a large oscillation in the voltage in the EC loop, which then can be connected to a loudspeaker.

Though varying combinations of semiconductors can be fabricated into many different solid-state devices, the operation of the device is strongly dependent on the chemistry of the elements making up the semiconductors. The bonding between elements making up semiconductors determines the electronic band structure and the size of the band gap. The number of valence electrons determines the filling of those bands and thus the electronic properties. Ongoing research efforts continue to discover new semiconductors with new possible applications. In addition, extensive effort is being invested to design smaller and smaller devices with the goal of moving from solid-state devices (based on crystalline materials) to single molecule devices.

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Solution Chemistry

The majority of chemical processes are reactions that occur in solution. Important industrial processes often utilize solution chemistry. "Life" is the sum of a series of complex processes occurring in solution. Air, tap water, tincture of iodine, beverages, and household ammonia are common examples of solutions.

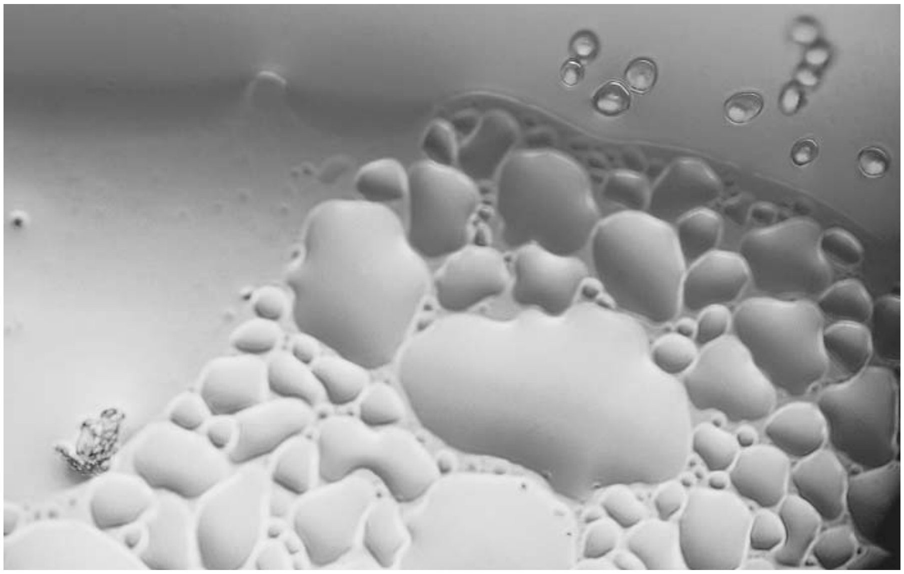
A solution is a homogenous mixture of substances with variable composition. The substance present in the major proportion is called the solvent, whereas the substance present in the minor proportion is called the solute. It is possible to have solutions composed of several solutes. The process of a solute dissolving in a solute is called dissolution.

heterogenous: composed of dissimilar parts

homogenous: composed of similar parts

Many common mixtures (like concrete) are **heterogeneous**—the components and properties of such mixtures are not distributed uniformly throughout their structures. Conversely, solutions are said to be **homogeneous** because they have uniform composition and properties. Solutions are intimate and random homogeneous mixtures of atomic-size chemical species, ions, or molecules.

In addition to their observed homogeneity, true solutions also have certain other characteristics. For example, components of a solution never separate spontaneously, even when a significant density difference exists between the components. Solutions also pass through the finest filters unchanged.



Droplets of a solution of water and oil, exposed to polarized light and magnified.

The components of a solution distribute themselves in a completely random manner, given sufficient time. For example, a lump of sugar dropped into a glass of water dissolves, and eventually molecules of sugar can be found randomly distributed throughout the water, even though no mechanical stirring has been employed. This phenomenon, called diffusion, is similar to the process of diffusion that occurs with gases. The molecules of sugar (as well as those of water) must be in constant motion in the solution. In the case of liquid solutions, the sugar molecules do not move very far before they encounter other molecules; diffusion in a liquid is therefore less rapid than diffusion in a gas.

Kinds of Solutions

Many commonly encountered solutions are those involving a solid that has been dissolved in a liquid, but there are as many types of solutions as there are different combinations of solids, liquids, and gases. Solutions in which the solvent is a liquid and the solute is a gas, liquid, or solid are very common. The atmosphere is a good example of a solution in which a gaseous solvent (nitrogen) dissolves other gases (such as oxygen, carbon dioxide, water vapor, and neon). Solutions of solids in solids are another example, and these are encountered most often among the various metal alloys.

Of all the liquid solvents used in the laboratory, in industry, and in the home, water is the most commonly employed and is the best of the inorganic solvents. The alcohols and numerous other types of compounds are classified as organic solvents; many of these are used in dry cleaning chemicals, nail polish removers, paint thinners, and many other similar purposes.

Concentration

The concentration of a solution is defined as the amount of **solute** present in a given quantity of solvent. Very often scientists speak of concentrated solutions, dilute solutions, or very dilute solutions, but these designations give only a rough relative qualitative idea of concentration. For example, a

solute: dissolved substance

"concentrated solution" contains a considerable quantity of solute as compared with a "dilute solution." Although such designations are only qualitatively useful, they are nevertheless widely used.

The most common way to express concentration is on the basis of the weight of solute per unit weight of solvent. For example, a salt solution may be prepared by dissolving 1.64 grams of sodium chloride in 100 grams of water. The concentration of this solution could also be expressed as 0.0164 grams of NaCl per 1 gram of water, or as 16.4 grams of NaCl per 1,000 grams of water. Thus, a statement of the concentration of a solution does not imply anything concerning the amount of solute or the amount of solvent present, but rather gives the ratio of solute to solvent in terms of some convenient (and arbitrary) units. Because the weight of a sample of a liquid is usually more difficult to determine experimentally than its volume, a practical unit of concentration is the weight of solute in a given volume of the solution; for example, a sugar solution may contain 50 grams of sugar per 100 milliliters of solvent.

Solubility

Solubility is a measure of the maximum amount of solute that can be dissolved in a given amount of solvent to form a stable solution. The composition of many solutions cannot be varied continuously because there are certain fixed limits imposed by the nature of the substances involved. Solid salt and sugar can be mixed in any desired proportions, but unlimited quantities of sugar (or salt) cannot be dissolved in a given amount of water; however, up to the solubility limit, solutions can be produced in any desired proportion.

When the solvent contains a maximum quantity of solute, the resulting solution is said to be saturated. The saturation point varies according to the solute. For example, 100 grams of pure water at 25°C (77°F) can dissolve no more than 35.92 grams of NaCl to form a stable saturated solution, but this same amount of water at 25°C dissolves only 0.0013 grams of calcium carbonate. The solubility in these examples is expressed in grams of solute per 100 grams of water, but any suitable units could be used. Water can dissolve any amount of a solute less than that required for a saturated solution. Tables of the solubilities of many substances can be found in various chemistry texts.

In some cases there is no upper limit to the amount of a solute that a given quantity of solvent can dissolve, and these substances are said to be miscible in all proportions. Completely miscible substances give homogeneous mixtures (solutions); for example, a mixture of any two gaseous substances is homogeneous. Often, liquids such as alcohol and water can be mixed in all proportions to give homogeneous mixtures.

When a saturated solution has been achieved, a dynamic equilibrium exists between the solute in solution and any undissolved solute. Molecules of the solute (or atoms or ions, depending upon the nature of the solute) are continuously going into solution, but since the solution is already saturated, an equal number of molecules of the solute leave the solution and redeposit on the excess solid solute. A state of equilibrium exists when these two processes occur at the same rate, the net result being a constant amount of solute in solution. A saturated solution can therefore be defined more precisely as a solution that is in equilibrium with an excess of the solute at a given temperature.

In some instances it is possible to prepare a true solution that contains an excess of the equilibrium amount of solute; this condition is called supersaturation. Supersaturated solutions are unstable. If left undisturbed, they may remain in this state for an indefinite period of time. However, the excess solute can be brought out of solution by a slight agitation or by the addition of any solid particle (dust, a small crystal of solute, etc.) that can act as a center for crystal growth, returning the solution to its normal saturated state.

Conditions That Affect Solubility

In general, three major factors—pressure, temperature, and the nature of the solute and solvent—influence the solubility of a solute in a solvent. Not all these factors are equally important in a specific instance.

Pressure. Changes in pressure have little effect on the solubility of solid or liquid solutes in a liquid solvent, but pressure has a much greater influence on the solubility of a gaseous solute. A commonly observed phenomenon that supports this is the effervescence that occurs when the cap of a bottle of ordinary soda water is removed. Soda water contains carbon dioxide gas dissolved in water under pressure; when the cap is removed, the pressure of the gas on the liquid is decreased to atmospheric pressure. Since carbon dioxide gas leaves the solution at this lower pressure, it follows that the solubility of carbon dioxide in water is dependent upon the pressure of the carbon dioxide above the liquid. The results of this simple observation are summarized in Henry's Law, which states that at any specified temperature, the extent to which a gas dissolves in a liquid is directly dependent upon the pressure of the gas.

Temperature. In general, a change in temperature affects the solubility of gaseous solutes differently than it does the solubility of solid solutes, because the solubility of a gas in a liquid solvent decreases with increasing temperature. With relatively few exceptions, the solubility of solids in liquids increases with an increase in temperature. In some instances, the increase in solubility is very large; for example, the solubility of potassium nitrate in water at 25°C is about 31 grams of KNO_3 per 100 grams of water and about 83 grams of KNO_3 per 100 grams of water at 50°C (122°F). On the other hand, the solubility of some solutes, such as ordinary table salt, shows very little dependence on temperature. Often this difference in solubility can be used as an advantage in the preparation, isolation, or purification of substances by the process of crystallization. In general, it is not possible to arrive at any reliable generalization concerning the influence of temperature upon the solubility of liquids in liquids. In some cases the solubility increases with an increase in temperature, in some cases it decreases, and in others there is very little effect.

The nature of solute and solvent. Crystalline substances consist of a regular arrangement of atoms, molecules, or ions; in the latter case, the forces that hold the crystal together are electrostatic in nature. For an ionic crystal to dissolve in water, the water molecules must be able to shield the charges of the positive and negative ions from each other. The attractive forces between the ions in solution are less than those in the solid state because of the solvent molecules; hence, the ions behave more or less independently in solution. In general, the relative solubilities of ionic substances are a measure of the magnitude of the electrostatic forces that hold the crystals together.

Properties of Solutions

Pure liquids have a set of characteristic physical properties (melting point, vapor pressure at a given temperature, etc.). Solutions in a solvent exhibit these same properties, but the values differ from those of the pure solvent because of the presence of the solute. Moreover, the change observed in these properties in going from the pure solvent to a solution is dependent only upon the number of solute molecules; these properties are called colligative properties. The properties of a solvent that show a predictable change upon the addition of a solute are melting point, boiling point, vapor pressure, and osmotic pressure.

Melting and boiling points. Solutions exhibit higher boiling points and lower melting points than the parent solvent. The increase in boiling point and decrease in melting point is dependent upon the number of solute particles in the solution. The greater the number of solute particles (i.e., the concentration), the greater the boiling point elevation and melting point depression. A common application of this effect in some parts of the world is in the use of antifreeze solutions in the cooling systems of automobiles in cold climates. “Antifreeze” compounds are usually organic liquids that are miscible with water so that large freezing point effects can be attained.

Vapor pressure All liquids exhibit a vapor pressure, the magnitude of which depends on the temperature of the liquid. For example, water boils at 100°C, which means that at 100°C the vapor pressure of water is equal to the atmospheric pressure allowing bubbles of gaseous water (steam) to escape from the liquid state. However, the vapor pressure of a solution (at any temperature) is less than that of the solvent. Thus, boiling water ceases to boil upon the addition of salt because the salt solution has a lower vapor pressure than pure water. The salt solution will eventually boil when the temperature of the solution increases bringing about an increase in vapor pressure sufficient to again form bubbles. Note in this example that the boiling point of water increases with the addition of salt; thus, the boiling point elevation and the vapor pressure depression are related.

Osmosis. This property of solutions is perhaps the least familiar of the colligative properties, but in a sense it is more important than those already mentioned. In 1748 French clergyman and physicist Jean-Antoine Nollet observed that certain animal membranes are selectively permeable to different molecules. Since then, many examples of semipermeable membranes have been discovered, including animal bladder or gut tissues, eggshell lining, and certain vegetable tissues. A semipermeable membrane may be defined as a material that allows molecules of one kind to pass through it but prevents the passage of other kinds of molecules or allows the passage of different kinds of molecules at different rates. Membranes often permit the passage of solvent molecules and prevent the passage of solute molecules.

The phenomenon of osmosis is of far-reaching importance in biology, medicine, and related areas. Many animal and vegetable membranes are semipermeable, and the process of osmosis plays an important role in the transfer of molecules through cell walls in biological processes. Osmosis is responsible in part for the germination of seeds and for the rising of sap into the branches and leaves of trees. The preservative action of sugar solutions (e.g., preserves, jellies) is believed to depend upon osmotic processes; bacteria are literally dehydrated. SEE ALSO Water.

J. J. Lagowski

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Space Chemistry ***See Astrochemistry.***

Space Flight ***See Rocketry.***

Spectroscopy

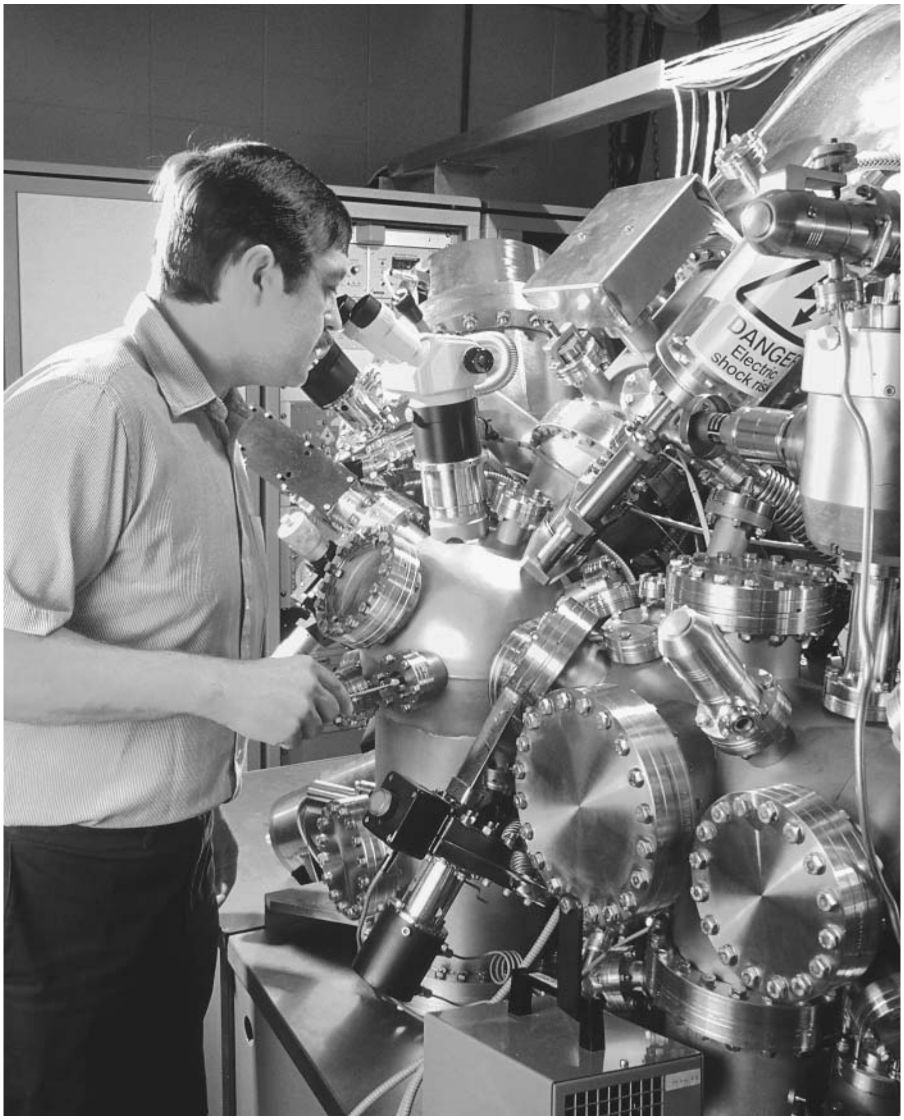
photon: a quantum of electromagnetic energy

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

Spectroscopy is the measurement of interactions between electromagnetic radiation and matter. Electromagnetic radiation, which includes light, has characteristics of waves and particles. Each "particle" of light, or "**photon**," has a discrete amount of energy that can be transferred to a molecule. The transverse waves of electromagnetic radiation possess a constantly changing magnitude of electric and magnetic fields in directions that are **perpendicular** to the direction in which the wave is traveling. These changes in the electric and magnetic fields can cause changes in molecules. Electromagnetic radiation can be transmitted, absorbed, or reflected by matter, and each region of the spectrum can be used to investigate different aspects of the structure and properties of molecules, depending on the amount of energy imparted to the molecule. The absorption of radiation by matter is a quantized process, in that a molecule will only absorb radiation of certain discrete frequencies. These frequencies are determined by well-defined spacings of energy levels in the molecule under investigation. The absorption of photons of high energy cause large changes (often irreversible) in the molecules and correlate to moving electrons to higher energies.

Ultraviolet-Visible Radiation

Electromagnetic radiation is often characterized by its wavelength—the distance between successive peaks in the wave. Radiation with wavelengths between 100 and 700 nanometers (3.94×10^{-6} and 2.76×10^{-5} inches) is termed ultraviolet-visible radiation. The transmittance (T) of a sample is the amount of light transmitted (P) by a sample divided by the amount of light transmitted by a blank (P_0)—$T=P/P_0$. The absorbance (A) of a solution is the negative logarithm of the transmittance—$A=-LOG(T)$. The



Electron spectroscopy is used for measuring concentrations, rates of absorption, and molecular structure.

absorbance of a sample is proportional to the length of the sample that is in the path of the probe radiation and the number of the molecules in the beam path. A plot of the absorbance or transmittance versus the wavelength of radiation is called a spectrum.

When molecules absorb photons in the ultraviolet and visible regions of the spectrum—corresponding to waves with wavelengths between 190 and 1,100 nanometers (7.48×10^{-6} and 4.33×10^{-5} inches)—electrons are promoted to higher electronic energy levels. Since molecules absorb photons with energies that match the difference in energy between their electronic energy levels, only a portion of white light is absorbed by a given molecule, giving it color. The color of light absorbed by a molecule is subtracted from white light, and the remaining light will be the complement of the light absorbed. Ultraviolet-visible spectra show the relative spacing of energy levels in molecules. Generally, molecular energy levels are stabilized when a molecule possesses alternating double bonds and the energy of the photons that these molecules absorbed shifts to lower wavelengths. This phenomenon explains the observation that ethylene, possessing one C=C bond, absorbs light of 180 nanometers (7.09×10^{-6} inches) and is colorless, while beta-carotene, possessing eleven alternating C=C bonds, absorbs at 450 nanometers (1.77×10^{-5} inches) and appears orange in color. Light absorbance in the ultraviolet and visible regions is used to determine the concentration of molecules in solution and of atoms in the gas **phase**. Chemists can determine the concentration of lead in drinking water with absorption spectroscopy.

phase: homogeneous state of matter

Nuclear Magnetic Resonance Spectroscopy

Radio waves can be used to probe the electronic environment of the nuclei of atoms. The nuclei of atoms spin in a clockwise or counterclockwise fashion and create a magnetic field. This field can have the same or opposite field as a superconducting magnet surrounding the sample. When radio waves of a particular frequency are applied to the sample, the spin of these nuclei will change. The frequency of radiation absorbed by molecules in a magnetic field is determined by the types of bonds and the way these bonds are connected. Chemists measure the absorption of radio waves by molecules using a technique called nuclear magnetic resonance spectroscopy. This type of spectroscopy can also be used to determine areas of the body that are diseased, through a technique called magnetic resonance imaging.

Microwave Spectroscopy

Microwaves with long wavelengths cause molecules to rotate faster when they are absorbed. Polar bonds in molecules like water and sugar act as handles for the microwave radiation to grab on to, and the rotational energy can be greatly increased by short exposures to microwaves. This fact explains why polar molecules heat up quickly in microwave ovens. By measuring the wavelength of absorption through microwave spectroscopy, researchers can determine the size of the molecule.

Infrared Radiation

The absorption of infrared radiation (1 to 1,000 micrometers, or 0.0000394 to 0.0394 inches) causes bonds in molecules to vibrate. A bond in the molecule must undergo a change in the dipole moment when the infrared radiation is absorbed. The stiffer the bond, the more energy is required to cause the bond to stretch. Therefore the frequency required to cause C–N, C=N, and C≡N bonds to stretch increases from left to right. Often the infrared spectrum is considered to be a fingerprint of the molecule. Matching a sample's spectrum with a standard spectrum can positively identify the sample. This technique is used to measure emissions in automobile exhaust.

Fluorescence

Fluorescence is the process by which molecules emit light. When an electron moves to a level of lower energy, light can be given off with a frequency that matches the spacing between the original and final levels. The electron must initially be placed in a higher energy level by the absorption of light at short wavelengths. In fluorescence, the molecule loses some of this excess energy by emitting light at longer wavelengths instantaneously. This

voltage: potential difference expressed in volts

process is observed in sodium streetlights, where sodium atoms in the gas phase have been excited by an applied **voltage** and the electrons relax to lower energy levels and give off yellow light at 589 nanometers (2.32×10^{-5} inches). Fluorescent dye molecules on clothing are excited by ultraviolet light, and these molecules give off energy of longer wavelengths, as electrons in the molecules relax to lower energy levels. The fluorescence of molecules is very sensitive to the polarity, temperature, and viscosity that the molecule resides in. Unlike absorbance, fluorescence is not measured on a background and can quantitate very low amounts of materials. Richard Mathies and coworkers have detected single molecules in solution by fluorescence spectroscopy.

X Rays and Gamma Rays

X rays and gamma rays have enough energy to remove electrons from atoms and molecules and thereby ionize them. The wavelengths of x rays that are absorbed are determined by the distance that an electron is from the nucleus. Furthermore, the regular spacing of atoms in a molecule can create a diffraction pattern of x rays. By examining the diffraction pattern, researchers can accurately determine the arrangement of atoms in a molecule.

Applications

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

Many scientists use spectroscopy on a daily basis to gain insight into the structure of molecules or the concentration of atoms or molecules in a sample. The chemist uses radio waves and infrared radiation to determine the structure of a new molecule. The geologist uses **ultraviolet radiation** to determine the concentration of a particular element in a rock or mineral. The microbiologist uses fluorescence measurements to determine the concentration of bacteria in solution. SEE ALSO RYDBERG, JOHANNES.

G. Brent Dawson

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Stanley, Wendell

AMERICAN BIOCHEMIST
1904–1971

Wendell Stanley shared the Nobel Prize in chemistry in 1946 with John Northrop, awarded to them “for their preparation of enzymes and virus proteins in a pure form,” and with James Sumner “for his discovery that enzymes can be crystallized.” In 1926 Sumner had crystallized the enzyme urease; in 1930 Northrop had crystallized pepsin; and in 1935 Stanley had crystallized tobacco mosaic virus. Stanley’s result and subsequent findings demonstrated that an infectious agent could possess some of the properties of a chemical molecule. Stanley concluded: “Tobacco mosaic virus is regarded as an autocatalytic self-reproducing protein which, for the present, may be assumed to require the presence of living cells for multiplication.”

Large batches of tobacco plants infected with tobacco mosaic virus and ground up while frozen were thawed in buffer solution containing alkaline sodium phosphate, and the solution was filtered. The filtrate at lowered pH was treated with concentrated ammonium sulfate. The precipitate contained virus, which was extracted and reprecipitated (by acidification in the presence of 20 percent saturated ammonium sulfate) as small “needles.”

Stanley’s achievement was soon reproduced in England by Frederick Bawden and Norman Pirie, who were also able to show that the tobacco mosaic virus and other plant viruses contained **ribonucleic acid** (RNA). Stanley initially considered the RNA to be a contaminant, but later investigations by Seymour Cohen showed RNA to be a very large molecule having a molecular mass of up to 2 million daltons. Surprisingly, the thought that the viral RNA might be the genetic element of the virus was not tested until 1956.

American biochemist Wendell Stanley, corecipient, with John Howard Northrop, of the 1946 Nobel Prize in chemistry, “for their preparation of enzymes and virus proteins in a pure form.”

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

Wendell Meredith Stanley was born in Ridgeville, Indiana, in 1904. On graduation from the University of Illinois in 1926 he aspired to be a football coach. He shortly afterward changed course and embarked on an extremely productive period as a graduate student, with the chemist Roger Adams as his instructor. He received a Ph.D. in chemistry from the University of Illinois in 1929 and stayed there another year, at the end of which he went to work for a year with Heinrich Wieland in Munich. He returned to the United States in 1931, having been given a post at the Rockefeller Institute in New York. In 1932 he moved to the Princeton branch of the institute, where Northrop was also a faculty member. In 1948 he was appointed professor of biochemistry and director of the virus laboratory at the University of California at Berkeley. In 1958 he became a professor of virology. He died suddenly in Spain in 1971, aged sixty-six. SEE ALSO Ribonucleic Acid.

Keith L. Manchester

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Starch

Starch is the chief storage form of carbohydrate in plants and the most important source of carbohydrate in human nutrition. A starch molecule is a polysaccharide assembled from the simple sugar **glucose**; it can contain anywhere from five hundred to several hundred thousand glucose molecules joined by **covalent bonds** into a single structure. In addition to its impor-

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

covalent bond: bond formed between two atoms that mutually share a pair of electrons tance in human nutrition, starch has many industrial applications: it is used in the manufacture of paper, textiles, pharmaceuticals, and biodegradable polymers, and it is an additive in foods.

Chemically, starch is composed of two different molecules, amylose and amylopectin. In amylose, the glucose molecules are linked in a "linear" fashion; however, the tetrahedral chemistry of carbon (and the bond angles that result from this chemistry) gives amylose an overall spiral shape. Amylopectin, on the other hand, has a linear arrangement of glucose molecules that includes, at regular intervals, a different kind of linkage between two adjacent glucoses. This different linkage results in the formation of a branched structure and an overall treelike shape for this molecule. Plant starch is typically 20 to 30 percent amylose and 70 to 80 percent amylopectin. The classic test for the presence of starch is reaction with iodine. If starch molecules are present in a substance, the addition of iodine yields a deep blue color, which results from I_2 being trapped inside the spiral structures of amylose molecules.

Starch molecules are broken down by enzymes known as amylases. The digestibility of a specific starch is influenced by its physical form. In plants starch is present in microscopic granules, which impair the enzymatic digestion of starch molecules obtained from plants. Cooking starch-containing items results in the hydration of starch molecules and the swelling of starch granules, increasing the rate and enhancing the enzymatic breakdown of starch. Amylases also convert starch to glucose. SEE ALSO CARBOHYDRATES; POLYSACCHARIDES.

Matthew A. Fisher

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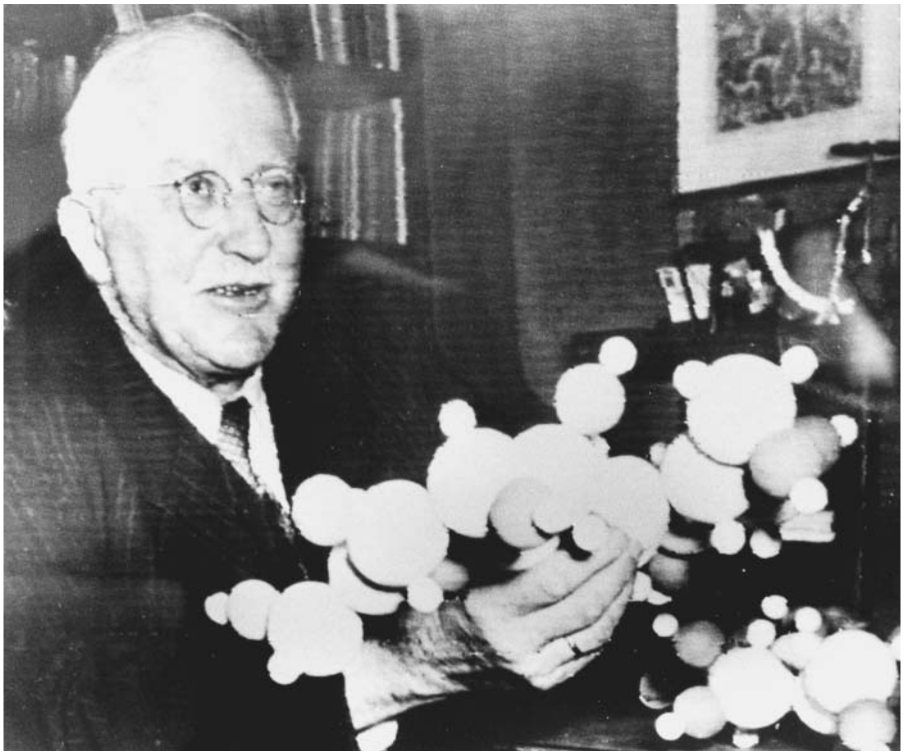
Staudinger, Hermann

GERMAN CHEMIST
1881–1965

Hermann Staudinger was one of the most influential organic chemists of the twentieth century. His wide-ranging research interests included the investigation of many kinds of molecules, ranging from small organic compounds to large polymers. He is generally considered to be the father of macromolecular (polymer) chemistry and won the 1953 Nobel Prize in chemistry for his discoveries in that field.

Staudinger was born in Worms, Germany, on March 23, 1881. He at first planned to study botany at the University of Halle, but he subsequently followed his father's advice and switched to chemistry. After graduating from



German chemist Hermann Staudinger, recipient of the 1953 Nobel Prize in chemistry, "for his discoveries in the field of macromolecular chemistry."

Halle with a degree in chemistry in 1903, Staudinger moved to the University of Strasbourg and became an academic lecturer there in 1907. Subsequent academic appointments took him to Karlsruhe, Zurich, and, finally, Freiburg.

Although Staudinger's work on ketenes, diazo compounds, oxalyl chloride, and pentavalent phosphorus compounds is still relevant, he is more recognized for his seminal contributions to macromolecular chemistry. Staudinger started working on macromolecules in the early 1920s. Following his move to Freiburg in 1926, he discontinued his investigations of small organic compounds and concentrated exclusively on the chemistry of what he believed were high molecular weight compounds.

It was a risky career move for Staudinger, and one that put him at odds with many of the leading organic chemists of the time. He proposed (without much proof to back up his proposal) that macromolecules were long-chain molecules of identical or nearly identical units that were linked by **covalent bonds**. Today it is known that many of Staudinger's ideas were essentially correct, but in the 1920s most chemists disagreed with him. They viewed macromolecules as colloidal aggregates of small molecules and did not believe that covalent bonding was involved.

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

Staudinger's colleague, Dr. Heinrich Wieland, told him to drop his idea of large molecule organic compounds and assured him that a sample of purified rubber would be shown eventually to be composed of low molecular weight compounds. During a lecture in Zurich in 1925, Staudinger was verbally attacked for advocating the idea of covalent bonding in macromolecules.

Despite the attacks, Staudinger was determined to convince his detractors that his ideas on the structures of macromolecules were sound. To prove his point he carried out a series of experiments designed to yield more understanding of the chemical and physical properties of polymers. He began with natural rubber. He and J. Fritschi hydrogenated the double bonds present in natural rubber polymer molecules in an autoclave and found that the isolated product had properties similar to those of the starting rubber. From this Staudinger concluded that natural rubber was not a colloidal substance, but a long-chain macromolecular substance.

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

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

He gathered more evidence by synthesizing polymers from **formaldehyde** and from styrene. The homologous formaldehyde-derived polymers spanned the molecular size range, from small molecules to large macromolecules. From the results Staudinger concluded that polymers were molecules whose repeating units were linked by covalent bonds, and that they had characteristic **functional groups** at their ends. The polystyrene polymers were prepared under varying reaction conditions and had a range of molecular weights and physical properties. These data were also consistent with covalent bonding, but not with colloidal association.

Staudinger's ideas were gaining popularity, but it was a 1928 paper by Herman Mark and Kurt Meyer that finally convinced chemists that Staudinger had been right. Mark and Meyer used x-ray crystallography to probe the structure of a crystallized polymer and found that polymers were indeed long-chain molecules in which repeating units were linked by covalent bonds.

Staudinger spent the next twenty or so years building up macromolecular chemistry and helping to lay the foundation for today's multibillion-dollar polymer industry. He retired in 1951 and received the 1953 Nobel Prize in chemistry for his work on polymers. He died on September 8, 1965. SEE ALSO POLYMERS, NATURAL; POLYMERS, SYNTHETIC.

Thomas M. Zydowsky

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Steel

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

Steel is an **alloy** of iron with about 1 percent carbon. It may also contain other elements, such as manganese. Whereas pure iron is a relatively soft metal that rusts easily, steel can be hard, tough, and corrosion-resistant. Used to make almost everything from skyscraper girders, automobiles, and appliances to thumb tacks and paper clips, steel is one of the world's most vital materials. Among all the metals, iron is second only to aluminum in natural abundance, making up 4.7 percent of the earth's crust, and occurring mainly as its various oxides. The main product made from iron is steel, the least expensive and most widely used of all metals.

A steel worker is catching a sample of molten steel in a crucible during the manufacturing process.

History

It appears that ancient peoples were using iron as early as 4000 B.C.E. for making various tools, weapons, and other objects. They apparently obtained the iron from meteorites. The composition of those earliest iron artifacts was higher in nickel than native iron ores on Earth, in keeping with the composition of meteorites. In fact, the word "iron" comes from an ancient term meaning "metal from the sky." It is interesting to note that when Admiral Robert Peary visited Greenland in the 1890s, he found that the Inuit had for many years been making iron tools from a 30-ton iron meteorite that had fallen there centuries earlier.

While it is not known exactly when people learned how to remove iron from its ores, by 1200 B.C.E. iron ore was being mixed with burning wood or charcoal and turned into hot masses from which iron metal could be "wrought" by repeated hammering. Placing the iron back in burning charcoal seemed to make it harder and stronger. The iron picked up carbon from the charcoal, especially along its surface, turning it into the hard material that has come to be known as steel.

During the first millennium B.C.E. a highly superior steel product was made in India, in a region near Hyderabad. Well known for its strength and its wavy patterned surface, it was especially desirable for making sword blades. Some think that the ore found in that area just happened to have the right impurities to give the steel special properties. The hot iron was repeatedly forged and folded to produce a metal of extremely high quality that became famous all over the ancient world. It was especially sought after by Europeans, who called it "wootz"; by Moors living in Spain, who used it to make their Toledo blades; and by Arabs, who used it in their famous Damascus swords.

Making Steel

Over the years various countries have excelled in making steel. During the eighteenth century a relatively small amount of steel was made, but Sweden was the main producer. In the nineteenth century Great Britain became dominant. In the twentieth century the United States was the largest steel producer in the world until about 1970, when it was surpassed by the Soviet Union. At the start of the twenty-first century, China led the world in steel production.

Three primary installations in an integrated steel plant are the blast furnace, the steel furnaces, and the rolling mills. The blast furnace converts iron ore to pig iron; the steel furnaces convert the pig iron to steel; and the rolling mills shape the steel into sheets, slabs, or bars.

Blast furnace. A blast furnace is a chimney-like structure in which iron ores (mainly FeO, Fe_2O_3, and Fe_3O_4) are converted into iron metal. Iron ore, coke, and limestone are loaded into the top of the furnace, while air is blown in from below. The coke is converted to carbon monoxide (CO), which then acts as the reducing agent:

$$2\ C + O_2 \rightarrow 2\ CO$$

$$3\ CO + Fe_2O_3 \rightarrow 2\ Fe + 3\ CO_2$$

The molten iron falls to the bottom of the furnace, and the limestone reacts with silicate impurities to form a molten slag, which floats on top of the iron. The two layers are drawn off separately, and the iron is poured into molds. Because the molten iron yields ingots that resemble little pigs, the product is referred to as "pig iron."

Steel furnaces. In the steel furnace, sulfur and phosphorus impurities and excess carbon are burned away, and manganese and other alloying ingredients are added. During the nineteenth century most steel was made by the Bessemer process, using big pear-shaped converters. During the first half of the twentieth century, the open hearth furnace became the main type of steel furnace. This gave way mid-century to the basic oxygen process, which used pure oxygen instead of air, cutting the process time from all day to just a few hours. In the twenty-first century, most new steel plants use electric furnaces, the most popular being the electric-arc furnace. It is cheaper to build and more efficient to operate than the basic oxygen furnace. In the electric-arc furnace a powerful electric current jumps (or arcs) between the electrodes, generating intense heat, which melts the iron scrap that is typically fed into it. The most modern process for making steel is the continuous process, which bypasses the energy requirements of the blast furnace. Instead of using coke, the iron ore is reduced by hydrogen and CO derived from natural gas. This direct reduction method is especially being used in developing countries where there are not any large steel plants already in operation.

TYPES OF STEEL

Carbon Steel. This is the most widely used kind of steel. Its carbon content is under 2 percent and is usually less than 1 percent. It often also contains a little manganese.

Stainless Steel. This is the most corrosion-resistant kind of steel. It normally contains at least 12 percent (and sometimes up to 30 percent) chromium, and it usually also contains nickel. A very popular stainless steel formulation is 18-8, 18 percent chromium and 8 percent nickel.

Alloy Steels. These contain a little carbon, and sometimes silicon, but they mainly contain added metals, such as manganese (hardness), nickel (strength), molybdenum (improved wear), tungsten (high temperature strength), chromium (corrosion resistance), and vanadium (toughness).

Galvanized Steel. This steel is coated with zinc to protect against corrosion. The coating is usually done by a hot dip process.

Electroplated Steel. This steel has a coating of another metal, usually tin, applied by the use of an electric current. Tin-plated steel is widely used for making cans and other containers.

Tool Steel. This is very hard steel made by tempering (heating to a very high temperature and then quickly cooling).

Damascus Steel. This was a very high quality ancient steel with a beautiful wavy surface pattern used in making sword blades. It seems to have come mainly from India.

Wootz Steel. This was actually a European mispronunciation of *ukku*, the very fine steel made in ancient India that they called "wook." (It is probably the same material as Damascus steel.)

Finishing processes. A final step in processing steel is shaping. Liquid steel can be cast into ingots or various other forms. They can then be sent to rolling mills. There are hot rolling mills and cold rolling mills. Various kinds of steel slabs are rolled into sheets, strips, bars, or other kinds of products. Sometimes the steel is forged into shape with hammers or presses, or the hot steel is extruded through dies to give it some desired shape. For example, steel wire is made by drawing hot steel rods through smaller and smaller dies. Some steel is finished by grinding or polishing, and some is coated with zinc or electroplated with tin.

World Steel Production

The three top steel producers in the world are China, the United States, and Japan, in that order. The United States and Japan each produce around 100 million tons (90 million metric tons) of steel per year, and China had an output in 2000 of about 140 million tons (127 million metric tons). Iron and steel make up approximately 90 percent of all the metal produced in the world. The largest steel company in the United States is United States Steel, which produces about 20 percent of the country's steel.

Steel plants vary widely in size. Some large integrated plants include coke ovens, blast furnaces, several kinds of steelmaking furnaces, and various mills for rolling the steel into sheets or slabs. Some companies dig their own ore and run their own coal mines and limestone quarries, and some even operate their own railroads and barges. Other steel plants consist of a single electric furnace for melting scrap with a small mill for turning the melted steel into bars. These scrap recycling plants are known as

A steel bridge in Portland, Oregon. Steel's strength and resistance to corrosion make it an alloy useful for many purposes.

"minimills," and they now account for about half of steel production in the United States. There were about 160 steel plants operating in the United States in 2003, and most of them were minimills. SEE ALSO IRON.

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Steroids

Steroids are a family of **lipid** molecules that includes cholesterol, steroid hormones, and bile salts. These amphipathic molecules (containing both **hydrophobic** and **hydrophilic** regions) are derived from two-carbon acetyl-CoA

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

hydrophobic: a part of a molecule that repels water

hydrophilic: a part of a molecule having an affinity for water units, whose combination leads to the formation of isoprenoids (five-carbon **isoprene** molecular units), and finally to the formation of a seventeen-carbon tetracyclic hydrocarbon, the steroid skeleton. Figure 1 shows the basic steroid skeleton structure, made up of three six-membered rings and one five-membered ring. The fused six-membered cyclohexane rings each have the **chair conformation**. Each member of the steroid family has a structure that differs from this basic skeleton in the degrees of unsaturation within the ring system and the identities of the hydrocarbon side chain substituents attached to the rings. These substituents are in most cases oxidized to alcohol, **aldehyde**, **ketone**, or **carboxylic acid functional groups**.

The general term *sterol* refers to a subgroup of steroids that contain an alcohol functional group, which is signified by the -ol ending. Steroids are found predominantly in **eukaryotic cells**, with cholesterol being the most abundant steroid molecule. It contains twenty-seven carbons, has an alcohol functional group at C-3, a methyl group at C-13, and a branched aliphatic hydrocarbon (eight carbons) unit at the C-17 carbon atom. It is the basic building block for all the other steroid molecules. The **biosynthesis** of other steroids from cholesterol yields molecules that have fewer carbons, are more polar and more oxidized, and have smaller and more oxidized hydrocarbon units at C-17. It should be emphasized that cholesterol and most steroids contain predominantly single (C–C) bonds and take on non-planar structures. Intracellular cholesterol is predominately found as part of (embedded in) the plasma cell membranes. Because of cholesterol's bulky structure, it does not embed well into the lipid bilayer structure of a membrane and as a result disrupts the order or regularity of the membrane. Increasing levels of embedded cholesterol, which can be as high as 25 percent of membrane volume, correlates with increasing the fluidity (as opposed to rigidity) of the membrane.

The level of extracellular cholesterol in blood serum correlates with the degree of advancement of atherosclerosis and the development of coronary heart disease. The serum cholesterol is obtained from diet and from biosynthesis, which occurs primarily in the liver of mammals. The usual metabolic pathway for cholesterol biosynthesis involves a sequence of more than twenty reactions, each catalyzed by a specific enzyme. The committed and the rate-limiting step in the sequence is the **synthesis** of a six-carbon molecule, mevalonate, catalyzed by the enzyme 3-hydroxy-3-methylglutaryl CoA reductase (HMG CoA reductase). The development of drugs that inhibit the activity of HMG CoA reductase (and that reduce levels of serum cholesterol), has led to a decline in coronary heart disease. These drugs have structures similar to that of mevalonate and serve as **competitive inhibitors** of HMG CoA reductase. The binding of a competitive inhibitor to the enzyme and of the substrate mevalonate to the same enzyme are mutually exclusive events. One of the most potent inhibitors of HMG CoA reductase is the drug lovastatin, which binds very strongly at the active site of the enzyme, and, as a result, serum cholesterol levels in humans are decreased by as much as 20 percent.

The hydrophobic, water-insoluble cholesterol is transported in blood to cells predominantly as part of high density and low density lipoprotein particles (HDLs and LDLs, respectively). LDLs transport cholesterol to extrahepatic tissues. The LDL particles bind to LDL **receptors** on the cell

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

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")

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

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

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

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

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

biosynthesis: formation of a chemical substance by a living organism

synthesis: combination of starting materials to form a desired product

competitive inhibitor: species or substance that slows or stops a chemical reaction

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

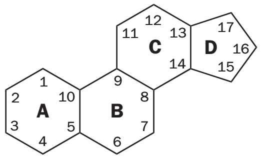

Figure 1. Steroid skeleton.

membranes, facilitating cholesterol deposition at the cells, for use primarily as a component of the membrane. HDLs carry out a similar transport function but also return cholesterol to the liver, where it can be metabolized. In this way HDLs decrease the levels of the cholesterol that contributes to the deposition of plaque in arteries and is implicated in heart disease. In a number of cases, patients have been found to have defective genes that **code** for the LDL receptors. In these cases the LDL particles cannot deposit the cholesterol at cell sites. The LDLs remain in the blood, and eventually their lipid molecules accumulate on the arterial walls, which can lead to blockage of arteries and a heart attack.

code: mechanism to convey information on genes and genetic sequence

Cholesterol is the precursor of other important steroid **metabolites**, which include bile salts and steroid hormones. Bile salts, which are the major breakdown product of cholesterol, resemble detergents, which are amphipathic molecules (having both polar and **nonpolar** regions). Their primary function is to **emulsify** dietary lipids. This interaction between bile salt and lipid increases the surface area of exposed lipid, which greatly enhances the ability of lipase enzymes to get access to and **hydrolyze** lipid molecules, thereby promoting their absorption and digestion. Bile salts are synthesized and secreted by the liver, stored in the gall bladder, and pass through the bile duct and into the small intestine. Bile salts are the major metabolic product of cholesterol, their manufacture accounting for the consumption of approximately 800 mg/day of cholesterol in a normal human adult. (On the other hand, less than one-tenth that amount of cholesterol is utilized for steroid hormone synthesis.) A major bile salt is glycocholate.

metabolites: products of biological activity that are important in metabolism

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

emulsify: process of forming an emulsion; of suspending one phase of an immiscible pair of phases in the other

hydrolyze: to react with water

Cholesterol is also the precursor of all the steroid hormones, which can be subdivided into five major classes. The first and second classes of hormones, the mineralocorticoids and the **glucocorticoids**, are synthesized in the adrenal cortex. The mineralocorticoids (e.g., aldosterone) regulate the body's ion balance by promoting the reabsorption of inorganic ions, such as Na^+, Cl^-, and $HCO3^-$, in the kidney. As a result, they are involved in the regulation of blood pressure. The glucocorticoids (e.g., cortisol) regulate gluconeogenesis and, in pharmacological doses, inhibit the inflammatory response. The third class includes **progesterone**, associated with the female reproductive cycle and synthesized in the cells of the corpus luteum; it prepares the lining of the uterus for implantation of the ovum and is essential for the maintenance of pregnancy. The sex hormones are synthesized in the male and female gonads and in the placenta. These hormones, the fourth and fifth classes, are **androgens** (primarily testosterone) and the estrogens (primarily estradiol). These two classes of hormones are associated with the development of the secondary sexual characteristics of males and females, respectively. They exert powerful physiological effects in humans because of their importance in the regulation of a variety of vital metabolic processes.

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

progesterone: steroid found in the female reproductive system: formula $C_{21}H_{30}O_2$

androgen: group of steroids that act as male sex hormones

Steroid hormones, like all hormones, are chemical messengers. They are synthesized in the cells of an endocrine gland, secreted by the cells into the bloodstream, and travel to target organs in which they direct cell-to-cell communication and the "global regulation" of **metabolism** in a multicellular organism such as humans. The levels of the steroid hormones are also highly regulated, with levels in the blood or in cells being very small, typically less than **micromolar** amounts. Because of their hydrophobic

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)

micromolar: relating to a solution of a substance that is in the concentration range of micromoles per liter, or 10^{-6} moles per liter

The anabolic steroid Durabolin causes a muscle cell to store more nitrogen, facilitating muscle growth.

character, they must associate with carrier molecules for their transport in the blood.

In contrast to **polypeptide** hormones that bind to hormone receptor proteins embedded in the plasma membranes of cells, the hydrophobic steroid hormones pass from the bloodstream into cells readily via **passive diffusion** across the membrane. Although the steroid hormones can in principle enter all cells, the only cells that are responsive to steroid hormones are those cells that contain proteins called steroid hormone receptors. These receptors reside in an inactive state either in the cytoplasm or in the cell nucleus. There are specific hormone receptors for each of the hormone types: **estrogen**, androgen, progesterone, glucocorticoid, and mineralcorticoid. As a result of the hormone binding to the recognition site of its hormone receptor, an inactive receptor is transformed into a functionally active one. These active hormone-receptor complexes are **ligand**-activated **transcription** factors, which are then able to migrate to the **DNA** in the nucleus and bind to the promoter regions of a specific subset of genes. This stimulates the transcription of genes that are sensitive to the presence of the

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

passive diffusion: mechanism of transporting solutes across membranes

estrogen: female sex hormone

ligand: molecule or ion capable of donating one or more electron pairs to a Lewis acid

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

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

expressed: made to appear; in biochemistry—copied

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

anabolism: metabolic process involving building of complex substances from simpler ones, using energy

hormone. These genes are only **expressed** or transcribed when the hormone is present. The messenger **RNA** that is produced is then translated into a new set of proteins. As a result of this stimulation of gene expression, the metabolic character of the cell is dramatically changed.

Anabolic steroids are synthetic substances related to male sex hormones (androgens). Although it is illegal in the United States to possess or distribute anabolic steroids for nonmedical use, a "black market" for them exists, and many amateur and professional athletes take them to enhance performance. In many cases, the athletes take doses that are extremely high—perhaps 100 times the doses that might be prescribed for medical use. As a result, they put themselves in real danger of short-term and long-term health problems. Blood testing, as has been used in the Olympic Games, can detect, identify, and quantify the presence of anabolic steroids in the blood of athletes, which can lead to the disqualification of an athlete. SEE ALSO Cholesterol; Cortisone; Estrogen; Lipids; Testosterone.

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Stimulants

The substances referred to as stimulants are a variety of compounds that excite the central nervous system or alter the body's metabolic activity. Some stimulants enhance alertness and increase energy whereas others affect emotions and oppose psychological depression.

One way in which chemical stimulants function is to mimic or enhance the effects of hormones that prepare animals for "fight or flight" when they are faced with threatening situations. They bring about an increased heartrate, increased blood pressure, and an increased rate of respiration. One way in which such hormones (or their imitators) prepare the body for sudden action is to increase the breakdown of glycogen and **glucose** in order to meet the increased demand for energy. The best examples of these hormones are the catecholamines (epinephrine, also known as **adrenalin**, and norepinephrine, also known as noradrenalin). The hormones bind to **receptors** on target muscle cell membranes and prompt formation of cyclic adenosine monophosphate (cAMP), known as a "second messenger" because it transmits a signal to many intracellular molecules involved in **metabolism** (epinephrine and norepinephrine being first messengers). In order for a subsequent message to be received (and for intracellular alterations related to fight or flight to be maintained), hormones and second messengers must be rapidly removed from cell surfaces once they have delivered their messages. An enzyme classified as a phosphodiesterase degrades cAMP to a form that is inactive. Some of the most common stimulants, such as caffeine and related compounds in tea and chocolate, inhibit the phosphodiesterase enzyme so that cAMP levels remain high enough to maintain the alerted state.

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

adrenalin: chemical secreted in the body in response to stress

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

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)

Speed is a stimulant that excites the central nervous system.

A second way in which stimulants exert their effects is by inhibiting the neurochemistry that involves the transmission of signals from one nerve cell to another. When a nerve cell receives a signal, that signal is propagated to the far end of the long nerve cell. In order for that signal to be transmitted to the next nerve cell, molecules called neurotransmitters are released into the spaces (synapses) between the cells. The neurotransmitters bind to specific receptors on the receiving cell, thus passing on the signal. In order to prepare for a new signal, neurotransmitters must be removed from the intercellular space through reuptake or degradation.

Cells can also recover from the signal for the fight or flight reaction by taking hormones that they have released back up into themselves. Cocaine interferes with the reuptake of adrenalin by cells in the cortex of the brain, thus intensifying the effects of adrenalin and producing a sense of euphoria and (sometimes) hallucinations. Cocaine use leads to psychological dependency and can cause convulsions, respiratory failure, and death.

Amphetamines are drugs that mimic the effects of epinephrine, or adrenalin. Because effects such as mental illness and brain damage can result from overuse of amphetamines, they currently have limited medical use. Metamphetamines are similar to amphetamines in structure and action but have fewer undesirable side effects. Ritalin (methylphenidate), commonly used to treat attention deficit disorder, has essentially the same mode of action as amphetamines. Ritalin abuse by middle and high school students has become a common concern.

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

Because of their adverse effects, the Food and Drug Administration (FDA) has taken action to remove two over-the-counter products that have amphetamine-like action: ephedrine, an agent with actions similar to those of epinephrine and the main active ingredient in the herb ephedra, used for weight loss and in energy-enhancement cold medicines; and weight loss products that contain phenylpropanolamine, which can raise blood pressure and increase the risk of stroke.

Opiates such as morphine and codeine are thought to enhance the release by neurons of the neurotransmitter dopamine; the release of dopamine leads to a sense of euphoria. These drugs are addictive and are often abused. In general, all antipsychotic medications work by blocking dopamine receptors in the forebrain. Nicotine mimics the action of the neurotransmitter **acetylcholine** at receptors having to do with the transmission of signals between autonomic nerve cells and skeletal muscle. SEE ALSO CAFFEINE; EPINEPHRINE; METHYLPHENIDATE; NEUROCHEMISTRY; NEUROTRANSMITTERS; NOREPINEPHRINE.

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

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Stoichiometry

Stoichiometry refers to the ratios of products and reactants in a chemical reaction. It is a fundamental concept in chemistry, and we shall give a more exact description later.

Early Stoichiometry

The masses of the starting materials and of the products of chemical reactions were of obvious interest to early chemists. The earliest measurements may have been made by prehistoric **metal** workers who weighed a metal ore with a primitive balance and compared the weight with that of the extracted metal. Weighing was the most common and most accurate measurement that chemists could make for many centuries. An early example is the work of Belgian chemist Johann van Helmont in the early seventeenth century. Van Helmont weighed a large pot containing a growing plant at intervals and tried to show that the gain in weight was fully accounted for by the water added. He did not measure the carbon dioxide gas taken up or the oxygen released by the plant and so his conclusion was not valid, although the measurements were roughly correct.

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

Whether or not pure substances have the same proportion by mass of their constituents was by no means initially obvious. Around 1800 two French chemists, Claude Berthollet and Joseph Proust, supported opposite views on this topic. If a metal such as lead is heated in air, there is a gradual color change as lead oxide is slowly formed. Berthollet argued for a combination of "indefinite proportions" as this transformation occurs: the reactant is lead, the product is lead oxide, and there is an indefinite number of **intermediates**. Proust argued for "definite proportions" in that the system would at all times consist only of lead mixed with lead oxide (for simplicity we can ignore that more than one oxide of lead exists). The ratio of lead to lead oxide would change as the reaction proceeded but the system would have only two components. The wide acceptance of English

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

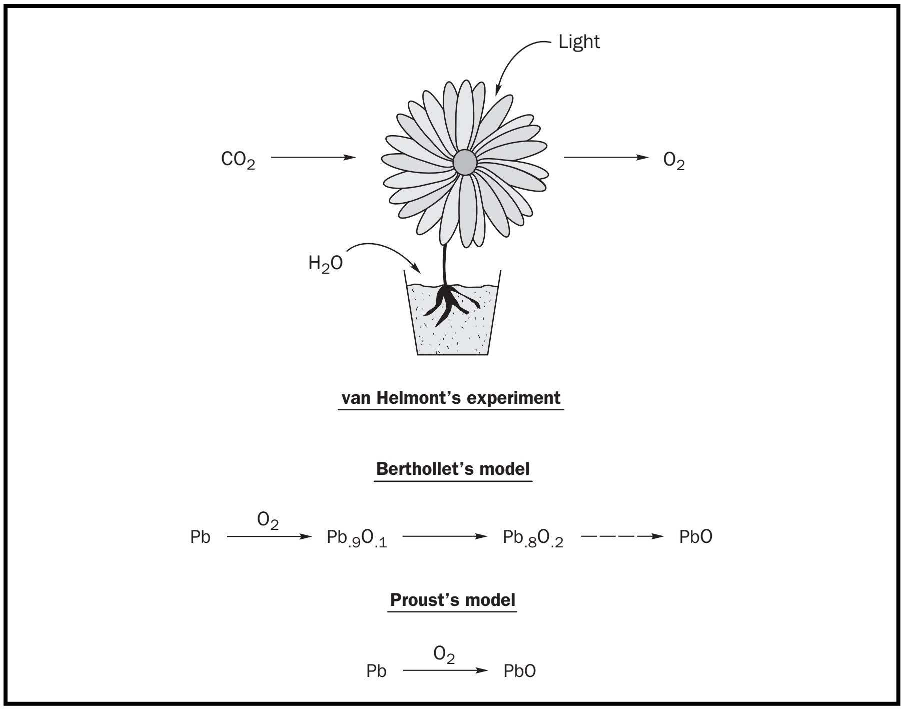

Figure 1. Early experiments to test the masses of reactants and products of chemical reactions.

chemist and physicist John Dalton's **atomic theory** a few years later convinced most chemists that Proust was right and that there was a Law of Definite Proportions for pure compounds.

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

The term "stoichiometry" was devised by German chemist Jeremias Richter in 1792 to describe the measurement of the combining ratios of chemical elements by mass. The term has since been expanded to include the combining ratios of substances in any chemical reaction. Richter studied mathematics with philosopher Immanuel Kant and wrote a thesis on the use of mathematics in chemistry. He was convinced that all chemical changes could be described in terms of simple whole-number ratios. He put forward the Law of Reciprocal Proportions, stating that if two chemical elements unite separately with a third element, the proportion in which they unite with the third element will be the same or a multiple of the proportion in which they unite with each other. This law has disappeared from most chemistry textbooks, but a companion law, the Law of Multiple Proportions, has survived.

The Law of Multiple Proportions states that when two elements combine to form two or more different compounds, the weights of one compound that can combine with a given weight of the second compound form small whole number ratios. For example, consider one experiment in which 10.0 grams of sulfur is combined with 10.0 grams of oxygen to form an oxide of sulfur, and another experiment under different conditions in which 3.21 grams of sulfur is combined with 4.82 grams of oxygen to form a different oxide. For each 10.0 grams of sulfur used in the second experiment, 15.0 grams (4.82 × 10.0/3.21) of oxygen is used. The ratios of the masses of oxygen that combine with a fixed mass of sulfur are 10.0:15.0, which is equal to the whole number ratio 2:3. This conforms to the Law of Multiple Proportions. (See Figure 2.)

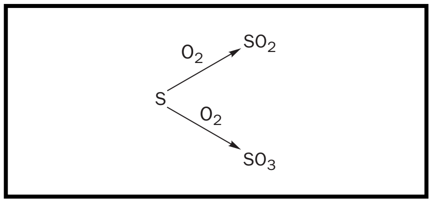

Figure 2.

The Laws of Reciprocal and Multiple Proportions have ceased to have predictive scientific value. Their importance lies in the fact that they provided evidence that Dalton needed in 1807 to postulate his atomic theory. The reason for Richter's whole number ratios has since become obvious: the simple ratios occur because atoms, although having different masses, react in simple ratios. Dalton's insistence that atoms cannot be split in chemical reactions holds true in modern chemistry.

Balancing Chemical Equations

Chemical equations are an indispensable way of representing reactions. They are routinely used to calculate masses of reactants and products. In the case of the examples used above for the Law of Multiple Proportions, the equations are:

$$S + O_2 = SO_2 \tag{1}$$

$$2S + 3O_2 = 2SO_3 \tag{2}$$

Note that we do not write the second equation as:

$$S + 3O = SO_3 \tag{3}$$

reagent: chemical used to cause a specific chemical reaction

because O (an oxygen atom) means something very different from O_2 (an oxygen molecule). Chemical equations also introduce the concept of a limiting **reagent**, or the reactant that is used up first in a reaction, when one or more components are in excess of the stoichiometric amount.

The balancing of chemical equations is a common exercise in elementary stoichiometry. It is not always appreciated, however, that some chemical equations are ambiguous in that they can be balanced in more than one way. Consider, for example, the following equation:

$$H^+ + ClO_3^- + Cl^- \rightarrow Cl_2 + ClO_2 + H_2O \tag{4}$$

where the dashed arrow signifies an unbalanced equation. It may be balanced as follows:

$$4H^+ + 2ClO_3^- + 2Cl^- = Cl_2 + 2ClO_2 + 2H_2O \tag{5}$$

Both sides of this equation have four H-atoms, six O-atoms, four Cl-atoms, and a total charge of zero. Equation 5 can also be balanced as:

$$16H^+ + 4ClO_3^- + 12Cl^- = 7Cl_2 + 2ClO_2 + 8H_2O \tag{6}$$

Here both sides have 16 H-atoms, 12 O-atoms, 16 Cl-atoms, and a total charge of zero. How can both equations balance, and which is correct? To answer the first question, many equations can be written as the sum of two or more component reactions. In this case the following related reaction can be used:

$$8H^+ + 2ClO_2 + 8Cl^- = 5Cl_2 + 4H_2O \tag{7}$$

If equation (5) is doubled and added to equation (7), the result is equation (6). Alternatively, equation (5) could be tripled and added to equation (7) to obtain yet another balanced equation with the same reactants and products in different stoichiometric amounts. There is therefore no limit to the number of balanced equations.

Deciding which equation is "correct" is often difficult because one of many competing pathways may take precedence in a reaction, depending on the energy requirements of the system (the thermodynamic limitations) and the speed of the reactions (the kinetics of the system). In the example above, analysis shows that equation (5) is thermodynamically unfavorable at room temperature while equation (6) is favorable.

Non-Stoichiometric Compounds

Most of chemistry is governed by simple whole-number ratios of molecules and atoms. Simple stoichiometry, although valid for the vast majority of mole ratios, is not universal: there are compounds with non-integral mole ratios. Substances such as **alloys** and glasses created problems for the initial acceptance of Dalton's atomic theory. There are, in addition, simple non-stoichiometric compounds that have varying ratios of constituent atoms. Such compounds are generally crystalline solids with defects in their crystal lattices; the lack of simple stoichiometry may give them important properties. Wustite, an oxide of iron, is an example of a non-stoichiometric compound. Its formula can be written $Fe_nO_{1.000}$, where n may have values varying from 0.88 to 1.00 and its physical and chemical properties will vary somewhat depending on the value of n.

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

Current Applications of Stoichiometry

Most chemical reactions are complex, occurring via many steps. In such cases, can an overall reaction be written that describes the stoichiometry of a system under consideration? Consider an example in which sulfur is burned in oxygen to simultaneously form sulfur dioxide (mostly) and some sulfur trioxide:

$$S + O_2 \rightarrow SO_2 \tag{8}$$

$$S + 1.5\ O_2 \rightarrow SO_3 \tag{9}$$

(Note that the "1.5" in reaction (9) means 1.5 moles, not 1.5 molecules.) If the two reactions are added, the resulting equation is: $2S + 2.5\ O_2 \rightarrow SO_2 + SO_3$. This representation of the reaction is plainly wrong because it states that one mole of SO_2 is obtained for every mole of SO_3, whereas most of the products consist of SO_2. The reason for this inconsistency is that the arrows in reactions (8) and (9) mean "becomes"; they are not equivalent to equals signs because they involve time dependence. In order to obtain an overall stoichiometric description of the reaction, both equations (8) and (9) are necessary, as is knowledge about their relative importance in the overall reaction.

Stoichiometry also has biochemical applications. In this case, the systems are biological networks. A typical biological network might be the central **metabolism** of a bacterium living in the gut under anaerobic conditions. This system consists of multiple processes that occur simultaneously involving reactions catalyzed by many enzymes. At the same time that reactants such as **glucose** are being consumed, many different metabolic products are being formed, and the combined reactions provide energy for the overall process. By doing experiments in which some genes in the bacterium have been deactivated, and then analyzing the "metabolic balance sheets," it becomes possible to identify which genes are essential for the overall process and which have no effect. It then becomes possible

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)

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

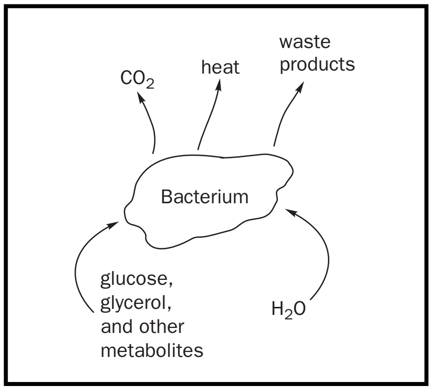

Figure 3. The stoichiometry of a complex reacting system like polluted air in sunlight is very complicated.

to predict the properties of mutants of the bacterium. SEE ALSO Equations, Chemical.

Sidney Toby

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Storage Protein

Storage proteins serve as reserves of **metal** ions and amino acids, which can be mobilized and utilized for the maintenance and growth of organisms. They are particularly prevalent in plant seeds, egg whites, and milk.

Perhaps the most thoroughly studied storage protein is ferritin, which stores iron. Iron is a mineral required by all living things; it is a component of heme, which is found in the transport protein hemoglobin, as well as of cytochromes, molecules taking part in cell **metabolism** (including drug metabolism). Free iron in solution, on the other hand, is able to participate in free radical reactions that damage proteins, **lipids**, and nucleic acids. Therefore, within organisms, in addition to serving as an iron reserve, ferritin provides a safeguard against potentially harmful side effects of iron.

Ferritin is a complex of 24 **polypeptide** chains that form a nearly spherical shell around a core of up to 4,500 iron atoms stored as iron oxide–hydroxide (ferrihydrite) complexes. Ferritin is able to store and release iron in a controlled fashion.

Proteins are made from amino acids, and many storage proteins serve as reserves of amino acids in embryonic and developing organisms. This is true of both animals and plants. Two well-known storage proteins in animals are casein and ovalbumin. Casein, found in mammalian milk, and ovalbumin, found in egg white, both provide a developing organism with a ready source of amino acids and organic nitrogen.

Plant storage proteins are found in high concentrations in seeds, especially in leguminous plants, in which the storage proteins constitute up to 25 percent of the dry weight of the seed. These proteins have no known enzymatic function and often exist within separate **vesicles** (packets) in the seeds. In addition to their importance to the germinating seed, these plant storage proteins are a valuable source of human nutrition. SEE ALSO Iron; Lipids; Nucleic Acids; Proteins; Toxicity; Transport Protein.

Paul A. Craig

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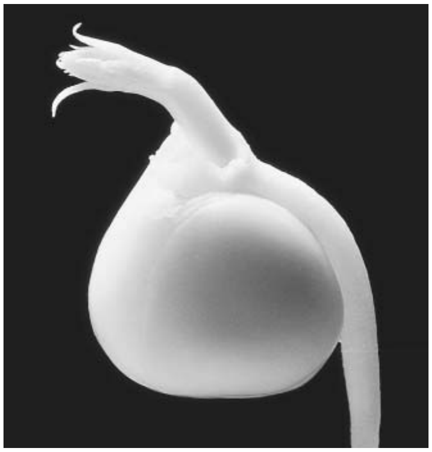
metal: element or other substance the solid phase of which is characterized by high thermal and electrical conductivities

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)

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

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

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



Storage proteins are a source of amino acids for growing organisms, such as this germinating garden pea.

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Strontium

MELTING POINT: 769°C
BOILING POINT: 1,383°C
DENSITY: 2.54 g/cm^3
MOST COMMON IONS: Sr^{2+}

38
Sr
STRONTIUM
87.62

Strontium is the thirty-eighth element in the Periodic Table and the sixteenth most abundant element in Earth’s crust. It was first recognized by Adair Crawford in 1790, who named the substance “strontianite,” after the Scottish town of Strontian where samples were originally obtained. However, it was Sir Humphrey Davy who actually isolated strontium in elemental form in 1808, using his electrolysis apparatus.

There are four stable **isotopes** of strontium that are found naturally. In addition there are about twenty radioactive isotopes, including strontium-90, a deadly by-product of **nuclear**-bomb detonations. The natural forms of strontium are relatively nontoxic. Similar to calcium both physically and chemically, elemental strontium is a soft, shiny **metal**. Like calcium and other alkaline earth metals, it is easily oxidized and thus not found naturally in its free elemental state. Instead, it almost always is found in the +2 **oxidation** state, forming such compounds as strontium oxide (SrO), strontium sulfate ($SrSO_4$, from the mineral celestite), strontium carbonate ($SrCO_3$, from the mineral strontianite), and strontium chloride ($SrCl_2$). Strontium nitrate, $Sr(NO_3)_2$, is used to produce the brilliant red color seen in some fireworks and signal flares and is also used in making “tracer bullets” that can be seen when fired at night. Other strontium compounds are sometimes used in the manufacture of special glasses. Yet overall, strontium is not a very important element industrially or commercially. SEE ALSO Davy, Humphry

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

nuclear: having to do with the nucleus of an atom

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)

David A. Dobberpuhl

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Strutt, John (Lord Rayleigh)

ENGLISH PHYSICIST
1842–1919

John William Strutt was born at Langford Grove in Essex, England, and was the first child of John James Strutt, the second Baron Rayleigh. In 1861 Strutt ventured to Cambridge University where he studied at Trinity College, the same institute attended by Isaac Newton. Strutt received his B.A. in 1865 and was elected a fellow of Trinity College.

English physicist John William Strutt, the third Baron Rayleigh, who discovered argon.

Since in those days there were no university laboratory facilities, Strutt established his own at the family home, Terling Place. There he started research in electrodynamics, color vision, radiation scattering, acoustics, and other experimental phenomena that could be explained in terms of wave motion. In 1870 he published his classic paper "On the Theory of Resonance" that established Strutt's reputation as a serious scientist capable of handling both experimental and mathematical problems. In 1871 he followed up with his well-known theory of light scattering by small particles (now called Rayleigh scattering) and explained how this phenomenon is responsible for the blue color of the sky.

Upon the death of his father in 1873, Strutt inherited the family title and became the third Baron Rayleigh. With the exception of a short period (1879–1885) as the Cavendish Professor of Experimental Physics at the University of Cambridge, Lord Rayleigh spent the rest of his life working at Terling Place. He published a total of 446 publications covering many areas of physics.

inert: incapable of reacting with another substance

Strutt's best-known work, and one for which he was awarded the Nobel Prize in physics in 1904, was his unexpected discovery of the first rare **inert** gas argon. This element was discovered during his attempts to determine more reliable atomic weights by making very precise density measurements on gases. For nitrogen he found that when extracted from the atmosphere, it was heavier than nitrogen obtained by the decomposition of pure ammonia gas. He suspected that the nitrogen obtained from the air contained an impurity, and when Strutt published his density results, he requested suggestions on how to identify the impurity and correct it.

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

William Ramsay, a professor of chemistry at University College, Bristol, took up the challenge, and, knowing that nitrogen could be removed from air by passing it over heated magnesium, he was able to isolate a pure sample of the material that was the cause of Rayleigh's difficulties. Also he showed, by its emission spectra, that it was a new species. Since the gas was found to be chemically inert, it was given the name argon, from the Greek word *argos*, meaning "inert." Ramsay and Rayleigh published a joint paper on the discovery of this new element in 1895, pointing out that its **atomic weight** of 40 and its properties did not fit into the Periodic Table current at that time. Ramsay went on to discover other inert gases now known as helium, neon, krypton, xenon, and radon and was honored for this work with the Nobel Prize in chemistry at the same time that Lord Rayleigh received the same award in physics. SEE ALSO Argon; Ramsay, William.

John E. Bloor

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Substrate

A substrate is the substance upon which an enzyme acts in an enzymatic reaction. Enzymes are biological catalysts that increase the rate of chemical reactions by decreasing the activation energy required for that reaction. An enzyme catalyzes a chemical reaction converting a substrate reactant to a product. An individual enzyme generally has more than one substrate and may be specific to several reaction **intermediates** that are part of an overall reaction.

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

The three-dimensional structure of an enzyme determines its substrate binding specificity. A simple hypothesis proposed by German chemist Emil Fischer in 1894 suggested that the specificity of an enzymatic reaction could be likened to a lock and key. In the lock and key hypothesis, the geometric **complementarity** of the structures of the enzyme (the lock) and the substrate (the key) accounts for the specificity of the reaction. Although scientists were not able to determine the actual three-dimensional structures of enzymes and substrates until many years later, the basic idea of the lock-and-key hypothesis has held. A more refined hypothesis, known as the induced fit hypothesis, proposes that the binding of the substrate by the enzyme changes the structure of the enzyme, resulting in an even greater affinity of the enzyme for the substrate. The site on an enzyme that binds the substrate (known simply as the substrate binding site) is most often a pocket or cleft in the approximately globular structure of the enzyme.

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

The term *substrate* has another meaning in chemistry. Some chemical syntheses are carried out in mixed phases; for example, the reactants exist in solution but the reaction itself occurs at the surface of a solid. The identity of the solid, specified in experimental protocols, influences the **synthesis** reactions, and the solid is referred to as the substrate. SEE ALSO Fischer, Emil Hermann.

synthesis: combination of starting materials to form a desired product

Robert Noiva

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Sugars ***See Carbohydrates.***

Sugar Substitutes ***See Artificial Sweeteners.***

Sulfa Drugs

Sulfa drugs were the first synthetic drugs with widespread antibiotic activity to be put into clinical use. In the 1930s German chemists observed that certain dyes used to stain bacteria stopped microbial growth. Gerhard Domagk, a pathologist at I. G. Farbenindustrie, performed a series of experiments on mice infected with streptococcus bacteria and observed that mice injected with an orange-red dye called Prontosil survived bacterial infection. Prontosil is an **azo dye** that had not shown antibacterial activity during

azo dye: synthetic organic dye containing an –N=N– group earlier **in vitro** tests. However, **in vivo**, the dye is transformed into sulfanilamide, a compound with antimicrobial activity (see Figure 1). Domagk had such faith in Prontosil's anti-infectious properties that he is reported to have injected the dye into his daughter when she had septicemia. In 1939 Domagk was awarded the Nobel Prize in physiology or medicine for his discovery.

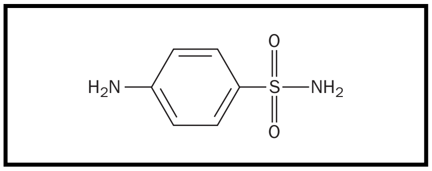

Figure 1. Structure of sulfanilamide.

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

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

biosynthesis: formation of a chemical substance by a living organism

folic acid: pteroylglutamic acid; one of the B complex vitamins

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

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

Once sulfanilamide was recognized as an active antimicrobial agent, scientists synthesized thousands of **sulfonamides** to test for bactericidal activity. It was later realized that sulfonamides do not actually kill bacteria; they interfere with bacterial growth and replication. Sulfa drugs are bacteriostatic. They inhibit an enzyme necessary for the **biosynthesis** of **folic acid** in bacteria. Folic acid is necessary for the biosynthesis of **thymine** and the purine bases, the building blocks of **DNA**. Bacteria that are sensitive to sulfa drugs are unable to acquire folic acid from their environment and, in the presence of sulfonamides, are unable to synthesize the folic acid essential for cell growth and multiplication. Sulfonamides do not harm their human hosts, however, because, unlike susceptible bacteria, humans acquire folic acid from their diet and lack the enzyme necessary for synthesizing folic acid. SEE ALSO ALLOSTERIC ENZYMES; ANTIBIOTICS; INHIBITORS; PENICILLIN.

Nanette M. Wachter

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Sulfur

16
S
SULFUR
32.064

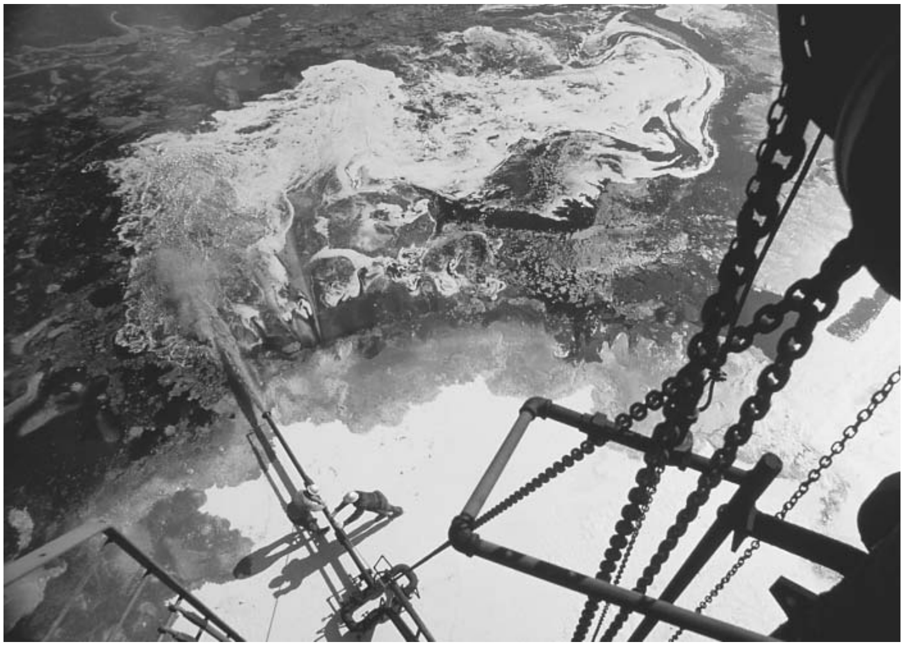
MELTING POINT: 115.2°C
BOILING POINT: 444.6°C
DENSITY: 2.06 g/cm^3
MOST COMMON IONS: S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, $S_2O_6^{2-}$, SO_4^{2+}

combustion: burning, the reaction with oxygen

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

Sulfur has been known since prehistoric times. Because it is flammable, alchemists regarded sulfur as essential to **combustion**. The chemical properties of sulfur and its compounds, including the reaction of sulfur with mercury (Hg) to form a red solid, mercuric sulfide (HgS), and the use of sulfuric acid (H_2SO_4) as a solvent of **metals**, were discovered at about C.E. 250–300. Gunpowder, a mixture of sulfur, charcoal, and potassium nitrate (KNO_3), was first used for military purposes in China in C.E. 904.

Sulfur is a tasteless, odorless, nonmetallic element. Sulfur along with selenium (Se) and tellurium (Te) are called chalcogens. The valences of sulfur are 2, 4, and 6, which can be represented by compounds such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and barium sulfate ($BaSO_4$), respectively. Pure sulfur is insoluble in water. The most stable variety of sulfur, rhombic sulfur, is a yellow crystalline solid.



A vat of sulfur in Port Sulphur, Louisiana. Sulfur is an important crop nutrient and is the thirteenth most abundant element in Earth's crust.

In Earth's crustal composition, sulfur ranks thirteenth in abundance, with an estimated concentration of 0.05 percent. Sulfur exists in elemental form, as metallic sulfides, as sulfates, and, when combined with carbon and nitrogen, in organic forms. Most of the world's sulfur resource is located in North America. It is distributed, in descending order according to share of that resource, as follows: the United States and Canada have 26 percent and 22 percent, respectively, followed by Russia (11%), Saudi Arabia (5%), Japan (5%), Poland (4%), Germany (4%), and France (2%); the remaining 21 percent is distributed in other countries.

Sulfur is commercially important in the manufacture of chemicals such as sulfuric acid. The chemicals, in turn, are used in the manufacture of sulfa drugs, **vulcanized rubber**, acid batteries, dyes, and so on. In agriculture, sulfur is the fourth most important crop nutritive element, after nitrogen, phosphorus, and potassium. Its use in fertilizers is increasing rapidly. Sulfur is also used to manufacture poultry feed additives, pesticides, and parasiticides. SEE ALSO CHALCOGENS.

vulcanized rubber: chemical process of mixing rubber with other materials like sulfur; it strengthened rubber so it could be used under hot or cold conditions; discovered by Charles Goodyear

Guang Wen

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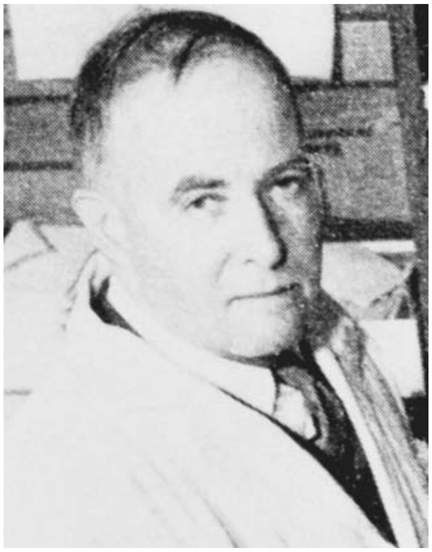
Sumner, James

AMERICAN BIOCHEMIST
1887–1955

James Sumner received the Nobel Prize in chemistry in 1946 (which he shared with John Northrop and Wendell Stanley), "for his discovery that



American biochemist James Batcheller Sumner, corecipient of the 1946 Nobel Prize in chemistry, "for his discovery that enzymes can be crystallized."

enzymes can be crystallized." In asserting that enzymes were proteins, Sumner had to battle the considerable opposition of European chemists for many years, particularly that of Richard Willstätter's group in Munich, who believed that enzymes belonged to an as yet unknown class of chemical compounds.

Sumner wrote in his Nobel Lecture: "I decided in 1917 to attempt to isolate an enzyme. . . . I desired to accomplish something of real importance. In other words I decided to take a 'long shot.' . . . Since the jack bean *Canavalia ensiformis* appeared to be extraordinarily rich in urease, I could see no reason why this enzyme could not be isolated in pure form and characterized chemically." The task took nine years.

Sumner's earliest research facilities were primitive. His laboratory did not even possess an ice chest. He noted, also in his Nobel Lecture: "I would leave cylinders of 30 percent alcoholic extracts on window ledges and pray for cold weather." (He frequently became discouraged.)

Treatment of the jack bean meal with 30 percent alcohol dissolved most of its urease but failed to dissolve other proteins, hence he achieved a considerable purification. Sometime in 1926, it occurred to him that he might achieve even greater purification by using dilute acetone instead of alcohol. A filtered acetone extract, chilled overnight, contained no visible precipitate. However, there was precipitate. In Sumner's own words: "Upon observing a drop of the liquid under the microscope it was seen to contain many tiny crystals. . . . I centrifuged off some of the crystals and observed that they dissolved readily in water. I then tested this water solution. It gave tests for protein and possessed a very high urease activity. I then telephoned to my wife, 'I have crystallized the first enzyme.'"

Willstätter and his collaborators challenged Sumner's claim that urease was a pure protein. After 1926 Sumner and collaborators provided further evidence that urease was indeed a protein molecule and that Willstätter's objections were based on incorrect experimentation. In 1930 Northrop had shown that pepsin was a protein, and in 1937 Sumner isolated catalase in pure crystalline condition. Sumner's initially controversial claims were thus fully vindicated.

James Batcheller Sumner was born in Canton, Massachusetts, in 1887. As a young man of seventeen he suffered a tragic misfortune. While he was out hunting with a companion, the companion accidentally shot him in the left arm, which had to be amputated above the elbow. (Sumner was left-handed.) With amazing courage and determination he taught himself to get along with one arm, and to use his right in activities for which he had previously used only his left. He continued on as a keen sportsman and, despite his disability, came to excel in tennis.

In 1906 Sumner entered Harvard College, graduating in 1910 with a degree in chemistry. He earned a Ph.D. in biological chemistry in 1914 for research carried out under Otto Folin on the formation of urea in animals. When Sumner first applied to do graduate work, Folin suggested he take up law, as he would never be able to carry out laboratory assignments as a one-armed man. Thus challenged, Sumner went on to show how skilled an experimentalist he could become.

In 1914 Sumner became an assistant professor of biochemistry at the Ithaca division of the Cornell University Medical College and was promoted to full professor in 1919. In 1938 he moved to the Cornell School of Agriculture, where in 1947 a laboratory of enzyme chemistry was established under his direction. Active to the last, he died in 1955 of cancer, aged sixty-seven. SEE ALSO Proteins; Willstätter, Richard.

Keith L. Manchester

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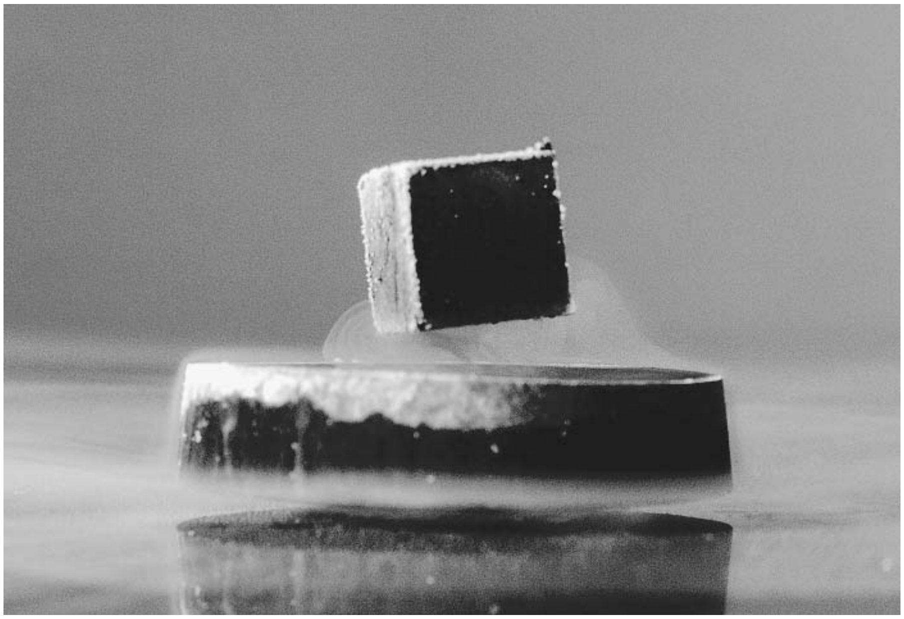
Superconductors

Superconductivity, which is defined as the absence of resistance in a conducting material to a continuously flowing electric current, is a special property that a sizable number of substances attain suddenly at very low temperatures. The substances (called superconductors) include elements, **alloys**, compounds, and nonstoichiometric ceramic materials. Superconductors also exhibit perfect diamagnetism; that is, magnetic fields cannot penetrate them (the Meissner effect), and small powerful magnets actually float (levitate) above flat superconductor surfaces. A superconductor's critical transition temperature, T_C, is the temperature above which no superconductivity can be obtained. For elements, alloys, and simple compounds, very low critical transition temperatures (T_C 23 K) mean that the cooling effects of liquid helium (B.P. = 4 K) are needed to bring about and to maintain their superconductivity. The discovery in 1986 that nonstoichiometric ceramics containing copper and oxygen can have much higher T_C values has provided a new impetus for developing superconducting materials.

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

High Temperature Superconductors

In April 1986, K. Alex Müller and J. Georg Bednorz (with IBM in Switzerland) reported the superconductivity of a nonstoichiometric ceramic oxide of lanthanum, barium, and copper, $La_{2-x}Ba_xCuO_{4-y}$, with the then record high T_C of 35 K. Further experiments conducted by Müller, Bednorz, and others showed that slight modifications made to $La_{2-x}Ba_xCuO_{4-y}$ (x 0.2 and y is even smaller) could yield materials having T_Cs of 50 K. By early 1987, Paul C. W. Chu (at the University of Houston), Maw-Kuen Wu (at the University of Alabama), and their coworkers synthesized another ceramic oxide material, $YBa_2Cu_3O_{7-y}$, and observed that superconductivity in the material was attainable by cooling it with liquid nitrogen (B.P. = 77 K). This "high temperature superconductor" made possible



A magnet is hovering over a superconductor, demonstrating that magnetic fields cannot penetrate the superconductor, known as the Meissner effect.

superconductor applications that were impractical with the low temperature superconductors. (See Figure 1.)

Other nonstoichiometric ceramic oxides that contain copper in nonintegral **oxidation** states have been synthesized and evaluated. Several of these materials have even higher T_C's than that of $YBa_2Cu_3O_{7-y}$. The BSCCO series $Bi_2Sr_2Ca_n-1Cu_nO_{2n}+4+y$ (for $n = 1$ to 4) reaches a T_C maximum of 110 K for $Bi_2Sr_2Ca_2Cu_3O_{10+y}$; a similar $Tl_2Ba_2Ca_n-1Cu_nO_{2n}+4+y$ series reaches a maximum of 122 K for $Tl_2Ba_2Ca_2Cu_3O_{10+y}$; $HgBa_2Ca_2Cu_3O_{8+y}$ has a T_C of 135 K at ambient pressure; and $Hg_{0.8}Tl_{0.2}Ba_2Ca_2Cu_3O_{8.33}$ has a T_C of 138 K. Also, the T_C of $HgBa_2Ca_2Cu_3O_{8+y}$ has been reported to increase to 153 K at a pressure of 150,000 atmospheres and to 160 K at 280,000 atmospheres. Even higher T_C values have been claimed for portions of multiparticle ceramics, but no macroscopic material has shown unambiguous superconductivity at these higher temperatures (above 160 K).

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

Other new classes of superconductors that are being investigated include intermediate temperature range superconductors, such as magnesium diboride ($T_C = 39$ K), alkali-doped C_{60} (M_3C_{60} has a T_C of 33 K), and hole-doped C_{60} ($T_C = 52$ K). The latter result led Jan Hendrik Schon, Christian Kloc, and Bertram Batlogg (of Bell Labs) to the newer haloform-intercalated, high temperature C_{60} superconductors $C_{60} \cdot 2CHCl_3$ and $C_{60} \cdot 2CHBr_3$, with T_C values of 80 K and 117 K, respectively.

The theoretical interpretation of the high temperature superconductors is still under development. The copper oxide ceramic superconductors obtain their paired conducting electrons from copper in mixed oxidation states of I and II or II and III, depending on the particular system. The paired conducting electrons are called Cooper pairs, after Leon N. Cooper. Cooper's name also gives us the C of BCS; the BCS theory is an interpretation of superconductivity for low temperature superconductors (having T_C's of less than 40 K).

MEISSNER EFFECT

The Meissner effect is the repulsion of a magnetic field from the interior of a superconductor below its critical temperature. Whereas a weak magnetic field is totally excluded from the interior of a superconductor, a very strong magnetic field will penetrate the material and concurrently lower the critical transition temperature of the superconductor. W. Meissner and R. Ochsenfeld discovered the Meissner effect in 1933.

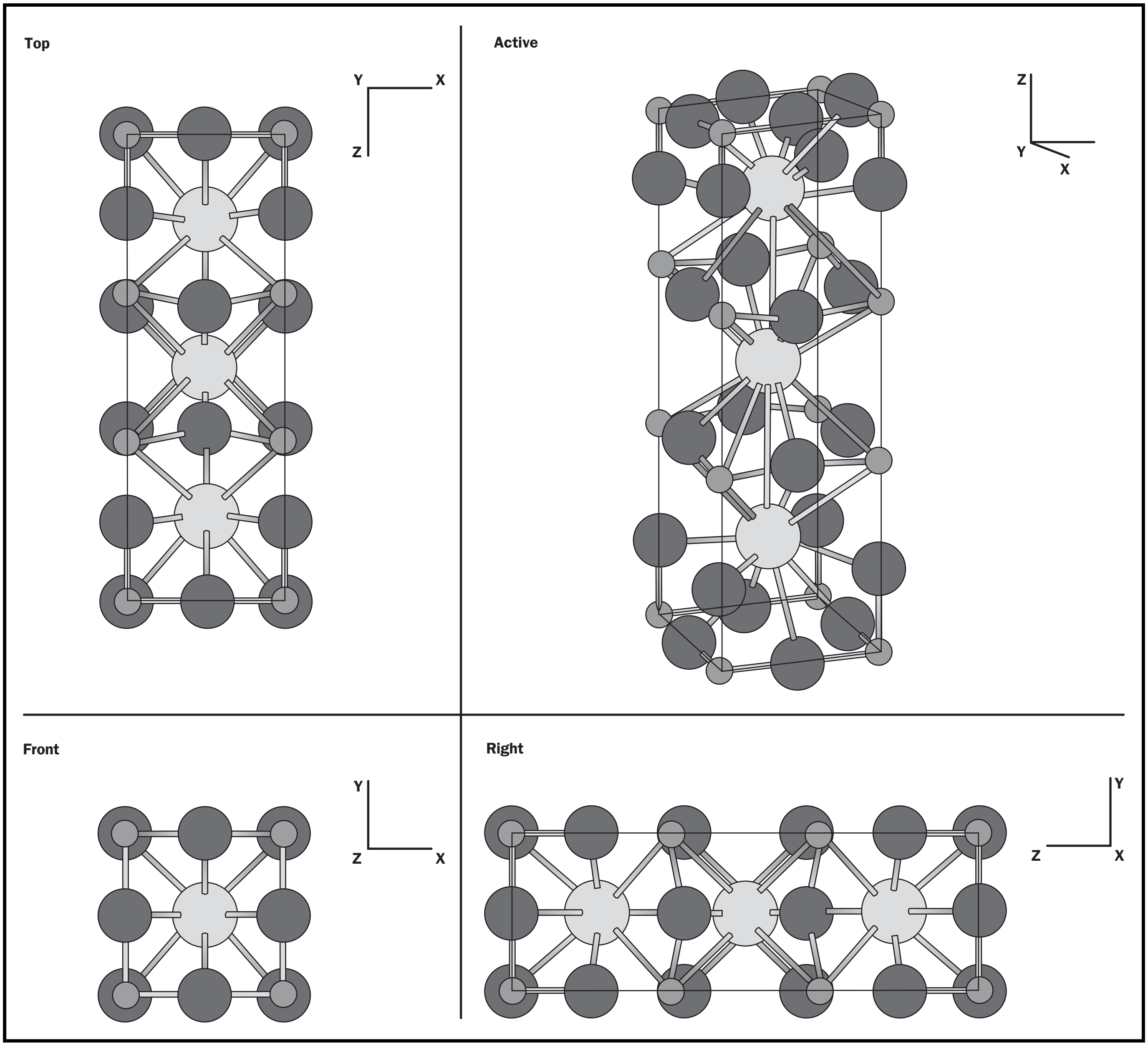


Figure 1. The crystal structure of $YBa_2Cu_3O_{7-y}$. Redrawn from Naval Research Laboratory. Available from <http://cst-www.nrl.navy.mil/lattice/struk.picts/>.

Applications

Applications for superconducting materials include strong superconducting magnets without iron cores, which in turn have a variety of uses. These superconducting magnets are used in particle accelerators, **nuclear** magnetic resonance and magnetic circular dichroism instruments, magnetic resonance imaging devices in medicine, levitating trains, magnetic refrigerators, magnetic energy storage, and SQUIDS (superconducting quantum interference devices) for very sensitive magnetic field measurements (including biomedical magnetoencephalography). Most magnetic applications were developed with and still use the older low temperature superconductors, such as niobium-titanium alloy superconducting wire, which must be cooled with liquid helium. For example, the Fermilab Tevatron (1983) uses 1,000 liquid helium–cooled superconducting magnets in its four-mile (circumference)

nuclear: having to do with the nucleus of an atom

BCS THEORY

BCS theory, developed by John Bardeen, Leon Cooper, and Robert Schrieffer, provides complicated mathematical equations that satisfactorily explain the superconductivity of the classical low temperature superconductors with critical transition temperatures below 40 K. The theory includes Cooper pairs of electrons but does not explain the high critical transition temperatures of the newer ceramic superconductors.

proton-antiproton collider. The sudden quenching of superconducting magnets by vibrations, external fields, or accidental warming can be a serious problem, and the associated heat can cause extensive helium loss.

Cooling with liquid nitrogen rather than liquid helium is much more economical. The difficulty in molding the high temperature superconductors into strong and flexible forms (e.g., filaments or wires) and the greater T_C lowering that accompanies greater magnetic field strength have limited their use up to the present time. Several firms have developed methods to improve the transfer of charge among superconducting particles; and it appears that the best superconductors may be impure ones that allow (the more disordered) ceramic glass formation rather than ceramic crystallite formation. BSCCO superconducting transmission lines are being manufactured (by American Superconductor, Pirelli, and Intermagnetics General) but are currently competitive only when space or weight limitations are important. Superconducting filters for cellular communications, in which the lack of resistance provides filters that have minimal signal loss and are more discriminating in frequency tuning, are being marketed (by Superconductor Technologies, Illinois Superconductor [ISCO], and Conductus), and superconducting motors (American Superconductor) and generators (General Electric) are under development. SEE ALSO Ceramics; Cryogenics; Magnetism.

Ronald D. Archer

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Surface Chemistry

Wolfgang Pauli once stated that "the surface was invented by the devil," illustrating the complexity and difficulty of studying the surfaces of materials. This prompts a fundamental question: What is the surface of a material? The simplest definition is that the surface is the boundary at which the atoms that make up one material terminate and interface with the atoms of a new material. If the surface is considered to be just the outermost layer of atoms of a material, then it comprises on average only 10^{15} atoms per square centimeter (1 square centimeter equals 0.155 square inch), as compared to the bulk of the material, which consists of approximately 10^{23} atoms per cubic centimeter. Surface chemistry is important in many critical chemical processes, such as enzymatic reactions at biological interfaces found in cell walls and membranes, in electronics at the surfaces and interfaces of microchips used in computers, and the **heterogeneous catalysts** found in the catalytic converter used for cleaning emissions in automobile exhausts.

heterogenous: composed of dissimilar parts

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

The development of modern surface chemistry did not begin until the early 1960s as the tools needed to detect the small numbers of surface atoms relative to the bulk atoms (predominately through electron-based spectroscopies) became available. Almost thirty years later, the study of surface chemistry received another boost with the development of a new class of tools called scanned probe microscopies, which provide the ability to view the chemical changes of surfaces under different environmental conditions. Such tools were the first to allow for the direct three-dimensional mapping of positions of atoms at surfaces. These techniques changed the view of surfaces by offering scientists and engineers the ability to directly examine and modify surface chemistries at the atomic and molecular levels.

Seeing Is Believing: The Scanning Tunneling Microscope

In 1981 the first direct visualization of surface atoms was made using a new tool, the Scanning Tunneling Microscope (STM). This tool and the offshoots of its development, including the Atomic Force Microscope (AFM) and Near-field Scanning Optical Microscope (NSOM) have revolutionized the field of surface chemistry. For the first time many processes that occurred at surfaces and interfaces, such as catalytic reactions, could be directly probed. This revolution was so important that the inventors, German physicist Gerd Binnig and Swiss physicist Heinrich Rohrer, received the Nobel Prize in physics only five years later in 1986.

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

The STM utilizes the **quantum mechanical** phenomenon of tunneling to visualize the positions of atoms on surfaces. A sharp metal tip is attached to a piezoelectric translator, which can position the tip with angstrom (1 Å = 1 x 10^{-10} meters) precision. As the tip is scanned over the surface, electrons move between the tip and sample and a tunneling current is produced. This current is very sensitive to (i.e., exponentially dependent upon) the

TUNNELING

Tunneling is the process in which electrons can pass from one metal to another, even though they are not in contact. This process occurs by coupling of the electronic states between the two surfaces.

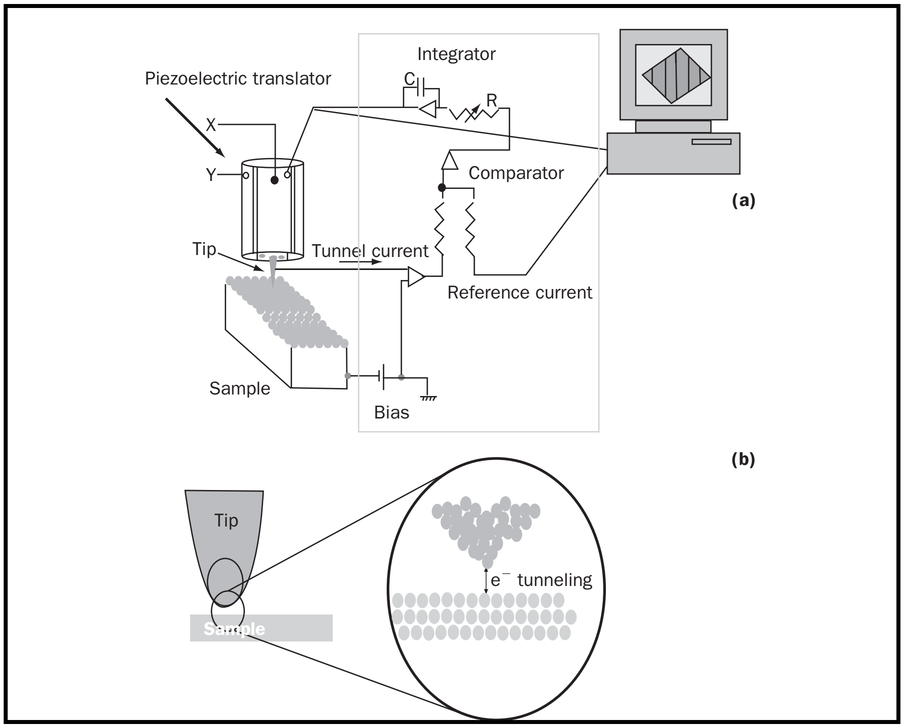

Figure 1. (a) A schematic of a scanning tunneling microscope (STM) showing the primary components including: the piezoelectric tip translator, the sample, the feedback loop, and the computer. (b) Because of the exponential distance dependence of the tunneling current, the majority of the tunneling between the tip and surface is through the closest atoms between the two.

distance between the tip and sample. By attempting to maintain a constant current using a feedback loop monitored by a computer, the piezoelectric receives a signal from the computer to raise or lower the tip as it scans over the surface (Figure 1). Plotting the changes in tip height and position produces a three-dimensional image of the surface, yielding the ability to view the locations of single atoms and to manipulate their atomic positions.

Numerous areas of research have benefited from this technique, including semiconductor technology, growth of metals, and heterogeneous catalysis. Shown in Figure 2 is an atomic resolution image of sulfur atoms on a rhodium surface. Because of the crystalline nature of the Rh surface, the S atoms position themselves in an ordered arrangement as they bond to the metal. Similarly, for surfaces such as silicon, the atomic positions can be viewed. STM revealed for the first time the organization of the structure of atoms on silicon surfaces, having a significant impact on the design of semiconductor devices. Shown in Figure 3 is an image of the Si(111)-(7×7) restructured surface as viewed by STM. Imaging of semiconductors such as Si as a function of voltage between the tip and sample allows for direct visualization of the occupied and unoccupied states, a direct view into the chemistry of the surface atoms.

PIEZOELECTRIC

A piezoelectric is a ceramic material (typically a mixture of Pb, Zr, Ti, and O) that changes size with applied voltage. Quartz is an example of a naturally occurring piezoelectric. Piezoelectric materials are used to control the tip position in scanned probe microscopes because the changes in the piezoelectric dimensions can be controlled with sub-angstrom precision.

Seeing the Rest of the World: Atomic Force Microscopy

While STM gave researchers the ability to probe atomic scale events at metal and semiconducting surfaces, many of the materials of interest to surface scientists fall outside these classes of materials, such as the surfaces of oxides and biological materials that lack conductivity. AFM is a tool that provides similar surface mapping of materials as STM, but can be used for systems that are nonconductive as well.

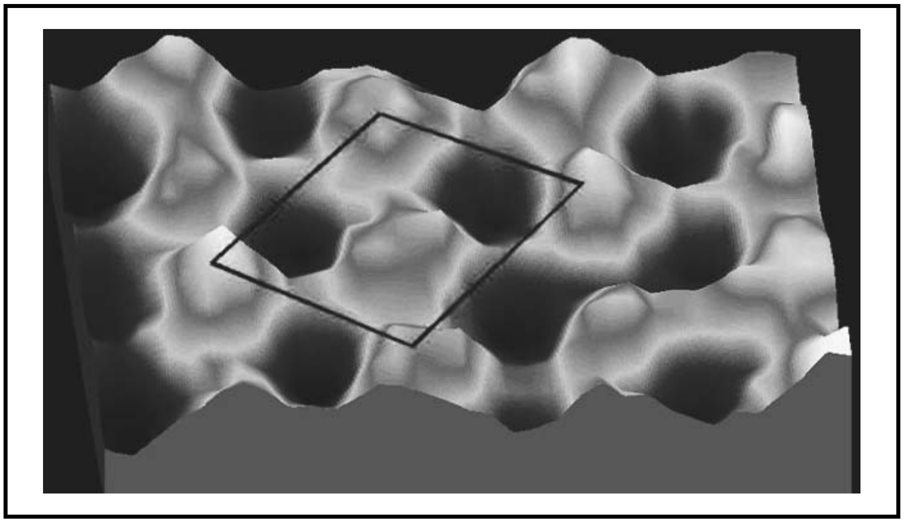

Figure 2. STM image of S atoms on a Rh surface (15 Å × 7 Å × 1.5 Å).

In AFM, a sharp tip on a cantilever is placed in contact with a surface. The forces acting between the tip and surface cause the cantilever to bend. Using a feedback loop, this force is held fixed as the tip is scanned and "feels" its way over the surface, producing an image of the surface topography (Figure 4). AFM measurements can be made in air or under liquids, which allows imaging of biologically important molecules and surfaces, within the nanoscale regime, under natural physiological conditions. AFM has also become an important tool in the measurement of surface properties ranging from basic structure to nanoscale mechanical properties such as friction, adhesion, and elasticity. The details of friction and adhesion are crucial at the nanoscale level, especially with the drive to move technology to even smaller length scales, leading to the development of microelectromechanical systems (MEMS) devices such as microscale motors, actuators, and switches. MEMS devices are currently used in critically important technologies such

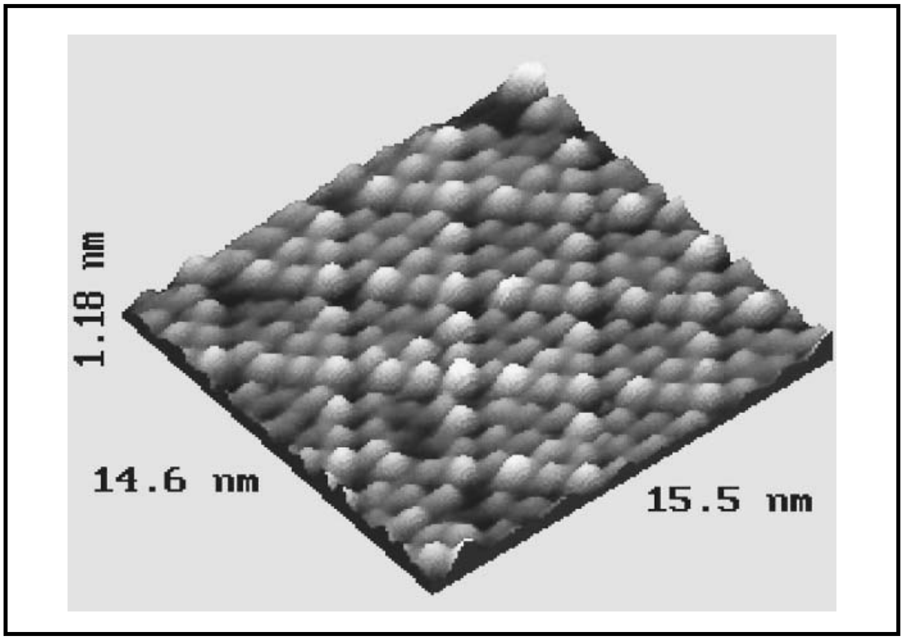

Figure 3. Topographic image (14.6 nm x 15.5 nm x 1.18 nm, 1 nm =10 Å) of a reconstructed Si(111) surface, showing the new outermost atomic positions.

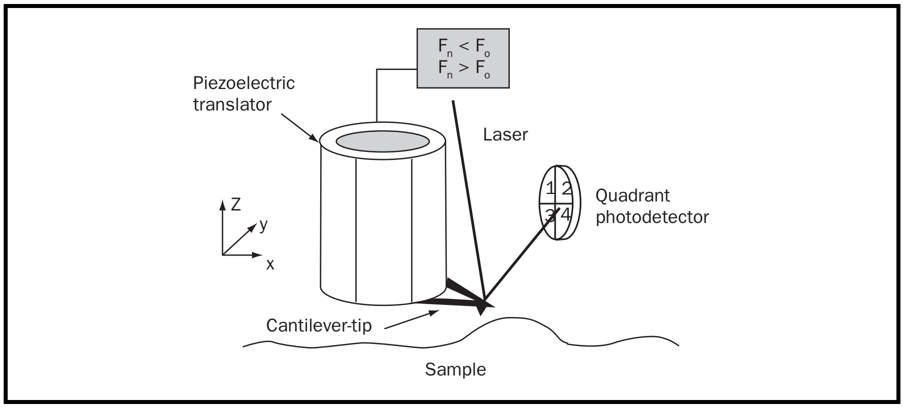

Figure 4. A schematic of an atomic force microscope (AFM), showing the primary components including: the piezoelectric translator, the sample, the cantilever-tip assembly, and the photodetector. In its simplest operating mode (contact mode), the feedback loop of the AFM maintains a constant force between the tip and sample. The force is monitored by measuring the deflection of the cantilever-tip assembly using a laser beam scattered into a quadrant photodetector.

as shock sensors for the deployment of airbags in automobiles. The surfaces of these devices are typically covered with silicon dioxide (glass); controlling the surface chemistry is essential in order to ensure the successful operation of the device.

Studies of adhesion by AFM have led the way to probing local chemical forces at surfaces allowing for the fundamental molecular forces between molecules to be measured directly. Other unique aspects of surface chemistry that AFM has been used to explore include the imaging of liquid surfaces. Modification of the AFM tip with metals allows for the local electric field between the tip and sample to be monitored. Changes in the dielectric properties such as the large contrast between water and many solid surfaces allow for the position of liquid droplets to be observed and for the structures of thin films of water to be probed. Due to the ubiquitous nature of water, the details of the surface chemistry of water are of key concern in a wide range of systems including the chemistry occurring in the stratosphere where ozone-depleting chemical reactions occur on ice surfaces.

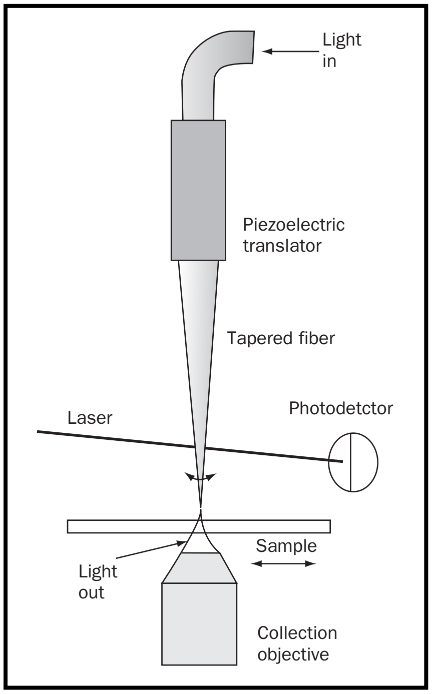

Figure 5. A schematic of a near-field scanning optical microscope, showing the primary components including: the piezoelectric tip translator, the sample, the fiber optic probe, and the photodetector. The fiber is oscillated from side to side and its oscillation measured in the photodetector to control the position of the fiber over the surface. The light leaving the end of the tip passes through the sample and is then collected in a typical microscope objective. The sample is scanned by moving it from side to side under the tip.

Squeezing Light: Near-field Scanning Optical Microscopy

The images that are generated by STM and AFM show structure but no true chemical composition. The details of the local chemistry on surfaces at the nanoscale level, however, are very important to understanding surface properties. Optical spectroscopy and microscopy provide a means of chemically identifying materials; in conventional microscopy, however, the resolution limit is approximately half the wavelength of the light used to illuminate the sample. Thus, spatial resolutions are typically limited to approximately 200 nanometers (7.9×10^{-6} inches) in the visible and approximately 5,000 nanometers (2.0×10^{-4} inches) in the infrared parts of the electromagnetic spectrum.

Near-field Scanning Optical Microscopy (NSOM) overcomes these limitations by “squeezing” the light through an aperture of approximately 50 nanometers (2.0 x 10^{-6} inches), typically using a tapered optical fiber just as is used in most telecommunications signal transmissions. By bringing the tapered fiber to within about 10 nanometers (3.9 x 10^{-7} inches) of a surface, the photons see only the local region of the surface where the tip is positioned (Figure 5). When the light is transmitted through the sample it is collected with a conventional microscope objective, spectroscopic as well as structural images of the materials on a surface can be observed. This approach has paved the way for single molecule spectroscopy and is opening new possibilities for the analysis of material properties at the nanometer scale. Technology is advancing into the infrared and microwave regions of the spectrum, allowing for the chemical composition and dielectric properties of materials to be probed with high spatial resolution. Figure 6 shows a near-field optical image of a polymer blend of polystyrene and polyethylacrylate, taken in the infrared region of the spectrum showing high spatial resolution spectroscopy.

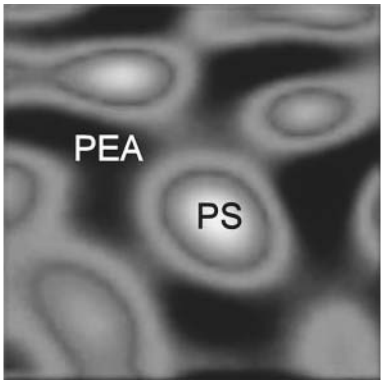

Figure 6. Infrared-NSOM image of a blended polystyrene/polyethylacrylate film (~1 micron thick) on Si. The image (8 μm x 8 μm), collected at 3125 cm^{-1}, shows the domains of polystyrene (PS) embedded within the polyethylacrylate (PEA). This chemical map of the surface has ~10 times higher spatial resolution than a conventional optical infrared microscope image. (Courtesy of Dr. Chris Michaels and Dr. Stephan Stranick, NIST.)

Nanostructures on Surfaces

The design of nanostructures on surfaces using scanned probe microscopies enables the custom design and manipulation of matter on the atomic and molecular level. An STM or AFM tip can be used as a “nanowriter,” placing and pushing around atoms and molecules on surfaces to make organized structures. Single atom positioning heralded by American physicist Donald Eigler at IBM showed the way in which atoms could be placed in complex structures using an STM to carry and position atoms on a surface with high precision. In 1987, using xenon atoms deposited on a nickel surface, researchers at IBM used the STM to write “I,” “B,” and “M” on a surface (Figure 7). Given the ability to write structures at this length scale, the entire Library of Congress could be written on the head of a pin. Although the timescale needed to write structures atom-by-atom makes this prohibitive as a general tool for large-scale lithography, the feasibility has been shown. This burgeoning area of nanotechnology has surface chemistry at its heart, as the detailed control of matter at the molecular level on surfaces is viewed as part of the next technological revolution.

The generation of nanostructures with AFM using dip-pen and nanografting patterning methods has shown great utility in the writing of complex molecules onto surfaces for use in nanoscale devices and sensors.

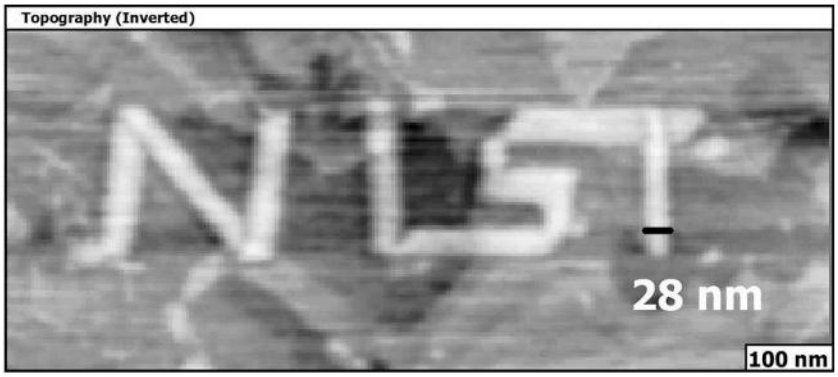

Figure 7. Nanowriting of a mercaptbenzoic acid layer into a background layer of dodecanethiol using nanografting. The height contrast is inverted to make the “nist” appear bright. The thickness of the “t” is only 28 nm. (Courtesy of Dr. Jayne Garno, NIST).

In dip-pen lithography an AFM tip "inked" with molecules is scanned along a surface in a controlled pattern. Under the appropriate conditions the molecules transfer from the tip to the surface, much as a fountain pen writes on a piece of paper.

Nanografting provides another means by which structures may be prepared on surfaces. In nanografting, a background layer of alkanethiols on gold is initially formed as a support matrix. When this surface is imaged in a background solution of a different molecule than the matrix, as the AFM tip scans through the matrix molecules, they are scraped away (mechanically removed) and replaced by the new molecules present in solution (Figure 8). This methodology has been successful in creating structures ranging from a few nanometers to tens of nanometers in dimension. Both of these approaches (and modifications thereof) are rapidly advancing the methodology of "nanowriting." SEE ALSO Catalysis and Catalysts; Nanochemistry.

James D. Batteas
James M. Helt

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Sustainable Energy Use

Most people agree that sustainable energy is energy that is derived from a fuel that is renewable or will never run out and that results in minimal environmental impact. Consequently, the fossil fuels coal, oil, and natural gas clearly do not provide sustainable energy. Once used, those fuels are not replenished, and while they are burned they contribute to various forms of air pollution.

An example of a renewable energy source is one derived from plant materials, such as wood or grain. Plants can be regrown to replace those used for energy. However, plants are sustainable energy sources only if they can be replaced as quickly as they are used. In many areas of the world, trees are being cut for lumber or fuel at a much faster pace than they can be regrown. Such practices are not sustainable.

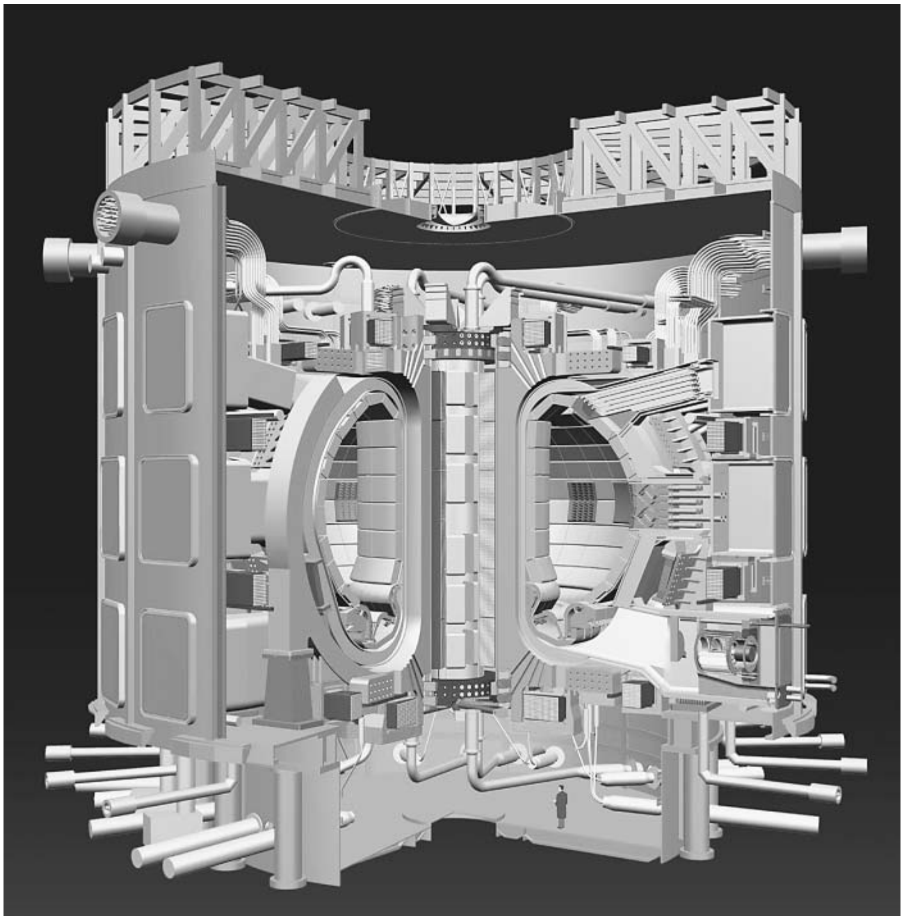
Plant materials, called **biomass**, are renewable and sustainable in the following examples:

biomass: collection of living matter

1. Anaerobic bacteria convert waste plant materials or animal manure to methane gas, and the methane gas (also present in natural gas) is burned either for heat or to make electricity (water is boiled and the steam turns a turbine).
2. Grain, such as corn, is converted to ethanol through a sugar fermentation process. Ethanol is then mixed with gasoline, a fossil fuel, before being burned in an automobile.

The sun and wind are major sustainable energy sources that do not directly use a "fuel." Solar energy is used for direct heating of homes and water, or it is converted directly to electricity using photovoltaic cells. Several large demonstration plants using various techniques to concentrate the solar energy have been built to convert solar energy into electric energy.

Wind is a sustainable source of energy in that it does not diminish with use like fuels.



A cutaway of the ITER tokamak device. A goal of the ITER project is to create sustainable energy by means of fusion.

The conversion of wind energy to electricity, using wind turbines, is now cost competitive with fossil-fuel sources of energy such as natural gas. Wind-turbine farms have been built in Europe and the United States. The land around them is still available for agricultural use. However, people have begun to resist the placement of wind farms in certain locations, citing noise, bird kills, and unsightly visual effects.

A future renewable energy source is hydrogen gas, which can be burned like natural gas or used in a fuel cell along with oxygen to make electricity, with only water as the final waste product. Hydrogen could replace natural gas if an economical method is found to extract it from water. The best future method is to use solar energy directly to "split" water to make hydrogen, and is a current area of research. An intermediate method, but still not used as of 2003, is to use photovoltaic cells to make electricity, which is used to electrolyze water to produce hydrogen. An unsustainable and energy-inefficient method is to use coal to make the electricity to electrolyze the water. As of 2003, fossil fuels, such as natural gas, are used to make hydrogen, which also is clearly unsustainable.

Some people have suggested fusion as a future energy source, based upon abundant supplies of deutrium in water and tritium from lithium and water. Technical problems have so far prevented this from occurring. SEE ALSO AIR POLLUTION; FOSSIL FUELS.

Charles E. Ophardt

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National Renewable Energy Laboratory. Available from <http://www.nrel.gov/>.

Renewable Energy Policy Project, CREST—Center for Renewable Energy and Sustainable Technology. Available from <http://www.crest.org/>.

Svedberg, Theodor

SWEDISH CHEMIST
1884–1971

Theodor Svedberg was a physical chemist whose work significantly affected the development of biochemistry in the twentieth century. He was born in Flerang, Valbo, in Sweden on August 30, 1884. He was educated at the Koping School and Orebro High School and earned B.A., M.S., and Ph.D. degrees at Uppsala University (the latter in 1908). His hobbies were painting and botany. He chose chemistry as his life's work because he believed chemistry to be a means of greater understanding of biological systems. Svedberg spent his entire professional life associated with Uppsala University, first as an assistant at the Chemical Institute in 1905 and then as a professor of physical chemistry starting in 1912. He was awarded a number of international prizes, including the Nobel Prize in chemistry in 1926. This honor was awarded for his groundbreaking work in the chemistry and physics of **disperse systems**.

Swedish chemist Theodor Svedberg, recipient of the 1926 Nobel Prize in chemistry "for his work on disperse systems."

disperse system: two-phase system in which one phase, the disperse phase, is distributed in the second phase, the dispersion medium

Svedberg's primary focus as a physical chemist was the field of colloid chemistry. Colloids are mixtures of very small particles that when dispersed in solvents are not dissolved, but are held in suspension by various actions of the solvent. Svedberg and his collaborators studied the interaction of colloid suspensions with light and their sedimentation processes. These studies showed that the gas laws could be applied to colloidal systems. Svedberg's Ph.D. thesis on the diffusion of platinum colloidal particles elicited a response from Albert Einstein, since it supported Einstein's theory concerning the **Brownian motions** of colloidal particles.

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

A more detailed study of the sedimentation of colloidal disperse systems required Svedberg's 1921 invention of the ultracentrifuge. This centrifuge is similar in principle to a regular laboratory centrifuge except that it rotates at very high angular velocities to provide centrifugal forces as high as 1,000,000 times the force of Earth's gravity. This force is capable of causing colloidal particles to separate into sedimentation bands of varying distances from the center of the centrifuge according to particle size. These bands are observed while the machine is running by photographing the bands, a technique called Schlieren photography. The sedimentation process of colloidal dispersions under these conditions is related to both the shape and mass of the particles. **Homogeneous solutions** of very large molecules such as carbohydrates, proteins, nucleotides (such as **DNA**), and manmade polymers also respond to high forces according to shape and molecular mass.

homogeneous solution: mixture of molecules that forms a single phase (solid, liquid, or gas)

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

In the early days of modern biochemical studies, the overall structure of proteins was not well understood. There were two major schools of thought. One theory posited that proteins are agglomerations of small molecules (Svedberg's theory, consistent with his colloid studies), and the second theory was that proteins are very large molecules. In 1921 Edwin Cohn of Harvard University, who subscribed to the large molecule theory, challenged Svedberg to subject a purified protein to the ultracentrifuge. If the protein were made up of smaller molecules, it would separate into a number of fractions with small molecular weights. If the protein was composed of only one type of very large molecule, the ultracentrifuge would show only one fraction of very high molecular weight. To Svedberg's surprise, the experiment showed that there was only one type of molecule and that proteins are, in fact, made up of a single sort of large molecule. This was a very important result in the understanding of proteins and other large molecules.

Although Svedberg is remembered for his very important work in colloids and artificial rubber, he must also be remembered as a scientist who was willing to test his own theory rigorously and change his point of view when experiment indicated a theory to the contrary. SEE ALSO COLLOIDS; EINSTEIN, ALBERT; PROTEINS.

Lawrence H. Brannigan

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Sweeteners *See Artificial Sweeteners; Disaccharides.*

Synge, Richard Laurence Millington

ENGLISH BIOCHEMIST
1914–1994

Richard Laurence Millington Synge's fascination with biochemistry came into being when he was a young man. In his 1952 Nobel Lecture, he revealed that, at the age of nineteen, after reading Sir Frederick Hopkins's presidential address to the British Association for the Advancement of Science, he suddenly realized "that living things must have wonderfully precise and complicated working parts on the molecular scale, and that biochemists had the best chance of finding out how these are put together and do their work" (Synge, "Applications of Partition Chromatograpy"). It was his desire to unravel the complicated molecules of biochemical importance that ultimately led to his collaboration with Archer J. P. Martin and to their development of liquid-liquid partition **chromatography**.

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

Having completed his undergraduate training in biochemistry and having acquired a familiarity with biochemical techniques, Synge launched into a chemical study of glycoproteins. A short time later he changed course: "Soon I found that my knowledge both of carbohydrate and protein chemistry was inadequate to the task" (Synge, "Applications of Partition Chromatography"). Synge moved on to work with Dr. D. J. Bell, under whose instruction he came to appreciate the power of liquid-liquid extraction as a method of separating the components of chemical mixtures.

It was as a graduate student at Cambridge University that Synge came into contact with Dr. Hedley R. Marston, who advised Synge to study the amino acid composition of wool. The acetylamino acids that were generated during the course of Synge's analysis of wool proteins were partitionable between chloroform and water. Synge was encouraged to consult with Martin on how best to achieve this partitioning.

The collaboration between Martin and Synge eventually culminated in a demonstration of partition chromatography to the Biochemical Society at its meeting at the National Institute for Medical Research in London, on June 7, 1941, followed by the publication of their results in *Biochemical Journal* (1941).

Although Synge did not pursue the further development of chromatographic methods with Martin, he did employ techniques that had been developed by Martin to investigate large peptides. From 1942 to 1948 Synge worked almost exclusively with antibiotic peptides of the gramicidin group, employing paper chromatography to elucidate their primary structures (amino acid sequences). Breaking up these peptides into dipeptide and tripeptide fragments, Synge recognized that identification of these fragments led back to the original sequences. That is, an A–B–C–D–E chain will give rise to the fragments A–B, B–C, C–D, and D–E, from which the original sequence can be unequivocally reconstructed. SEE ALSO GLYCOPROTEIN; MARTIN, ARCHER JOHN PORTER; PRIMARY STRUCTURE.

Todd W. Whitcombe

British chemist Richard Laurence Millington Synge, co-recipient, with Archer John Porter Martin, of the 1952 Nobel Prize in chemistry, "for their invention of partition chromatography."

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Synthesis, Chemical

Over twenty-one million chemical compounds were known as of 2003. Most have been synthesized by chemists; only a small fraction of these are compounds isolated from natural sources. The final proof of a naturally occurring compound's structure is established by synthesizing the compound from simpler molecules by means of identifiable and reproducible reactions.

Protecting Groups

When synthesizing a molecule with more than one functional group, it may be difficult to carry out a reaction with one group without unintentionally

$$\begin{array}{rcll} BrCH_2CH_2CHO + 2CH_3OH + H^+ & \longrightarrow & BrCH_2CH_2CH(OCH_3)_2 + H_3O^+ & (1) \\ BrCH_2CH_2CH(OCH_3)_2 + OH^- & \longrightarrow & CH_2{=}CHCH(OCH_3)_2 + Br^- + H_2O & (2) \\ CH_2CHCH(OCH_3)_2 + H_3O^+ & \longrightarrow & CH_2{=}CHCHO + 2CH_3OH + H^+ & (3) \end{array}$$

Figure 1. Protecting-group use.

interfering or reacting with another group. Use of a protecting group helps to prevent this. The protecting group must be removed after the desired reaction is completed. In the simple example shown in Figure 1, HBr could not be eliminated from the bromopropionaldehyde because the aldehyde group would react with the base. Protecting the aldehyde group by converting it to an acetal allows the HBr elimination to take place. Other examples can be noted: alcohols or phenols can be converted to esters or ethers, aldehydes or ketones to acetals, carboxylic acids to esters, and amino groups to amides.

Retrosynthetic Analysis

For synthesis of fairly complicated molecules, the concept of retrosynthetic analysis (also called the disconnection approach), stated formally as a principle by American chemist E. J. Corey, is generally employed. In this approach, the molecule is broken up into two or more parts called synthons. A symbol used to indicate a retrosynthetic step is an open arrow written from product to suitable precursors or fragments of those precursors (Figure 2). Each synthon is similarly broken up and the process repeated until the fragments are available starting molecules. The synthesis is essentially worked backwards to the actual process followed in the laboratory. Beginning in the 1960s the strategy of organic synthesis became sufficiently systematic that computers could be used for syntheses planning.

Some of the better-known compounds synthesized by retrosynthetic analysis are strychnine, penicillin, prostaglandins, progesterone, vitamin B12, biotin, L-hexoses, menthol, and taxol.

Coordination Compounds

A coordination compound or complex refers to the grouping that is formed when a metal ion or atom accepts a pair of electrons from a molecule or ion. Metal ions—even in very low concentrations—function as powerful catalysts in many important industrial organic processes, as well as with enzymes (catalysts in living tissues). The total number of electron-donor atoms or donor pairs bonded to a given metal atom or metal cation is referred to as the coordination number. The coordination number of a compound can range from two to twelve and determines geometrical shape and physical properties.

Coordination number zero corresponds to an isolated atom; coordination number one occurs for very simple molecule combinations such as Ni-NN that are stable only in very cold matrices such as argon. Coordination

$$\text{Target molecule} \Longrightarrow \text{Precursors}$$

Figure 2. Retrosynthetic analysis.

number three is fairly rare since the metal can still serve as acceptor to more Lewis bases. Coordination number four refers to the smallest number of ligands commonly found in transition metal complexes. Coordination number five was thought to be nonexistent or rare at one time; more recently, studies have revealed stable five-coordinate complexes. Most transition metal complexes have a coordination number of six and show octahedral geometry, although other geometry is possible. Coordination numbers greater than six are rare because of high ligand-ligand steric repulsion. Only small ligand atoms such as fluorine (F) and oxygen (O) have low enough repulsion to form stable seven-coordinate complexes. For coordination number eight, the number of examples is limited because of high ligand-ligand repulsion; most examples involve small ligand atoms. However, eight is a relatively favorable number for complexes of f-block elements (the lanthanides and actinides), since these are large in size and also have a larger number of valence orbitals. Higher coordination numbers of nine and ten are known that also involve f-block elements.

In 1937 English chemist Nevil V. Sidgwick suggested a rule (the octet rule for first-row p-block elements) for complex formation under which a metal can acquire ligands until the total number of electrons around it is equal to the number surrounding the next noble gas. This rule was later expanded as the eighteen-electron rule under which a d-block transition metal atom has eighteen electrons in its nine valence orbitals [five n d; one (n + 1) s, and three (n + 1) p] and will form the stablest compounds when engaged in nine bonding molecular orbitals containing eighteen electrons.

Catalysts

Catalytic processes abound in nature. From enzymes to mineral surfaces, catalysts increase the rate of a given reaction, often by reducing the activation energy that the reactants must overcome before they go on to form products. Catalysts have been developed for a wide spectrum of reactions; a common example is the catalytic converter, used in cars to reduce toxic emissions. Inexpensive transportation fuels, high-temperature lubricants, chlorine-free refrigerants, high-strength polymers, stain-resistant fibers, cancer treatment drugs, and many thousands of other products would not be possible without the existence of catalysts. Catalysts are also essential for the reduction of air and water pollution, contributing to the reduction of product emissions that are harmful to human health and the environment.

catalytic: the action or effect of increasing the rate of a reaction without itself being converted

Most catalysts can be described as either **homogeneous** or **heterogeneous**. Homogeneous catalysts are molecularly dispersed with the reactants in the same phase, which provides easy access to the catalytic site but can make the separation of catalyst and products difficult. Heterogeneous catalysts—usually solids—are in a different phase from the reactants, reducing separation problems but providing more limited access to the catalytic site. Approaches to dealing with these disparate properties include anchoring the catalyst to a soluble or insoluble support, effectively "heterogenizing" the catalyst, or designing the catalyst so that it is soluble in a solvent that, under some conditions, does not mix with the reaction product. Some reactions will not take place (or will take place at a slower rate) without a catalyst being present. Actually an intermediate reaction of one of the reagents with

homogenous: made of similar parts

heterogenous: made of dissimilar parts

This organic chemist is synthesizing a chemotherapy agent, which is among the chemical compounds that do not occur naturally.

the catalyst (or catalyst surface) takes place at a faster rate than without it being present.

Enantiomers. Different enantiomers (mirror image forms) of a given biomolecule can exhibit dramatically different biological activities. Enzymes have evolved to catalyze reactions with selectivity for the formation of one enantiomeric form over the other. Chemists have developed various synthetic small-molecule catalysts that can achieve levels of selectivity approaching (and in some cases matching) those observed in enzymatic reactions. American chemist William S. Knowles pointed out in his 2001 Nobel Prize address that the best synthetic catalysts demonstrate useful levels of enantioselectivity for a wide range of substrates. Such catalysts have been called "privileged chiral catalysts." Such generality of scope is not observed in enzymatic catalysis. SEE ALSO ACID-BASE CHEMISTRY; CATALYSIS AND CATALYSTS; COORDINATION COMPOUNDS; INORGANIC CHEMISTRY; ORGANIC CHEMISTRY.

A. G. Pinkus

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Synthetic Fibers ***See Fibers; Polyesters; Polymers, Synthetic.***

Szent-Györgyi, Albert

HUNGARIAN-BORN AMERICAN BIOCHEMIST
1893–1986

Albert Szent-Györgyi was surely one of the most important scientists of the twentieth century. His research interests included **vitamins**, enzymatic **oxidation** mechanisms, muscle contraction, and cancer. He won the 1937 Nobel Prize in physiology or medicine for his discovery of vitamin C and for his studies on the Krebs, or citric acid, cycle.

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

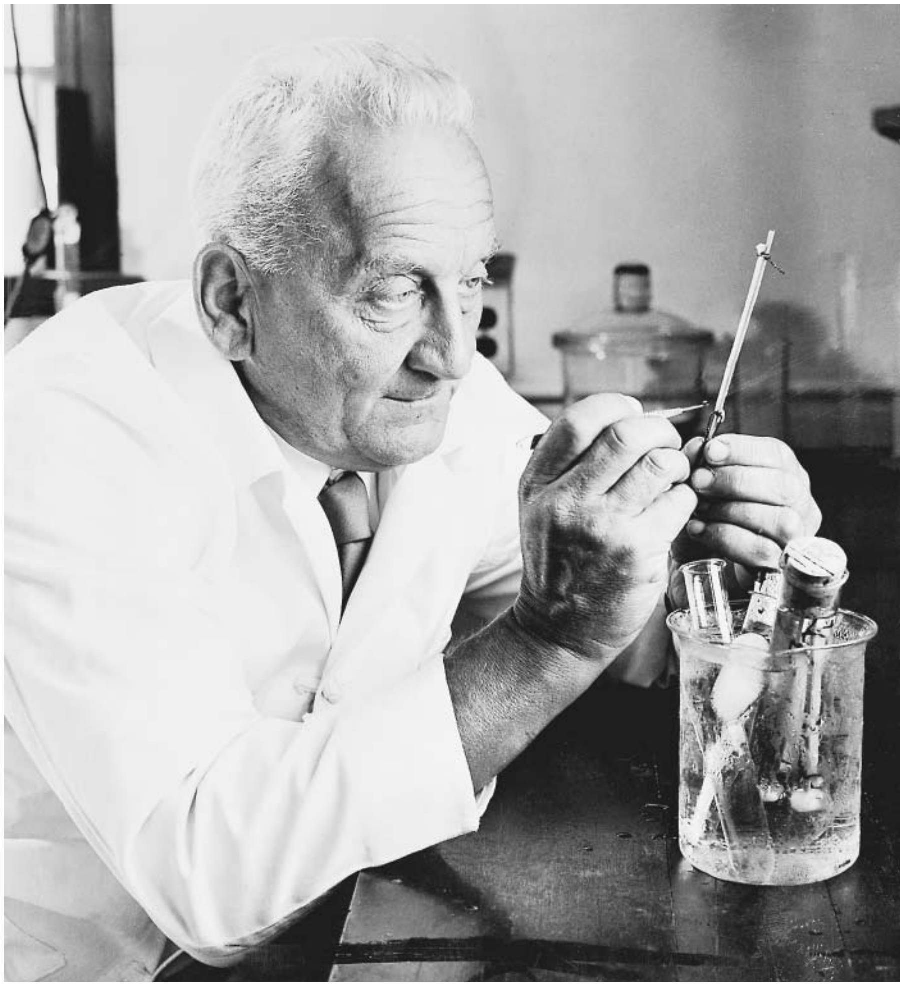
oxidation: process that involves the loss of electrons (or the addition of an oxygen atom)

Szent-Györgyi was born in Budapest, Hungary, on September 16, 1893. His father, Nicholas von Szent-Györgyi, was a prominent landowner. His mother, Josefine Lenhossek, belonged to a highly educated family: Her father and brother were both professors of anatomy at the University of Budapest.

Szent-Györgyi entered the University of Budapest in 1911. He stayed there until the outbreak of World War I, at which time he was drafted into the Hungarian army. Subsequently he served on the Italian and Russian fronts. After being wounded in action, Szent-Györgyi received a medal for bravery and was discharged. He completed his studies in Budapest and during the next decade worked at some of the world's leading academic research centers, including the University of Groningen, Cambridge University, and the Mayo Clinic.

In 1930 Szent-Györgyi returned to Hungary as a professor of medicinal chemistry. He joined the anti-Nazi resistance movement in Hungary during World War II and was for a while exposed to constant danger. He left Hungary in 1947 to join the staff of the Marine Biological Laboratory at Woods Hole, Massachusetts.

During his stay at Groningen, Szent-Györgyi identified a compound present in plant and animal tissues that blocked the enzyme-catalyzed oxidation of fruits and vegetables (the browning of a sliced apple exposed to air is the result of an enzyme-catalyzed oxidation). At Cambridge, he continued his work on this reducing substance and managed to isolate minute



Hungarian scientist Albert von Szent-Györgyi, recipient of the 1937 Nobel Prize in physiology or medicine, "for his discoveries in connection with the biological combustion processes, with special reference to vitamin C and the catalysis of fumaric acid."

quantities of it from adrenal glands. Upon his return to Hungary, he discovered that the reducing substance cured scurvy.

The discovery prompted Szent-Györgyi to search for a more abundant and reliable source of the compound, and eventually he was able to isolate kilograms of it from paprika (the dried, ground fruit of the pepper plant *capsicum annuum*). He named the new compound ascorbic acid, which means the acid that cures or prevents scurvy. (It also goes by the name of vitamin C.) Turkish invaders introduced paprika into Hungary in the sixteenth century and, historically, Hungary has been one of the world's leading exporters of paprika. Presumably large quantities of it were available to Szent-Györgyi, explaining why he looked to paprika to solve his supply problem.

Wanting to know the chemical structure of ascorbic acid, Szent-Györgyi gave a sample to Walter Haworth, a chemistry professor at the University of Birmingham in England and an expert in carbohydrate (sugar) chemistry. Haworth determined the complete chemical structure of ascorbic acid and shared the 1937 Nobel Prize in chemistry for his work.

An originator of many interesting and thought-provoking ideas, Szent-Györgyi died at Woods Hole on October 22, 1986. SEE ALSO ASCORBIC ACID.

Thomas M. Zydowsky

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t

Tantalum

MELTING POINT: 2,996°C
BOILING POINT: 5425°C
DENSITY: 16.65 g/cm^3
MOST COMMON IONS: Ta^{3+}, Ta^{4+}

73
Ta
TANTALUM
180.9479

Tantalum was discovered in 1802 by Swedish chemist Anders Gustav Ekeberg while analyzing Scandinavian minerals. He named the third-row early **transition metal** after the Greek god Tantalus, the son of Zeus, because the oxide was difficult to dissolve in strong acids.

Impure tantalum was isolated in 1825 by Swiss chemist Jean-Charles-Galissard de Marignac and, in purer form, by Heinrich Rose in 1844. It is found, in combination with its **congener** niobium, in tantalite/columbite (Fe, Mn)(Ta, Nb)$_2$O$_6$ ore, with tantalite containing more tantalum than niobium. Its crustal abundance is 1.7 parts per million, with major deposits in Australia, Brazil, China, Africa, the former Soviet Union, and Canada. The ore is concentrated, refined to the oxide Ta$_2$O$_5$, converted to K$_2$TaF$_7$, and reduced to the **metal**.

Tantalum is a hard, **ductile**, dense, steel-blue (when unpolished) metal with the fourth highest melting point of all metals. It crystallizes in a body-centered cubic **lattice** with an atomic radius of 146 picometers. Tantalum has one stable **isotope**, ^{181}Ta; ^{180}Ta is a long-lived (half-life 1.2 x 10^{15} years) isotope.

Tantalum is not attacked at 25°C (77°F) by concentrated bases or acids (other than hydrofluoric acid or fuming sulfuric acid) because of its adhering, corrosion-resistant oxide film. Important compounds, spanning the **oxidation** state range of –3 to +5, include tantalum oxide, Ta$_2$O$_5$; the hard, refractory ceramic carbide TaC; the pentachloride TaCl$_5$; the refractory nitride TaN; reactive **organometallic compounds** with unusual molecular structures; and an interesting series of tantalum-tantalum bonded halide clusters (e.g., Ta$_6$Cl$_{18}^{4-}$) consisting of an octahedron of six tantalums with terminal and **octahedral** edge-bridging halides.

In 2000, 2,267 metric tons (5 million pounds) were produced for various applications, including: (1) electronic devices (79%), especially in capacitors for cell phones, portable computers, and video cameras where high volumetric efficiency and reliability are essential (the oxide coat on tantalum has a high dielectric constant and resistivity); (2) corrosion-resistant chemical process equipment; (3) filaments for evaporating metals; (4) high-temperature superalloys for gas turbines and jet engines; (5) high refractive-index optical lenses; (6) cutting tools; (7) screws and clips for surgical bone

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

congener: an element or compound belonging to the same class

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

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

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

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)

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces repair because of its biological inertness; and (8) radioluminescent x-ray image-intensifying phosphors for medical imaging.

Louis Messerle

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Taste Receptors

Two categories of chemical senses (gustation or taste and olfaction or smell) are important for organisms to respond appropriately to their environments. The sensation of taste detects environmental chemicals and may have initially helped organisms distinguish between new sources of food and potential poisons. There are five different tastes that humans recognize: saltiness, sourness, sweetness, bitterness, and *umami* (the meaty flavor of monosodium glutamate or parmesan cheese). The chemistry of stimuli is described here, as well as their interactions with proteins in the membranes of taste **receptor** cells. These initiate nervous signals traveling via the gustatory nucleus of the brain stem to the cerebral cortex where conscious recognition of taste occurs.

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

Humans have 2,000 to 5,000 taste buds found scattered over the surface of the tongue in small projections known as papillae (bumps). Each taste bud contains about 50 to 150 taste receptor cells that are relatively selective for the taste that they sense. Chemical stimuli interact with the membranes of taste receptor cells either by binding to membrane receptors (proteins with selective binding sites) or by directly changing the number of ions flowing across the membrane.

Ionic Taste Stimuli

Saltiness is sensed by taste receptor cells that respond primarily to sodium chloride. The proteins in the cell membranes involved in transforming the presence of salt into nervous signals are **epithelial** sodium channels that allow the sodium ions to enter the cells, initiate the release of chemical **neurotransmitters**, and stimulate adjacent gustatory afferent axons (nerve cells that carry taste information to the brain). Sourness (hydrochloric acid, citric acid, or acetic acid) is likewise sensed by taste receptor cells in ways that directly affect ion channels. Protons either enter via the epithelial sodium channels or block epithelial potassium channels to initiate the cellular response. The bitterness of quinine and calcium is also sensed by blocking potassium channels in taste receptor cell membranes.

epithelial: related to a tissue type characterized by thin sheets and usually serving a protective or secretory function

neurotransmitters: molecules released by one neuron to stimulate or inhibit another neuron or cell

Membrane Receptor Taste Stimuli

In contrast, other tastes including sweetness (as in sucrose, fructose, and artificial sweetener) are sensed by actually binding to specific membrane receptor proteins in taste receptor cells. The chemicals sensed as sweet bind to selective sites on a membrane receptor in a “lock-and-key” fashion (implying that only chemicals of a particular shape can fit in the binding site and initiate the response). Once the sweet chemical is bound, the membrane receptor initiates a series of chemical reactions inside the cell, leading eventually to a change in the flow of ions across the membrane and the release of neurotransmitter. Likewise, the bitterness of some chemicals is sensed by binding to other membrane receptors and then initiating a response. The taste of some amino acids is initiated by binding to a specific site on **chemical-gated** ion channels (channels that open when a chemical is bound) where the amino acid (the chemical) acts as the key. The *umami* taste of monosodium glutamate is sensed by binding to another type of membrane receptor (similar to the synaptic glutamate receptors of the brain) that allows ions to cross cell membranes.

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

Taste and smell are well-known chemical senses; however, the specific genes and proteins involved in some tastes have not yet been fully identified. SEE ALSO Artificial Sweeteners; Molecular Structure; Neurotransmitters.

Barbara E. Goodman

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Technetium

MELTING POINT: **2,157°C**
BOILING POINT: **4,265°C**
DENSITY: **11.5 g/cm^3**
MOST COMMON IONS: **TcO_5^{2-}, TcO_3^{-}, TcO_4^{2-}, TcO_4^{-}**

43
Tc
TECHNETIUM
98.906

The discovery of technetium in 1937 by the Italian scientists Carlo Perrier and Emilio Segré was an important affirmation of the configuration of the Periodic Table. The table had predicted the existence of an element with 43 protons in its nucleus, but no such element had ever been found. (In fact, technetium does not occur naturally on Earth, as all of its known **isotopes** are radioactive and decay to other elements on a timescale that is relatively small when compared with the age of the earth.) Perrier and Segré were able to observe technetium from molybdenum that had been bombarded with deuterons. They named the element technetium, from the Greek word *technetos*, meaning artificial. Technetium is produced in relatively large quantities during **nuclear fission**, so there is currently an ample supply of the element from nuclear reactors and nuclear weapons production.

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

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

Technetium looks like most other **metals**, silver-gray in color, but it is usually produced as one of its oxides, pertechnetate (TcO_4^{-}). Technetium has great chemical flexibility, and a wide variety of its compounds have been

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

prepared, generally paralleling the known compounds of rhenium. Technetium's radioactive nature and varied chemistry have helped to make it the most important element that is used in nuclear medicine. For diagnostic purposes, a compound containing technetium is prepared and injected into a patient, and then a large camera, typically made up of several gamma ray detectors, is passed over the patient. The technetium compound will have localized in specific organs, providing valuable information about organ function or the presence of abnormalities. The radiation dose to the patient is low, and the diagnostic procedure is considered less risky than exploratory surgery. Every year, millions of medical diagnostic scans that employ technetium are performed. SEE ALSO Nuclear Fission; Rhenium.

Jeffrey C. Bryan

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52
Te
TELLURIUM
127.60

Tellurium

MELTING POINT: 449.5°C
BOILING POINT: 990°C
DENSITY: 6.25 g/cm^3
MOST COMMON IONS: Te^{2-}, Te_2^{2-}, Te^{4+}, TeO_5^{2-}, TeO_4^{2-}

Tellurium was discovered in gold ores by Franz Joseph Müller von Reichenstein, the chief inspector of mines in Transylvania (Romania), in 1782. Tellurium was named, however, by M. Klaproth, who continued Müller von Reichenstein's work and isolated the element in 1798. Its name originates from the Latin *tellus*, which means "earth."

SOME BINARY COMPOUNDS OF TELLURIUM

	Compound	Chemical formula
Hydrides	tellurium hydride	H_2Te
Fluorides	tellurium (IV) fluoride	TeF_4
	tellurium (VI) fluoride	TeF_6
Chlorides	tellurium chloride	Te_2Cl
	tellurium (II) chloride	$TeCl_2$
	tellurium chloride	Te_3Cl_2
	tellurium (IV) chloride	$[TeCl_4]_4$
Bromides	tellurium bromide	Te_2Br
	tellurium (II) bromide	$TeBr_2$
	tellurium (IV) bromide	$[TeBr_4]_4$
Iodides	tellurium (I) iodide	TeI
	tellurium iodide	Te_2I
	tellurium (I) iodide	Te_4I_4
	tellurium (IV) iodide	$[TeI_4]_4$
Oxides	tellurium (II) oxide	TeO
	tellurium (IV) oxide	TeO_2
	tellurium (VI) oxid	TeO_2

Some binary compounds of tellurium.

Tellurium is used in photocopiers to enhance picture quality.

Tellurium is a comparatively rare element, is seventy-third in order of crustal abundance (approximately 0.001 ppm), and is occasionally found as the native **metal**. Many of its minerals occur together with the sulfides of chalcophilic metals (e.g., Cu, Ag, Au, Zn, Cd, Hg, Fe, Co, Ni, Pb, As, Bi). It is obtained from anode slime produced in the electrolytic refining of Cu. Tellurium has eight naturally occurring **isotopes**; the most abundant ones are ^{130}Te (33.8%) and ^{128}Te (31.7%). Crystalline tellurium has a silvery-white appearance and exhibits a metallic luster but is usually obtained as a dark gray powder. It is brittle and easily pulverized. Tellurium is a p-type semiconductor and shows varying conductivity with crystal alignment (its electrical resistivity is approximately 1 ohm cm at 25°C). Its conductivity increases slightly with exposure to light. It can be **doped** with silver, copper, gold, tin, and other elements. Other **nuclear** and physical properties include: atomic radius: 160 pm; ionic radius: 221 pm (Te^{2-}); 97 pm (Te^{4+}); 56 pm (Te^{6+}); and **ionization** energy: 869 kJ/mol.

The main uses of tellurium are: as semiconductors; in the formation of **alloys** with lead (to prevent corrosion), cast iron (to improve machinability), copper, and stainless steel; in ceramic materials; tinting glass. SEE ALSO Chalcogens.

Thomas M. Klapotke
M. J. Crawford

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

dope: to add a controlled amount of an impurity to a very pure sample of a substance, which can radically change the properties of the substance

nuclear: having to do with the nucleus of an atom

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

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

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Temperature

In everyday terms, temperature is a measure of the "hotness" or "coldness" of a substance. More technically, temperature indicates the direction in which energy flows (as heat) when two objects are in thermal contact: energy flows as heat from a high temperature region to a low temperature region. In other words, temperature is simply an indicator of the expected direction of flow of energy as heat.

Temperature is not heat. Heat is energy in transition; temperature is the signpost of the expected direction of that transition. A large quantity of energy can flow as heat from one region to another even though the temperature difference between the regions is minute.

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

Temperature is not energy. A very large, cold block of **metal** will have a low temperature but may contain a very large amount of energy. A small block of the same material having the same temperature will contain less energy. This distinction is expressed by saying that temperature is an intensive property, a property independent of the size of the sample; whereas energy content is an extensive property, a property that does depend on the size of the sample. Thus, a sample taken from a tank of hot water will have the same temperature regardless of the size of the sample, but the energy content (more formally, the internal energy) of a large sample is greater than that of a small sample.

At a molecular level, the temperature of a system indicates the distribution of "populations" of energy levels within the system: the higher the temperature, the greater the proportion of molecules in a state of high energy. If the numbers of molecules in two energy states, separated by an energy difference ΔE, are N_{upper} and N_{lower}, then the temperature is

$$T = (\Delta E/k)\ \ln(N_{\text{lower}}/N_{\text{upper}}) \tag{1}$$

where k is Boltzmann's constant, a fundamental constant of nature. We see that the greater the ratio $N_{\text{lower}}/N_{\text{upper}}$ for a given energy difference, the higher the temperature. This molecular interpretation has a special significance in cases in which the only contribution to the overall energy is kinetic energy, which is the case in a perfect (ideal) gas. In that case, high temperature corresponds to a higher average speed of the molecules and a wider range of speeds in the sample. The average speed c of molecules of mass m at a temperature T is

$$c = (8kT/\pi m)^{1/2} \tag{2}$$

and so the average speed increases with the square root of the temperature.

Temperature is measured with a thermometer, a device in which a physical property of some component of the device changes when the device is put in thermal contact with a sample. That property may be the volume of a liquid (as in a mercury-in-glass thermometer) or an electrical property such as resistance. Electronic probes based on resistance changes in a semiconductor material are also used to measure temperature.

Three scales of temperature are still commonly encountered. The Fahrenheit scale is used in the United States for domestic purposes. On this

A woman is checking a baby's temperature. A high temperature indicates more energy in the body and possibly an illness.

scale, the freezing point of water is 32°F and its boiling point is 212°F. This scale has been discarded by virtually all other countries in favor of the Celsius scale, which is used for all scientific work. On the Celsius scale, the freezing point of water corresponds to 0°C and the boiling point corresponds to 100°C. A more fundamental scale is the Kelvin scale, which sets 0 at the absolute zero of temperature (corresponding to -273.15°C), and adopts a scale in which the triple point of water (the temperature at which ice, water, and water vapor coexist at **equilibrium**) is exactly 273.16 K. This scale ensures that the magnitude of the kelvin (as the unit for the Kelvin scale is called) is the same as that of the Celsius degree.

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

The Kelvin scale is used to express the thermodynamic temperature, denoted T, with $T = 0$ as the lowest possible temperature (when all motion has ceased). Temperatures on the Celsius and Fahrenheit scales are denoted θ (theta). Two important conversions are:

$$\theta/°\mathrm{C} = {}^5\!/_9(\theta/°\mathrm{F} - 32) \quad (3)$$

$$T/K = \theta/°\mathrm{C} + 273.15 \quad (4)$$

In chemistry, it is often necessary to keep a system at a constant temperature, for otherwise observations and measurements would provide a reading that was an average of a temperature-dependent property, such as reaction rate. One way to achieve a constant temperature is to immerse the system in a water bath containing a large volume of water, the temperature of which is controlled by a heater and a thermostat. A thermostat is a device for switching a current on and off according to whether the temperature of the system is above or below a selected value. It incorporates a temperature probe (a thermometer with an electric output) and electronic devices for interpreting the temperature and effecting the switching. The same principle is the basis of the thermostat that is used in homes.

phase: homogeneous state of matter

The chemical effects of greater temperature include changes in the rate of reaction and the position of chemical equilibrium. Almost all reactions proceed more rapidly at higher temperatures because the molecules (in the gas **phase**) collide more vigorously at higher temperatures. A thermodynamic consequence of changing temperature is that the equilibrium constant of an exothermic reaction decreases as the temperature is raised, so reactants are more favored at low temperatures than at high. This dependence is sometimes referred to as Le Chatelier's principle, but it is better to regard it as a consequence of thermodynamics and in particular of the second law of thermodynamics.

Although $T = 0$ is the lowest attainable temperature, it is possible to achieve negative temperatures. This seemingly paradoxical remark is resolved as follows. When a system has only two energy levels, all finite temperatures correspond to a distribution of populations in which more molecules occupy the lower state than the upper. However, it is possible by artificial means to invert the populations, so that briefly there would be more molecules in the upper state than the lower. It follows from equation 1 that T is then negative.

The thermodynamic justification for introducing the temperature into science is the Zeroth Law, which states that if system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then A and C would also be in thermal equilibrium with each other, if they were put in contact. The third law of thermodynamics is also relevant here: it states that absolute zero ($T = 0$) is not attainable in a finite number of steps. SEE ALSO CHEMISTRY AND ENERGY; ENERGY; HEAT; PHYSICAL CHEMISTRY; THERMODYNAMICS.

Peter Atkins

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Teratogen

Teratogen means, in Greek, "monster forming." Teratogens are chemicals that cause abnormalities in embryos. The most well-known is thalidomide, a drug originally designed to combat morning sickness in pregnant women. It caused the long bones in the arms or legs of fetuses to not develop properly, resulting in babies with severely stunted arms or legs.

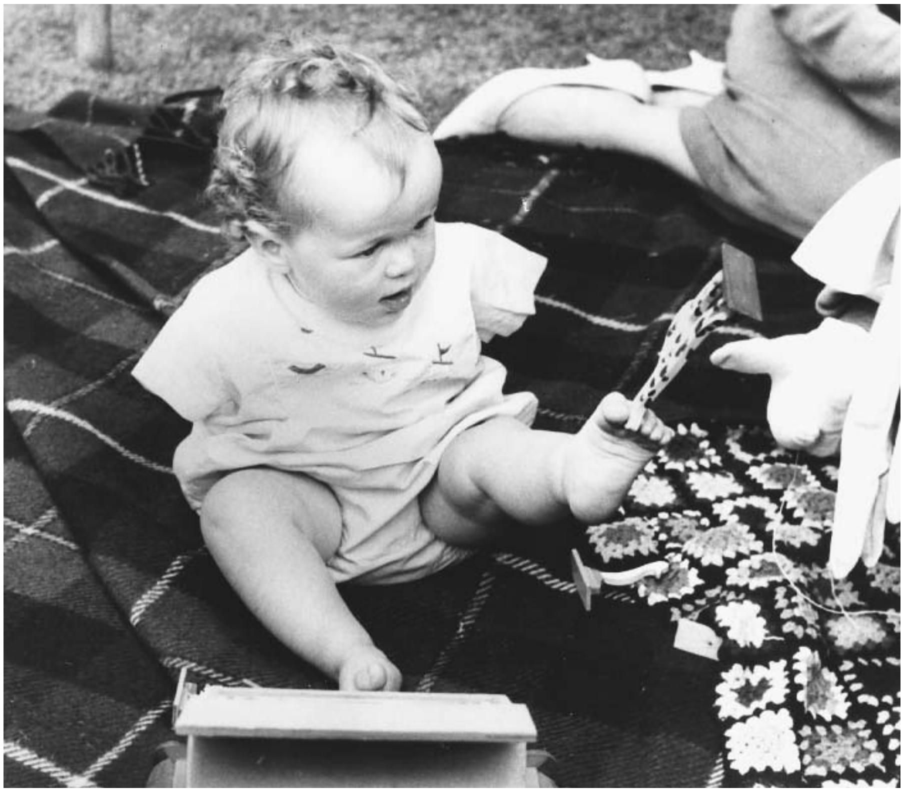
Teratogen is a type of mutagen that causes mutations in **somatic cells** (cells that are not part of the reproductive system). Mutagens induce mutations of deoxyribonucleic acid (**DNA**), the hereditary material in cells. The damage of DNA may either kill the cells or, when misrepaired, produce abnormal sequences that will be passed on to daughter cells. This may result in birth defects by injuring developing organs or by disorganizing growth and differentiation.

somatic cell: cells of the body with the exception of germ cells

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

Apart from thalidomide, the steroid hormones have also been identified as teratogens. The use of male sex hormones as a treatment for breast cancer has resulted in the masculinization of a number of female fetuses when such treatment was commenced prior to the twelfth week of gestation. In addition, the accepted practice of using **progesterone** from natural sources for the treatment of miscarriage led to the widespread use of synthetic hormones between 1950 and 1960. The result was the birth of more than 600 female babies with equivocal or frankly masculinized external genitalia. It

progesterone: steroid found in the female reproductive system: formula $C_{21}H_{30}O_2$



The teratogen thalidomide causes stunted arms and legs in babies. It was commonly used by pregnant women to combat morning sickness.

was found later that these synthetic compounds had appreciable androgenic (related to the male sex hormone) activity.

There are other chemicals suspected of being teratogenic because they are occasionally associated with malformations in the offspring of women treated during pregnancy. These include anticonvulsants and some oral hypoglycemics when taken at high doses during pregnancy. It is, however, very difficult to determine the teratogenesis of a drug. Long and costly surveys must be done on a very large population to associate a particular drug with birth defects. SEE ALSO Deoxyribonucleic Acid; Kelsey, Frances Kathleen Oldham; Mutagen; Toxicity.

Joseph Bariyanga

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Terbium

MELTING POINT: **1,356°C**
BOILING POINT: **2,480°C**
DENSITY: **8.253 g/cm^3**
MOST COMMON IONS: **Tb^{3+}, Tb^{4+}**

In 1787, near Ytterby, Sweden, Swedish army officer Karl Axel Arrhenius discovered a mineral that he named ytterite. In 1794 Finnish chemist Johan Gadolin, working with ytterite, isolated a mixture of oxides (yttria) from which Carl G. Mosander in 1843 isolated three fractions: the oxide of the element yttrium (Y) and two other mixtures of oxides (old erbia and old terbia). In 1878 Swiss chemist Marc Delafontaine worked with "old erbia" but called it new new terbia. Also in 1878 J. C. Galissard de Marignac and Delafontaine, working with "new terbia," isolated an oxide of a new element, terbium. The element has an abundance of 0.91×10^{-5} percent (by weight) in the igneous rocks of Earth's crust. Terbium's ground state electronic configuration is $[Xe]4f^{9}6s^{2}$. It has an atomic radius of 1.782 angstroms. Terbium has two crystallographic structures: α-Tb (room temperature to 1,310°C) and β-Tb ($>$ 1,310°C). Bastnasite (fluorocarbonates), monazite, and xerotime (phosphates) are the principal terbium-containing minerals.

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

Terbium has two **oxidation** states: 3+, the most important, and 4+. Tb^{4+} is a strong oxidizing agent. Tb^{3+} salts are generally colorless or very pale pink. The Tb^{3+} halides, except the fluoride compound, are soluble in water as well as in nitric acid, perchloric acid, and acetic acid. The hydroxide, oxide, phosphate, carbonate, and oxalate compounds are insoluble. A Tb^{4+} oxide with a composition approaching Tb_4O_7 (brown) is obtained via the **calcination** of several salts: carbonate, nitrate, and oxalate. The Tb^{4+} compounds TbO_2, with a fluorite-type **lattice**, and TbF_4 also exist.

calcine: to heat or roast to produce an oxide

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

Tb^{3+} compounds and complexes in most cases exhibit strong luminescence in the green portion of visible light. Ternary compounds such as

$\text{La}_{1-x}{-}y\text{Ce}_x\text{Tb}_y\text{PO}_4$ exhibit strong green emission radiation. Such kinds of compounds are called "phosphors" and are used to display color in television. Terbium is also used as an **alloy** material in compact discs. SEE ALSO Cerium; Dysprosium; Erbium; Europium; Gadolinium; Holmium; Lanthanum; Lutetium; Neodymium; Praseodymium; Promethium; Samarium; Ytterbium.

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

Lea B. Zinner
Geraldo Vicentini

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Terpenes

If you walk into a garden in bloom and breathe deeply, you are likely to encounter great smells. In many cases, the molecules that bring those scents to your nose are terpenes. Terpenes are a class of molecules that typically contain either ten or fifteen carbon atoms built from a five-carbon building block called **isoprene**. It is important to note these molecules are **volatile**—they tend to evaporate relatively easily—which allows them to reach one's nose and trigger the olfactory senses. Figure 1 shows the structure of several molecules in this category and identifies the plant from which they are derived.

isoprene: common name for 2-methyl-1,3butadiene, the monomer of the natural rubber polymer

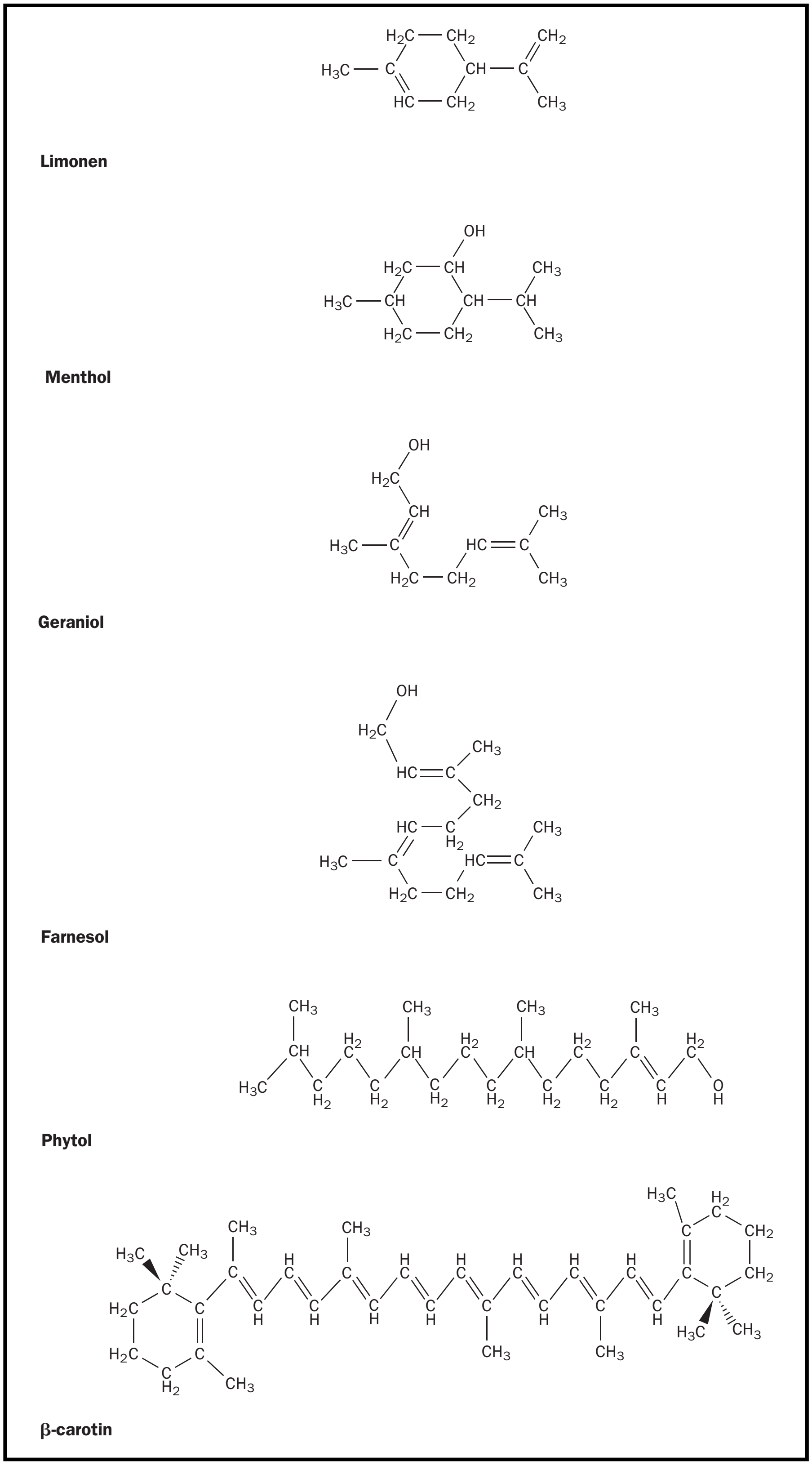
volatile: low boiling, readily vaporized

Because they share the common building block of isoprene, terpenes can be categorized based on how many terpene units they include. The "base" of this system is a two-isoprene unit, so monoterpenes have ten carbons. This category includes molecules such as camphor, menthol, and pinene. If three isoprenes are present, as in farnesol (shown in Figure 1), the category is called sesquiterpenes.

In plants, terpenes are typically found as a component of the essential oils. The name of this fluid suggests an important characteristic of this class of molecules. If humans have found these oils important enough to refer to them as essential, there is a reasonable chance that they have useful properties. Many terpenes such as menthol (shown in Figure 1) and camphor have medicinal values. You may have used a throat lozenge with menthol to help clear your sinuses the last time you had a cold.

Another use of terpenes may be found in coatings such as varnish. Varnish for musical instruments like violins can be made largely from the terpene pinene. The key to generating a coating such as varnish is to allow polymerization to occur. The fact that terpenes are built up from isoprene building blocks, much like any other polymer, suggests that polymerization is a possibility. When pinene (present in pine tree and made into turpentine) is exposed to air and sunlight, it will slowly polymerize and make a fine finish for wood.

β-carotene is a tetraterpene (structure shown in Figure 1); it has four isoprene units. This molecule, found in abundance in carrots, is useful in



Limonen

Menthol

Geraniol

Farnesol

Phytol

β-carotin

Figure 1. The structures of several terpene molecules and the plants from which they are derived.

human diets because it can be converted into **vitamin** A in the body. It also plays an important role in plants because it is among the pigments that absorb light in **photosynthesis**. When leaves change color in the fall, β-carotene is often responsible for this effect. SEE ALSO LIPIDS; MEMBRANE.

Thomas A. Holme

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

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

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Tertiary Structure

The tertiary structure is the complete three-dimensional structure of a **polypeptide** chain. Many polypeptides fold into compact, globular structures in which amino acid residues that are distant from each other in primary structure come into close proximity in the folded structure. Because of efficient packing, most water molecules are excluded from the protein's interior. It is the different interactions between the side chains of the amino acids that stabilize the tertiary structure. A major force stabilizing the tertiary structure is the **hydrophobic** interaction among **nonpolar** side chains in the core of the protein.

Additional stabilizing forces include **electrostatic interactions** between ionic groups of opposite charge, **hydrogen bonds** between polar groups, and **disulfide bonds**. Disulfide (S–S) bonds are formed between the thiol (S–H) groups of two cysteine side chains resulting in a **covalent bond** between the two side chains. Many physical and chemical agents, including heat, detergents, salts, **heavy metals**, strong acids and bases, organic solvents, and mechanical stress, can disrupt or destroy the three-dimensional structure of a protein. This process of destroying the three-dimensional protein structure is called denaturation. SEE ALSO PRIMARY STRUCTURE; QUATERNARY STRUCTURE; SECONDARY STRUCTURE.

Elizabeth S. Roberts-Kirchhoff

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

hydrophobic: water repelling

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

electrostatic interaction: force that arises between electrically charged particles or regions of particles

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

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

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

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

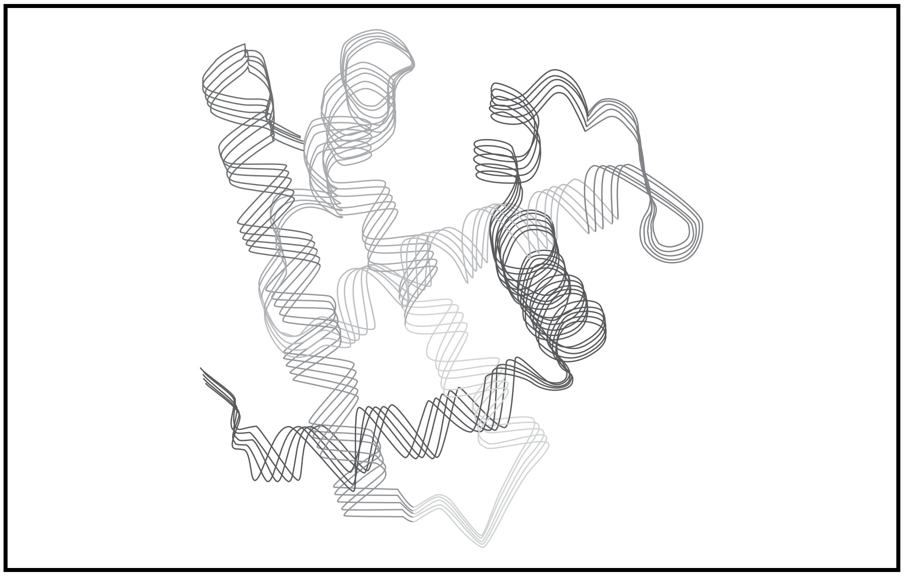

Figure 1. This structure of myoglobin illustrates a typical tertiary structure.

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Testosterone

androgen: group of steroids that act as male sex hormones

estrogen: female sex hormone

synthesis: combination of starting materials to form a desired product

Testosterone is a male sex hormone, one of a class of compounds known as **androgens**. Included in this group are testosterone, dihydrotestosterone, and androstenedione. Androgens are synthesized from cholesterol and are considered steroid hormones, a category of hormones that includes female sex hormones such as **estrogen**. The isolation and **synthesis** of testosterone were reported in 1935. Chemists Adolf Butenandt and Leopold Ruzicka later received the Nobel Prize in chemistry (in 1939) for this work and related discoveries.

basal metabolism: the process by which energy to carry out involuntary, life-sustaining processes is generated.

Testosterone (which is also present in small amounts in females) stimulates the growth of the male reproductive organs and promotes the development of the male secondary sex characteristics. It also affects body hair distribution, baldness, voice, and skin thickness and promotes each of the following: the formation of spermatozoa, protein formation, muscle development, bone growth, the retention of calcium, the rate of **basal metabolism**, and the number of red blood cells in the body.

excrete: to eliminate or discharge from a living entity

In males testosterone is manufactured and secreted overwhelmingly by the testes. After secretion, 97 percent of testosterone is bound by protein carriers in blood and circulates in the body for thirty to sixty minutes. At this point, it has either been absorbed by various tissues or degraded to inactive molecules. Much of the testosterone absorbed by tissues is reduced to dihydrotestosterone, a step that is essential for the actualization of some of testosterone's effects. Testosterone not absorbed by tissues will be degraded by the liver, and the products of this degradation will be **excreted** from the body. SEE ALSO Estrogen; Steroids.

Matthew A. Fisher

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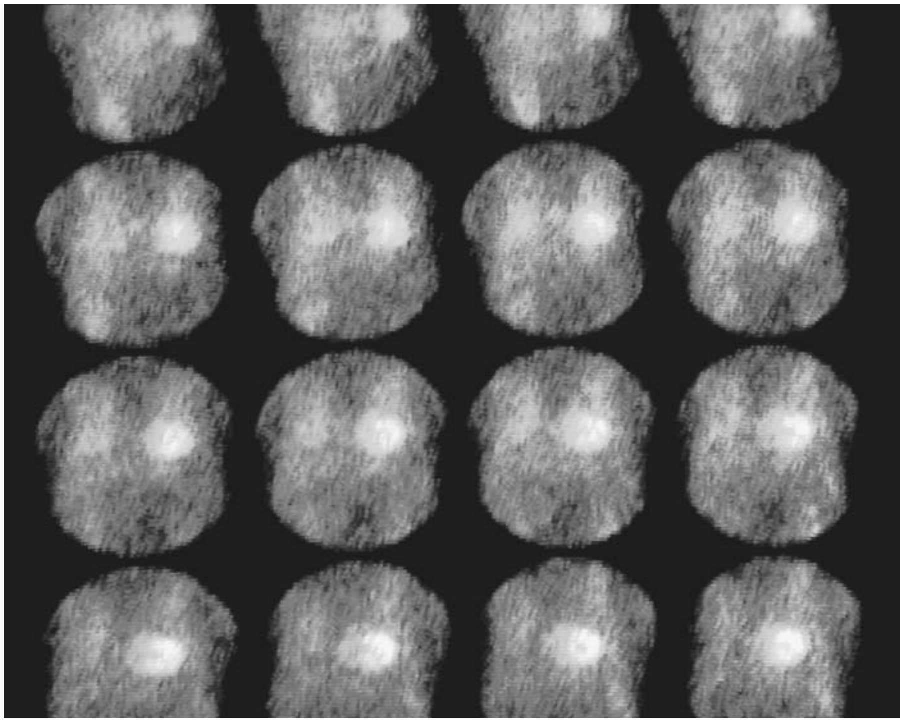
Thallium

81
Tl
THALLIUM
204.383

MELTING POINT: **302°C**
BOILING POINT: **1,457°C**
DENSITY: **11.8 g/cm^3**
MOST COMMON IONS: **Tl$^+$, Tl^{3+}**

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

Thallium was discovered in 1861 by the British chemist Sir William Crookes. While attempting a **spectroscopic** analysis of materials that contained tellurium, Crookes observed a previously unknown bright green line



The soft metal thallium is used in heart scans to evaluate the blood supply to the heart.

on his spectroscope (a machine that identifies the kinds of light emitted by elements at high temperatures). The name thallium comes from the Greek word *Thallos*, meaning "green twig," and was chosen by Crookes because the **spectral line** he had observed reminded him of a fresh green shoot.

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

The abundance of thallium in Earth's crust is estimated to be between 0.1 and 1 mg/kg (ppm). It is widely dispersed and is often associated with potassium minerals. Small deposits of the thallium-bearing minerals such as lorandite and the aptly named crookesite exist in Greece and Sweden, respectively.

Thallium **metal** is so soft that it can easily be cut with a knife. It has a metallic luster that slowly tarnishes upon exposure to air to give the metal a bluish-gray appearance (caused by the formation of Tl_2O_3). The thin layers of surface oxide prevent further **oxidation**. However, in moist air or water, the soluble hydroxide TlOH is formed. Thallium can exist in two oxidation states, (I) and (III). When heated in air, the metal oxidizes to Tl_2O. Thallium reacts vigorously with the **halogens**, forming dihalides of composition $2TlX_3$ where X = fluorine, chlorine, or bromine. Thallium is rapidly dissolved in nitric acid but rendered passive in sulfuric and hydrochloric acids due to the formation of insoluble Tl(I) salts.

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)

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

In biological systems, thallium is nonessential, (i.e., not required for organisms to complete their life cycles) and toxic at high concentrations. Thallium(I) mimics potassium. In humans it affects potassium-activated enzymes in the brain, muscles, and skin. Symptoms of thallium poisoning can easily be attributed to other causes, which in the past has made this element popular for homicides!

Currently, thallium is used in some electronic devices, in low melting point glass, and in the creation of low melting point **alloys**. SEE ALSO HALOGENS; POTASSIUM.

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

Brett Robinson

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Theoretical Chemistry

Theoretical chemistry is the discipline that uses quantum mechanics, classical mechanics, and statistical mechanics to explain the structures and dynamics of chemical systems and to correlate, understand, and predict their thermodynamic and kinetic properties. Modern theoretical chemistry may be roughly divided into the study of chemical structure and the study of chemical dynamics. The former includes studies of: (1) electronic structure, potential energy surfaces, and force fields; (2) vibrational-rotational motion; and (3) **equilibrium** properties of condensed-phase systems and macromolecules. Chemical dynamics includes: (1) bimolecular kinetics and the collision theory of reactions and energy transfer; (2) unimolecular rate theory and metastable states; and (3) condensed-phase and macromolecular aspects of dynamics.

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

A critical issue crossing all boundaries is the interaction of matter and radiation. Spectroscope experiments are used as both structural and dynamic probes and to initiate chemical processes (as in photochemistry and laser-induced chemistry), and such experiments must be understood theoretically. There are also many subfields of theoretical chemistry—for example, biomedical structure-activity relationships, the molecular theory of nuclear magnetic resonance spectra, and electron-molecule scattering—that fit into two or more of the areas listed.

Another source of overlap among the categories is that some of the techniques of theoretical chemistry are used in more than one area. For example, statistical mechanics includes the theory and the set of techniques used to relate **macroscopic phenomena** to properties at the atomic level, and it is used in all six subfields listed. Furthermore, the techniques of **quantum mechanics** and classical-mechanical approximations to quantum mechanics are used profitably in all six subfields as well. Condensed-phase phenomena are often treated with gas-phase theories in instances in which the effects of liquid-phase solvent or solid-state **lattice** are not expected to dominate. There are many specialized theories, models, and approximations as well.

macroscopic phenomena: events observed with human vision unassisted by instrumentation

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

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

Because quantum and statistical mechanics are also parts of physics, theoretical chemistry is sometimes considered a part of chemical physics. There is no clear border between theoretical physical chemistry and theoretical chemical physics.

Three Modes of Science

Modern science is sometimes said to proceed by three modes—experiment, theory, and computation. This same division may be applied to chemistry. From this point of view, theoretical chemistry is based on analytical theory, whereas computational chemistry is concerned with predicting the properties of a complex system in terms of the laws of quantum mechanics (or classical approximations to quantum mechanics, in the domains in which such classical approximations are valid that govern the system's constituent atoms or its constituent nuclei and electrons, without using intermediate levels of analytical chemical theory. Thus, in principle, computational chemistry assumes only such basic laws as the Schrödinger equation, Newton's laws of motion, and the Boltzmann distribution of energy states. In practice, though, computational chemistry is a subfield of theoretical chemistry, and predictions based on approximate theories, such as the dielectric continuum model of solvents, often require considerable computer programming and number crunching. The number of subfields of chemistry in which significant progress can be made without large-scale computer calculations is dwindling to zero. In fact, computational advances and theoretical understanding are becoming more and more closely linked as the field progresses. Computational chemistry is sometimes called molecular modeling or molecular simulation.

Electronic Structure

Perhaps the single most important concept in theoretical chemistry is the separation of electronic and nuclear motions, often called the Born-Oppenheimer approximation, after the seminal work of Max Born and Robert Oppenheimer (1927), although the basic idea must also be credited to Walter Heitler, Fritz London, Friedrich Hund, and John Slater. The critical facts that form a basis for this approximation are that electrons are coupled to nuclei by Coulomb forces, but electrons are much lighter—by a factor of 1,800 to 500,000—and thus, under most circumstances, they may be considered to adjust instantaneously to nuclear motion. Technically we would describe the consequence of this large mass ratio by saying that a chemical system is usually electronically adiabatic. When electronic adiabaticity does hold, the treatment of a chemical system is greatly simplified. For example, the H2 molecule is reduced from a four-body problem to a pair of two-body problems: one, called the electronic structure problem, considers the motion of two electrons moving in the field of fixed nuclei; and another, called the vibration-rotation problem or the dynamics problem, treats the two nuclei as moving under the influence of a force field set up by the electronic structure. In general, because the energy of the electronic subsystem depends on the nuclear coordinates, the electronic structure problem provides an effective potential energy function for nuclear motion. This is also called the potential energy hypersurface. The atomic force field (i.e., the set of all the forces between the atoms) is the gradient of this potential energy function.

Thus, when the Born-Oppenheimer approximation is valid and electronic motion is adiabatic, the end result of electronic structure theory is a potential energy function or atomic force field that provides a starting point for treating vibrations, equilibrium properties of materials, and dynamics. Robert Mulliken, Road Hoffman, Kenichi Fukui, John Pople, and Walter Kohn won Nobel Prizes in chemistry for their studies of electronic structure, including molecular orbital theory. Some important problem areas in which the Born-Oppenheimer separation breaks down are photochemical reactions involving visible and **ultraviolet radiation** and electrical conductivity. Even for such cases, though, it provides a starting point for more complete treatments of electronic-nuclear coupling.

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

Dynamics

In the subfield of theoretical dynamics, the most important unifying concept is transition state theory, which was developed by Henry Eyring, Eugene Wigner, M. G. Evans, and Michael Polanyi. A transition state is a fleeting intermediate state (having a lifetime on the order of 10 femtoseconds) that represents the hardest-to-achieve configuration of a molecular system in the process of transforming itself from reactants to products. A transition state is sometimes called an activated complex or a dynamical bottleneck. In the language of quantum mechanics, it is a set of resonances or metastable states, and in the language of classical mechanics, it is a hypersurface in phase space. Transition states are often studied by semiclassical methods as well; these methods represent a hybrid of quantum mechanical and classical equations. Transition state theory assumes that a good first approximation to the rate of reaction is the rate of accessing the transition state. Transition state theory is not useful for all dynamical processes, and in a more general context a variety of simulation techniques (often called molecular dynamics) are used to explain observable dynamics in terms of atomic motions.

Predictive Power

In the early days of theoretical chemistry, the field served mainly as a tool for understanding and correlating data. Now, however, owing to advances in computational science, theory and computation can often provide reliable predictions of unmeasured properties and rates. In other cases, where measurements do exist, theoretical results are sometimes more accurate than measured ones. Examples are the properties of simple molecules and reactions such as $D + H_2 \rightarrow HD + H$, or the heats of formation of reactive species. Computational chemistry often provides other advantages over experimentation. For example, it provides a more detailed view of phenomena such as the structure of transition states or a faster way to screen possibilities. An example of the latter is provided in the field of drug design, in which thousands of candidate molecules may be screened for their likely efficiency or bioavailability by approximate calculations—for example, of the electronic structure or free energy of desolvation—and, relying on the results of these calculations, candidates may be prioritized for **synthesis** and testing in laboratory studies. In conclusion, theoretical chemistry, by combining tools of quantum mechanics, classical mechanics, and statistical mechanics, allows chemists to predict materials' properties and rates of chemical processes, even in many cases in which they have not yet been measured or even observed in the laboratory; whereas for processes that have been observed, it provides a deeper level of understanding and explanations of trends in the data. SEE ALSO COMPUTATIONAL CHEMISTRY; MOLECULAR MODELING; QUANTUM CHEMISTRY.

synthesis: combination of starting materials to form a desired product

Donald G. Truhlar

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Thermochemistry

Thermochemistry is the study of the heat released or absorbed as a result of chemical reactions. It is a branch of thermodynamics and is utilized by a wide range of scientists and engineers. For example, biochemists use thermochemistry to understand bioenergetics, whereas chemical engineers apply thermochemistry to design manufacturing plants. Chemical reactions involve the conversion of a set of substances collectively referred to as "reactants" to a set of substances collectively referred to as "products." In the following balanced chemical reaction the reactants are gaseous methane, CH_4(g), and gaseous molecular oxygen, O_2(g), and the products are gaseous carbon dioxide, CO_2(g), and liquid water H_2O(l):

$$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(l) \tag{1}$$

Reactions in which a fuel combines with oxygen to produce water and carbon dioxide are called **combustion** reactions. Because natural gas consists primarily of methane, it is expected that reaction (1) will liberate heat. Reactions that liberate heat are termed exothermic reactions, and reactions that absorb heat are termed endothermic reactions.

combustion: burning, the reaction with oxygen

The heat associated with a chemical reaction depends on the pressure and temperature at which the reaction is carried out. All thermochemical data presented here are for reactions carried out under standard conditions, which are a temperature of 298 K (24.85°C) and an applied pressure of one **bar**. The quantity of heat released in a reaction depends on the amount of material undergoing reaction. The chemical formulas that appear in a reaction each represent 1 mole (see article on "Mole Concept") of material; for example, the symbol CH_4 stands for 1 mole of methane having a mass of 16 grams (0.56 ounces), and the 2 O_2(g) tells us that 2 moles of oxygen are required. Thermochemistry also depends on the physical state of the reactants and products. For example, the heat liberated in equation (1) is 890

bar: unit of pressure equal to one million dynes per square centimeter

phase: homogeneous state of matter consisting of gases, liquids, or solids

kilojoules (kJ); if, however, water in the gas **phase** is formed, $H_2O(g)$, the heat released is only 802 kJ. Reversing a reaction like (l), which liberates heat, yields a reaction wherein heat must be supplied for the reaction to occur. The following reaction absorbs 890 kJ.

$$CO_2(g) + 2\ H_2O(l) \rightarrow CH_4(g) + 2\ O_2(g) \tag{2}$$

Energy and Enthalpy

Thermochemical changes are often discussed in terms of the "system" and the "surroundings." The system is regarded as the reaction products and reactants, whereas the surroundings consist of everything else in the universe. A boundary separates the system from the surroundings. The first law of thermodynamics relates the energy change belonging to a system to the amount of work and heat crossing the boundary. A statement of the first law applied to chemical reactions in which only heat and work cross the boundary is given by the expression:

$$U_{\text{products}} - U_{\text{reactants}} = \Delta U = q + w \tag{3}$$

Here U_{products} represents the energy of the products and $U_{\text{reactants}}$ represents the energy of the reactants. The heat associated with the reaction is given as q, and w represents work done during the transformation of reactants to products. If the volume of the system changes during the reaction and the applied pressure remains constant, the work carried out is termed pressure-volume work. For example, reaction (2) converts one mole of gas and two moles of liquid to a total of three moles of gas. The volume of the system increases during the reaction because, under standard conditions, a mole of gas occupies more volume than a mole of liquid. The work of expanding a system against atmospheric pressure is experienced when one inflates a balloon, and this work can be shown to be equal to $-P\Delta V$. Here P represents the atmospheric pressure and ΔV represents the change in volume of the system.

The first law of thermodynamics also states that U is a state function. State functions are very important in thermodynamics; they depend only on the present state of a system and not on its past history. Neither q nor w are state functions. An understanding of the concept of state function is furthered by considering the example of one's taking a trip from San Diego, California, to Denver, Colorado. The change in altitude that one experiences during this trip does not depend on the route taken and, thus, is similar to a state function. In comparison, the distance traveled between the two cities does depend on the route one follows; similarly, q and w are path-dependent quantities.

If a process such as a chemical reaction is carried out at a constant pressure in a way that involves only pressure-volume work, then $-P\Delta V$ can be substituted for the work term in equation (3). Thus, we have:

$$\Delta U + P\Delta V = q_p \tag{4}$$

The symbol q_p represents the heat accompanying a chemical change carried out at constant pressure; in our previous example this would be equivalent to our specifying the exact route of travel between the two cities. The **enthalpy** of a system H is related to the energy of a system by the expression:

enthalpy: the sum of the energy in a system added to the product of its volume and pressure

$$H = U + PV \tag{5}$$

For a process or reaction carried out at constant pressure:

$$\Delta H = \Delta U + P\Delta V = q_p \tag{6}$$

Enthalpy, like energy, is a state function. Thus, equation (6) shows that, for a reaction carried out at constant pressure, q_p depends only on the reactants consumed and the products formed. The enthalpy change associated with a reaction carried out under standard conditions is termed the heat of reaction and is given the symbol ΔH^0, with the superscript denoting standard conditions. Endothermic reactions have a positive ΔH^0 whereas exothermic reactions have a negative ΔH^0. The change in enthalpy accompanying the conversion of reactants to products in a chemical reaction determines the amount of heat liberated or absorbed by the reaction. For a reaction carried out at constant pressure the enthalpy change depends only on the reactants and products.

Hess's Law

Because enthalpy is a state function, the heat associated with a reaction does not depend on whether the reaction proceeds from reactants to products in a series of steps or in a single step. This is the basis for Hess's law, which states that if two reactions are combined to yield a third reaction, the sum of the ΔH^0s for the first two reactions is equal to the ΔH^0 for the third. For example, consider the conversion of gaseous methane to liquid methanol:

$$CH_4(g) + 1/2\ O_2(g) \rightarrow CH_3OH\ (l) \tag{7}$$

and the subsequent combustion reaction:

$$CH_3OH(l) + 3/2\ O_2(g) \rightarrow 2\ H_2O(l) + CO_2(g) \tag{8}$$

Combining reactions (7) and (8) by adding them together gives reaction (1). Thus, the ΔH^0 for combined reactions (7) and (8) must equal −890kJ. If the ΔH^0 for reaction (8) is known to be −681 kJ, then the ΔH^0 for reaction (7) can be calculated by Hess's law to equal −209 kJ. Born-Haber cycles represent an application of Hess's law to reactions associated with the formation of salts, such as potassium chloride. Born-Haber cycles can be used to determine the enthalpy change accompanying the breakup of the potassium chloride **lattice** into isolated potassium and chlorine ions. SEE ALSO Energy; Heat; Physical Chemistry; Temperature; Thermodynamics.

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

Michael Eastman

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Thermodynamics

Thermodynamics is the science of heat and temperature and, in particular, of the laws governing the conversion of thermal energy into mechanical, electrical, or other forms of energy. It is a central branch of science that has important applications in chemistry, physics, biology, and engineering.

Thermodynamics is a logical discipline that organizes the information obtained from experiments performed on systems and enables us to draw conclusions, without further experimentation, about other properties of the system. It allows us to predict whether a reaction will proceed and what the maximum yield might be.

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

Thermodynamics is a macroscopic science that deals with such properties as pressure, temperature, and volume. Unlike **quantum mechanics**, thermodynamics is not based on a specific model, and therefore it is unaffected by our changing concepts of atoms and molecules. By the same token, equations derived from thermodynamics do not provide us with molecular interpretations of complex phenomena. Furthermore, thermodynamics tells us nothing about the *rate* of a process except its likelihood.

energy: the capacity to do work

entropy: measure of the amount of energy unavailable for work in a closed system

Applications of thermodynamics are based on three fundamental laws that deal with **energy** and **entropy** changes. The laws of thermodynamics cannot be derived; their validity is based on the fact that they predict changes that are consistent with experimental observations.

The first law of thermodynamics is based on the law of conservation of energy, which states that energy can neither be created nor destroyed; therefore, the total energy of the universe is constant. It is convenient for scientists to divide the universe into two parts: the system (the part of the universe that is under study—for example, a beaker of solution) and the surroundings (the rest of the universe). For any process, then, the change in the energy of the universe is zero. Chemists are usually interested only in what happens to the system. Consequently, for a given process the first law can be expressed as

$$\Delta U = q + w \tag{1}$$

where ΔU is the change in the internal energy of the system, q is the heat exchange between the system and the surroundings, and w is the work done by the system or performed on the system by the surroundings. The first law is useful in studying the energetics of physical processes, such as the melting or boiling of a substance, and chemical reactions—for example, **combustion**. The heat change occurring as part of a process is measured with a calorimeter. For a constant-volume process, the heat change is equated to the change in the internal energy ΔU of the system; for a constant-pressure process, which is more common, the heat change is equated to the change in the enthalpy ΔH of the system. Enthalpy H is a thermodynamic function closely related to the internal energy of the system, and is defined as

combustion: burning, the reaction with oxygen

$$H = U + PV \tag{2}$$

where P and V are the pressure and volume of the system, respectively.

The first law of thermodynamics deals only with energy changes and cannot predict the direction of a process. It asks, for example: Under a given set of conditions of pressure, temperature, and concentration, will a specific reaction occur? To answer the question we need a new thermodynamic function called entropy S. To define entropy, we need to use a quantum mechanical concept. The entropy of a system is related to the distribution of energy among the available molecular energy levels at a given temperature.

The greater the number of energy levels that have significant occupation, the greater the entropy.

The second law of thermodynamics states that the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process. The mathematical statement of the second law of thermodynamics is given by

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \tag{3}$$

where the subscripts denote the universe, the system, and the surroundings, respectively. The greater than portion of the "greater than or equal to" sign corresponds to a spontaneous process, and the equal portion corresponds to a system at equilibrium. Because processes in the real world are spontaneous, the entropy of the universe therefore constantly increases with time.

As is not the case with energy and **enthalpy**, it is possible to determine the absolute value of entropy of a system. To measure the entropy of a substance at room temperature, it is necessary to add up entropy from the absolute zero up to 25°C (77°F). However, the absolute zero is unattainable in practice. This dilemma is resolved by applying the third law of thermodynamics, which states that the entropy of a pure, perfect crystalline substance is zero at the absolute zero of temperature. The increase in entropy from the lowest reachable temperature upward can then be determined from heat capacity measurements and enthalpy changes due to phase transitions.

enthalpy: the sum of the energy in a system added to the product of its volume and pressure

Because it is inconvenient to use the change in entropy of the universe to determine the direction of a reaction, an additional thermodynamic function, called the Gibbs free energy (G), is introduced to help chemists to focus only on the system. The Gibbs free energy of a system is defined as $G = H - TS$, where T is the absolute temperature. At constant temperature and pressure, ΔG is negative for a spontaneous process, is positive for an unfavorable process, and equals zero for a system at equilibrium. The change in Gibbs free energy can be related to the changes in enthalpy and entropy of a reaction, and also to the equilibrium constant of the reaction, according to the equation $\Delta G° = -RT \ln K$, where $\Delta G°$ is the change in Gibbs free energy under standard-state conditions (1 bar), R is the gas constant, and K is the equilibrium constant.

Many chemical reactions can be classified as either **kinetically** controlled or thermodynamically controlled. In a kinetically controlled process the products are thermodynamically more stable than the reactants, hence the reaction is favorable. However, the rate of reaction is often very slow due to a high activation energy barrier. The conversion of the less stable **allotropic** form of carbon, diamond, to the more stable graphite is an example: The process can take millions of years to complete. In a thermodynamically controlled reaction the reactants may have a number of kinetically accessible routes to follow to form different products, but what is eventually formed is governed by relative thermodynamic stability. In protein folding, for example, a denatured protein may have many possibilities of **intermediate** conformation; however, the conformation it finally assumes, which corresponds to the physiologically functioning protein, is the most stable state thermodynamically. SEE ALSO CHEMISTRY AND ENERGY; ENERGY; HEAT; KINETICS; PHYSICAL CHEMISTRY; TEMPERATURE.

Raymond Chang

allotrope: a different physical form of an element in the same state of matter

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

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Thiamin

B **vitamins** are complex, water-soluble organic chemicals, often containing heterocyclic ring systems (containing one or more atoms other than carbon atoms); they cannot be synthesized by humans and are, therefore, required nutrients. Each of these vitamins is converted by the body into a coenzyme. Coenzymes are cofactors essential to the **catalytic** activity of enzymes.

Thiamin is also known as vitamin B_1. In the body it is converted to thiamin pyrophosphate (TPP), an essential coenzyme serving enzymes involved in the breakdown of nutrient molecules for energy. Thiamin deficiency in its severest form causes beriberi.

Thiamin is converted to TPP via the transfer of a pyrophosphate group to thiamin from **adenosine triphosphate (ATP)**.

In animals TPP-dependent decarboxylation reactions are essential to the production of energy needed for cell **metabolism**. In these reactions α-ketoacids are converted to acyl CoA molecules and carbon dioxide. The reactions (e.g., the conversion of **pyruvate** to acetyl CoA) are an important part of the breakdown of carbohydrates, and of the conversion of several classes of molecules (carbohydrates, fats, and proteins) to energy, carbon dioxide, and water in the citric acid cycle. In other organisms, in addition to its participation in the above reactions, TPP is a required coenzyme in alcohol fermentation, in the carbon fixation reactions of **photosynthesis**, and in the **biosynthesis** of the amino acids leucine and valine.

Major food sources of thiamin are fortified breads, cereals, pasta, whole grains (especially wheat germ), lean meats (especially pork and liver), fish, peanuts, dried beans, peas, and soybeans. Fruits and vegetables are not high in thiamin but are a significant source of thiamin if they are consumed in large enough amounts. The daily value (DV) of thiamin for adults is 1.5 milligrams (5.3×10^{-5} ounces). Thiamin deficiency virtually does not occur in North America. Because thiamin is water-soluble and easily removed from the body there is no known toxicity.

Beriberi has been found in people who eat polished rice (with husks discarded) and few other foods, as thiamin is in the husks of grains. Beriberi is associated with damage to the nervous system, brain, heart, and blood vessels. It is fatal if not treated with adequate amounts of thiamin. Lesser deficiencies of thiamin lead to weakness and fatigue. These lesser deficiencies respond rapidly to thiamin unless they are complicated by another condition, for example, alcoholism. SEE ALSO COENZYME.

Vivienne A. Whitworth

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

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

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

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)

pyruvate: anion of pyruvic acid produced by the reaction of oxygen with lactic acid after strenuous exercise

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

biosynthesis: formation of a chemical substance by a living organism

CASIMIR FUNK (1884–1967)

Beriberi, a fatal disease, was prevalent at the turn of the nineteenth century among groups who ate large quantities of polished rice. Casimir Funk correctly theorized that the discarded polishings contained some nutrient for disease prevention. Funk isolated this item and called it a "vitamine," combining *vite,* meaning life, and amine.

—Valerie Borek

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Thomson, Joseph John

ENGLISH PHYSICIST
1856–1940

Joseph John Thomson, always known as "J. J.," was born in Manchester, England, on December 18, 1856. His fame derives primarily from his discovery of the electron in 1897. He studied physics and mathematics, first in Manchester, and in 1876 went to Trinity College, Cambridge University, and never left. He graduated in 1880 and in 1884 succeeded Lord Rayleigh as professor of physics and director of the Cavendish Laboratory. (When he retired from Cavendish in 1919 he passed the baton to Ernest Rutherford). Thomson made Cambridge a world center for atomic physics. He won the Nobel Prize for physics in 1906 for his work on the electron, and seven of his research associates went on to win Nobel Prizes. The electron could almost be said to have been a family heirloom, as his son, George Paget Thomson, won the Nobel Prize for physics (in 1937) for showing the wave nature of the electron.

His early work in electromagnetism led him to say, in 1893: "There is no other branch of physics which affords us so promising an opportunity of penetrating the secret of electricity." He turned his attention to cathode rays, and his subsequent investigations of these rays led him to the idea that they consisted of bodies smaller than atoms. Thomson's main contribution to science was the clear identification of the electron and its characterization as an elementary, subatomic particle in 1897. He showed that cathode rays were deflected by both magnetic and electric fields, and he was able to measure a cathode ray's charge/mass (*e/m*) ratio. Figure 1 is a schematic of diagram of his apparatus, showing how a beam of electrons can be subjected to opposing electric and magnetic fields, which can be adjusted until their effects balance. This enabled him to estimate the mass of the electron as 1/1,837 of a hydrogen atom. The electron was the first subatomic particle to be discovered, and he made the inspired guess that it was a universal constituent of matter. He said: " . . . [W]e have in the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much

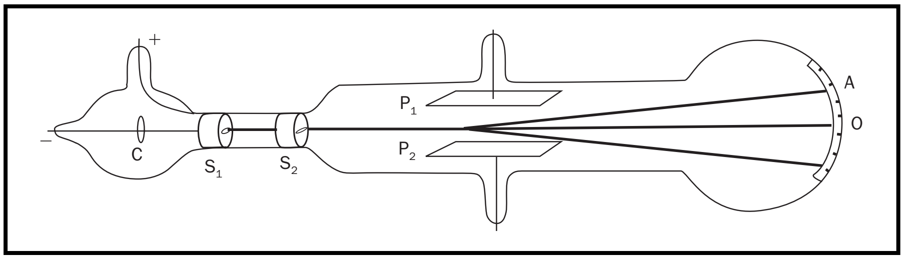
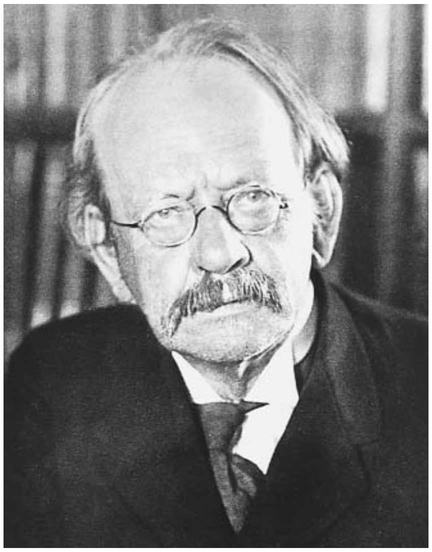


Figure 1. Basic features of Thomson's apparatus.

further than in the ordinary gaseous state: a state in which all matter . . . is of one and the same kind; this matter being the substance from which all the chemical elements are built up." He announced his discovery in the course of a public lecture at the Royal Institution in London, on April 30, 1897, in which he said: "Could anything at first sight seem more impractical than a body which is so small that its mass is an insignificant fraction of the mass of an atom of hydrogen?" Thomson referred to electrons as "corpuscles" (even in his 1906 Nobel lecture).



English physicist Sir Joseph John Thomson, recipient of the 1906 Nobel Prize in physics, "in recognition of the great merits of his theoretical and experimental investigations on the conduction of electricity by gases."

nuclear: having to do with the nucleus of an atom

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

Thomson devised the famous plum pudding model of the atom, in which electrons were compared to negative plums embedded in a positively charged pudding. The idea was wrong, and his successor at Cambridge, Ernest Rutherford, was soon to develop the **nuclear** model of the atom.

Thomson investigated positive rays, which consist of ionized atoms, beginning in 1906. He was able to use a combination of electric and magnetic fields to separate different charged atoms of elements on the basis of their charge/mass ratios. He was the first to show that neon contained two atoms of slightly different masses, in a paper published in 1913. As part of the conclusion of the paper he wrote: "There can, therefore, I think, be little doubt that what has been called neon is not a simple gas but a mixture of two gases, one of which has an atomic weight about 20 and the other about 22. The parabola due to the heavier gas is always much fainter than that due to the lighter, so that probably the heavier gas forms only a small percentage of the mixture." The two forms of neon were called **isotopes** by Frederick Soddy. One of Thomson's students, Frederick Aston, developed Thomson's idea of multiple species of an element, and in 1919 Aston produced the first mass spectrograph (an instrument that determined isotopic ratios), ancestor of today's mass spectrometer.

Thomson was a great advocate of pure research, in contrast to applied research, declaring: "[R]esearch in applied science leads to reforms, research in pure science leads to revolutions, and revolutions, whether political or industrial, are exceedingly profitable things if you are on the winning side." Thomson was knighted in 1908 and received many awards and honors. He died during the early part of World War II, on August 30, 1940, and is buried in Westminster Abbey near Sir Isaac Newton, in recognition of his great contributions to science. SEE ALSO MAGNETISM; SPECTROSCOPY.

Peter E. Childs

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Thorium

MELTING POINT: 1,750°C
BOILING POINT: 4,820°C
DENSITY: 11.724 g/cm^{-3}
MOST COMMON IONS: Th^{4+}

90
Th
THORIUM
232.0381

Thorium is a radioactive chemical element that belongs to the actinide series. Its ground state electronic configuration is $[Rn]5f^0 6d^2 7s^2$. Thorium was discovered by Jöns Jacob Berzelius in 1828. Its name is derived from "Thor," the god of war in the Scandinavian mythology. Thorium chemistry is dominated by the tetravalent thorium ion (Th^{4+}). Its ionic radius is very similar to that of the trivalent cerium ion (Ce^{3+}). For that reason it is no surprise that thorium occurs in nature together with the **rare earth elements**. Thorium is recovered commercially from the rare earth ore monazite (mainly $CePO_4$), which contains up to 9 percent ThO_2. Other thorium-containing minerals are thorite and thorianite. The most abundant **isotope** is ^{232}Th, with a half-life of 1.4×10^{10} years. None of the twenty-five known isotopes of thorium (with atomic masses ranging between 212 and 236) is stable.

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

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

Pure thorium is a silvery-white **metal** (melting point 1,750°C) that tarnishes upon exposure to air. Its density is 11.724 g/cm^{-3} at 25°C (77°F), similar to that of lead. The best-known application of thorium is its use in incandescent mantles for gas lamps. These mantles consist of a metal oxide skeleton (99% ThO_2 and 1% CeO_2). Thorium(IV) oxide is used by chemists

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

Thorium is used in incandescent mantles for gas lamps.

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

nuclear: having to do with the nucleus of an atom

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

as a **catalyst** in different organic reactions, and in the conversion of ammonia to nitric acid. Thorium is about three times as abundant as uranium, and therefore it may become an important **nuclear** fuel in the future. Because one of the disintegration products of thorium is the radioactive **noble gas** radon (^{220}Rn), good ventilation of areas and places where thorium is stored or handled is necessary. SEE ALSO Actinium; Berkelium; Einsteinium; Fermium; Lawrencium; Mendelevium; Neptunium; Nobelium; Plutonium; Protactinium; Rutherfordium; Uranium.

Koen Binnemans

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69
Tm
THULIUM
168.93421

Thulium

MELTING POINT: 1,545°C
BOILING POINT: 1,950°C
DENSITY: 9.32 g/cm^3
MOST COMMON ION: Tm^{2+}, Tm^{3+}

Thulium is a silver-grey metal with a bright luster. Swedish chemist Per Theodor Cleve discovered the metal in 1879 while processing the ore erbia. One of the materials Cleve extracted from the ore was a green substance he named “thulia”—a thulium oxide. The element’s name is derived from an ancient name for northern Europe, Thule.

Thulium is the least abundant of the naturally occurring rare earth elements, although it is believed to have a natural abundance similar to gold,

An army medic takes an x ray of a simulated injury during a field test of an atom-powered portable x-ray unit. Portable x-ray units are powered by thulium, obviating the need for electricity.

silver, and cadmium. Its abundance in the earth's crust is approximately 0.52 milligrams per kilogram. Thulium is commercially extracted from monazite (which is composed of up to 0.007 percent thulium) using ion exchange and solvent extraction techniques. It is also found in the minerals gadolinite, euxenite, and xenotime.

The most common isotope of thulium is ^{169}Tm, which has a natural abundance of 100 percent and is the only stable isotope. Other isotopes range from ^{145}Tm to ^{179}Tm and have half-lives ranging from 0.36 milliseconds (^{147}Tm) to 1.92 years (^{171}Tm). Examples of thulium compounds include thulium iodide (TmI_3), thulium fluoride (TmF_3), and thulium oxide (Tm_2O_3).

Thulium metal is soft, ductile, and malleable and can be cut with a knife. It tarnishes when in contact with air and reacts with water. Thulium has very few commercial uses. Radioactive thulium can be utilized as a power source for portable x-ray machines and is produced by irradiating the element in a nuclear reactor. Thulium may also be utilized to make magnetic ceramic materials found in microwave equipment. SEE ALSO CLEVE, PER THEODORE.

Stephanie Dionne Sherk

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Thymine *See Nucleotide.*

Tin

MELTING POINT: **231.9°C**
BOILING POINT: **2,270.0°C**
DENSITY: **7.31 g/cm^3**
MOST COMMON IONS: **Sn^{2+}, Sn^{4+}**

50
Sn
TIN
118.71

Tin makes up only about 0.001 percent of the earth's crust, but it was well known in the ancient world. Named after the Etruscan god Tinia, tin has the symbol Sn, which comes from the Latin word for tin, *stannum*, which is related to the word *stagnum* (dripping), because tin melts easily. Tin is primarily obtained from the mineral cassiterite (SnO_2) and is extracted by roasting cassiterite in a furnace with carbon.

Tin is a soft, pliable **metal**, but it is not used as such, because below 13°C, it slowly changes to a different allotype and forms a powder. Steel is plated with tin to make cans for food, and tin is also used in solders. Some tin compounds have been employed as antifouling agents in paint for ships and boats to prevent barnacles. However, even at low concentrations, these compounds are deadly to marine life, especially to oysters. Tin is thought to be an essential element for some living things, and this may also be true for humans.

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

A major use of tin has been as a constituent of **alloys**—such as bronze (tin and copper); pewter (tin and lead); superconducting wire (tin and nio-

alloy: mixture of two or more elements, at least one of which is a metal bium); Babbitt metal (tin, copper, and antimony); Bell metal (tin and copper); and fusible metal (tin, bismuth, and lead).

Stannous fluoride (SnF_2), a compound of tin and fluorine, is used in some toothpastes to decrease the incidence of caries.

George H. Wahl Jr.

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Titanium

22
Ti
TITANIUM
47.88

MELTING POINT: **1,668°C**
BOILING POINT: **3,287°C**
DENSITY: **4.54 g/cm^3**
MOST COMMON IONS: **Ti^{2+}, Ti^{3+}, TiO^{2+}**

Titanium is a strong, lightweight, silver-white **metal**. It was discovered in 1791 by Reverend William Gregor, a British cleric who established its presence in the mineral menachanite. The German chemist Martin Heinrich Klaproth named the element after the Titans, the sons of the earth goddess in Greek mythology. Pure titanium was not isolated until 1910, when American metallurgist Matthew A. Hunter heated titanium (IV) chloride ($TiCl_4$) with sodium at temperatures between 700°C and 800°C.

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

As the ninth most common element in the earth’s crust, titanium occurs at an abundance of 6,600 parts per million (ppm) or 5.63 grams per kilogram. Its chief sources are the minerals ilmenite ($FeTiO_3$), **rutile** (TiO_2), and sphene ($CaTiSiO_5$); ilmenite is the source of approximately 90 percent of titanium produced. Titanium is largely produced in the United States, Canada, Russia, Japan, Kazakhstan, Germany, France, and Spain.

rutile: common name of TiO_2; also a common structural type for compounds with the general composition AB_2

The most common **isotope** of titanium is ^{48}Ti, which has a natural abundance of 73.72 percent. Four other stable isotopes exist: ^{46}Ti (8.25%), ^{47}Ti (7.44%), ^{49}Ti (5.41%), and ^{50}Ti (5.18%). Most titanium is used in its dioxide (TiO_2) or metallic form.

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

Titanium’s physical properties (high melting temperature, resistance to corrosion, strength, light weight) make it an ideal additive to **alloys** used by the aerospace industry in rockets and jet aircraft, for ship components that are exposed to seawater, and for biomedical implants such as artificial joints or pacemakers. Titanium dioxide is utilized as a white pigment in paint, paper, plastics, and cosmetics. It is also used in some sunscreens because of its ability to absorb ultraviolet (UV) light.

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

Stephanie Dionne Sherk

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Todd, Alexander

BRITISH CHEMIST
1907–1997

Alexander R. Todd was born in Glasgow on October 2, 1907. His father was a businessman. Young Todd was educated at the Allan Glen School and Glasgow University. There he earned a B.S. and in 1928 left for the University of Frankfurt-am-Main, where he earned a Ph.D. in 1931 for his work on bile acids with W. Borsche. He returned to England that same year to study with Sir Robert Robinson; it was during this period that he completed very successful work on the colored materials of fruits, the anthocyanins. Todd journeyed home to Scotland in 1934 to join the staff of Edinburgh University. In 1938 he was appointed Sir Samuel Hall Professor of Chemistry and director of the Chemical Laboratories at the University of Manchester, posts he held until 1944. He then accepted a position as professor of organic chemistry at Cambridge University and became a fellow of Christ's College. He was named chancellor of the University of Strathclyde in 1975 and was a visiting professor at Hatfield Polytechnic until 1986.

The anthocyanin dyes that Todd researched while working with Robinson are important substances because they are part of the mechanism for protecting the plants' **DNA** from the deleterious effects of UV radiation during pollination and act as insect attractants during the pollination season. The structure for the red substance of cranberries is given in Figure 1.

While at Manchester, Todd began his work on nucleotides. These compounds are the structural units of the nucleic acids DNA and **RNA**. In 1949, while at Cambridge, he synthesized adenosine triphosphate (ATP; Figure 2) and later that same year flavin **adenine** dinucleotide (FAD). These nucleotides are the molecules that carry and transfer energy in virtually all living organisms. These discoveries are not only important in the elucidation of the energy transfer mechanisms, but they also set a precedent for the **synthesis** of nucleotides and the precursors of DNA and RNA. These accomplishments required the utmost skill in the art of organic synthesis because nucleotides are very difficult substances to prepare and characterize.

Todd also did significant work on the structure and synthesis of **vitamin** B_{12}, vitamin E, and a number of **alkaloids**. The most noteworthy of these contributions was the elucidation of the structure of tetrahydrocannabinol (THC), the active component of marijuana.

Todd was named president of the Royal Academy in 1975. He was also a member of the National Academy of Sciences (USA), the American Academy of Arts and Sciences, and several prestigious European societies. Todd served as the chairman of the British government's advisory committee on scientific policy from 1952 until 1964. He was awarded the Nobel Prize in chemistry in 1957 for his work on nucleotides and nucleotide coenzyme studies. He was knighted in 1954 and died in 1997. SEE ALSO NUCLEOTIDE.

Lawrence H. Brannigan

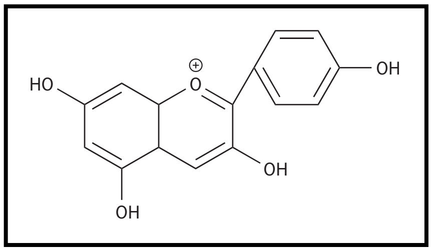

Figure 1. Red form of cranberry anthocyanin.

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

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

synthesis: combination of starting materials to form a desired product

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

alkaloid: alkaline nitrogen-based compound extracted from plants

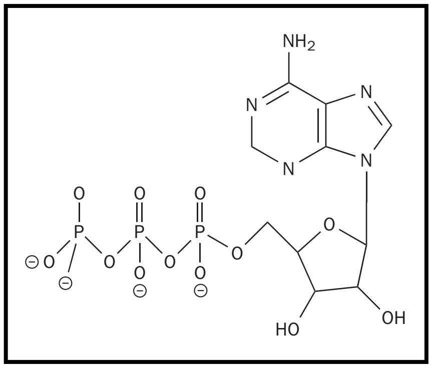

Figure 2. Structure of ATP.

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Toxicity

Toxicity is the capacity of a substance to poison. Swiss physician Paracelsus (1493–1541) defined poison as follows: "What is there that is not a poison? All things are poison and nothing without poison. Solely the dose determines that thing is not a poison." The toxicity of a substance is therefore not an inherent property but the detrimental manifestation of its biochemical effect in a living system. The severity of a substance's toxicity is the function of its interaction with the physiology of a particular organism. For example, chocolate is moderately toxic to canines but minimally to other animals. Ingested in very large quantities, even **vitamins** can exhibit toxicity in humans.

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

The comparison of two substances in terms of their relative toxicity is difficult because every substance has its own mode of action and target organ(s). Hence, the short-term poisoning potential (acute toxicity) of a substance is measured by the amount needed to kill half the population of a test species, called the LD50 (lethal dose for 50 percent). The measurement is expressed as milligrams per kilogram of body weight (mg/kg). For example, administering to mice a substance with an LD50 for mice of 10 mg/kg would kill 50 percent of a population of mice. In environmental studies, the term used to measure toxicity in air or water is LC50 (lethal concentration for 50 percent), defined similarly to LD50 and expressed as parts per million, parts per billion, or milligrams per liter (mg/l).

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)

The route of entry of a toxicant affects its LD50 value. Since the lethality of a substance is related to its ability to block vital cellular functions by interacting with specific biomolecules, the site of exposure, its dissemination speed, and the physiological importance of the target tissue all factor into its toxicity. For example, the common household pesticide dichlorovos has an LD50 for rats of 56 mg/kg if taken orally (through the mouth) and an LD50 of 15 mg/kg if injected intraperitoneally (into the abdominal cavity).

The toxicity of a chemical also varies from one animal to the next. The LD50 for the common insecticide Diazinon is 300 to 400 mg/kg in rats, while in birds it is 2.75 mg/kg. Theobromine, a chemical found in chocolate, is toxic to dogs but not to rodents. Although largely extrapolated from animal tests, a rating system for acute chemical toxicity for humans has been devised and is presented in Table 1.

Chronic or cumulative toxicity is manifested as a result of continuous exposure to a chemical. A common example is the "genotoxicity" of benzene, a chemical present in car exhausts and cigarette smoke. The **metabolism** of benzene in the liver results in the formation of highly reactive free-radicals. These in turn may cause damage to the genetic material of a cell, in some cases leading to cancer.

LD50

LD50 is the amount of a hazardous substance that results in the death of 50 percent of the individuals exposed. LD50 is commonly measured by exposing rats or mice to increasing amounts of the toxic substance until a dosage is reached that kills half the exposed animals within a certain time period (usually fourteen days).

—Dan M. Sullivan

TOXICITY RATING FOR HUMANS (70 KG BODY WEIGHT)

Rating/Class	Dose
6. Super toxic	<5 mg/kg
5. Extremely toxic	5–50 mg/kg
4. Very toxic	50–500 mg/kg
3. Moderately toxic	0.5–5 g/kg
2. Slightly toxic	5–15 g/kg
1. Practically nontoxic	>15 g/kg

SOURCE: Gosselin, et al. (1984). *Clinical Toxicology of Commercial Products.* Baltimore: Williams & Wilkens.

Table 1. Toxicity rating for humans (70 kg [154 lb.] body weight).

Although traditional investigations into the toxicity of chemicals in the natural environment have focused on animals, the toxicity of agrichemical and environmental pollutants to plants (phytotoxicity) has gained interest. Despite being well documented in literature, phytotoxicity is measured in various ways by agronomists and plant scientists; a standard quantification unit is therefore difficult to devise. SEE ALSO VENOM.

Hiranya S. Roychowdhury

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Transactinides

The term "transactinides" is used to refer to all elements beyond the actinides—that is, those elements with atomic numbers larger than 103. Lawrencium, with atomic number 103 and a full inner 5f electron shell, ends the actinide series. According to atomic relativistic calculations, the filling of the 6d electron shell takes place in the first nine of the transactinide elements (those with atomic numbers 104 through 112). They are placed as a 6d transition series under the 5d transition series in the Periodic Table of the chemical elements.✷ As of 2003 the discoveries of elements 104 through 111 had been confirmed, and element 112 was reported but not yet confirmed. The date of discovery and the names and symbols approved for each of these elements by the International Union of Pure and Applied Chemistry (IUPAC) in August 1997 and in August 2003 are given in Table 1, as is the date of discovery of the element that has been reported but not yet named. The naming of element 112 awaits a final IUPAC decision that there has been sufficient confirmation of its discovery to ask the discoverers to propose a name and symbol for consideration.

✷See Periodic Table in the For Your Reference section at the beginning of this volume.

All the known transactinides were first positively identified using physical rather than chemical techniques because of their very short half-lives

TRANSACTINIDE NAMES APPROVED BY IUPAC ON AUGUST 30, 1997, IN GENEVA, SWITZERLAND AND ON AUGUST 16, 2003 IN OTTAWA CANADA

Element	Name	Symbol	Year of Discovery#
104	Rutherfordium	Rf	1969
105	Dubnium (Hahnium)*	Db (Ha)*	1970
106	Seaborgium	Sg	1974
107	Bohrium	Bh	1981
108	Hassium	Hs	1984
109	Meitnerium	Mt	1982
110	Darmstadtium**	Ds**	1995
111***	――――	――	1995
(112)	――――	――	1996

Year of publication of discovery experiment.
* Many publications of chemical studies prior to 1997 use hahnium (Ha) for element 105.
** Name and symbol approved by IUPAC, August 16, 2003, Ottawa, Canada.
*** IUPAC has deemed evidence for discovery of this element sufficient and has asked the discovers to propose a name.

Table 1.

and small production rates. Production rates decrease from a few atoms per minute for element 104 to only a few atoms per week for element 111. Methods other than the classical chemical separation techniques for determining the atomic number (proton number) of a new element had to be developed. The production and study of both the chemical and **nuclear**-decay properties of the transactinides require special facilities and capabilities. These include preparation and handling of radioactive targets, access to an accelerator that can furnish high-intensity beams of the required light-to-heavy ions for irradiating the targets, and a method for rapidly transporting the desired short-lived **isotopes** to a suitable chemical or physical separation system. In the 1960s such facilities were available in Russia at the cyclotron at the Joint Institutes for Nuclear Research in Dubna and in the United States at the Heavy Ion Linear Accelerator (HILAC) at the Lawrence Berkeley Laboratory in California.

nuclear: having to do with the nucleus of an atom

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

From the mid-1960s to the early 1970s, the Russian and U.S. groups reported conflicting claims concerning the discoveries of elements 104 and 105, primarily due to the difficulty in positively determining the atomic number of the short-lived isotopes involved. Different techniques were used by the groups to attempt to provide positive proof of the discoveries. The U.S. group used an alpha-alpha correlation technique to identify the atomic number of alpha-decaying isotopes (alpha-decay is the emission of a $^{4}\text{He}^{2+}$ nucleus) of elements 104 and 105 by observing the time correlations between alpha-particles emitted by the parent element and those of the already known element 102 (nobelium) or 103 (lawrencium) daughter activities. The Russian group relied primarily on the detection of spontaneous **fission** (SF) decay. Spontaneous fission is one of the modes of decay found in elements of higher atomic number than actinium; in this process the nucleus "spontaneously" splits into two large "fission fragments." Half-lives for SF decay range from microseconds to billions of years (e.g., the SF-decay branch in plutonium-244 has a half-life of nearly 100 billion years). Detection of SF fragments is a very sensitive method, but the atomic number and mass of the fissioning nucleus are effectively destroyed in the fission process, so it is extremely difficult to identify the fissioning element with certainty. In the case of element 105, the Dubna group also performed an alpha-alpha correlation experiment, but these experiments were rather

fission: process of splitting an atom into smaller pieces inconclusive and did not agree with later confirmatory experiments. They also measured SF decay that they attributed to element 105 based on its half-life, proposed production reaction based on data from other experiments, and angular distribution of the products of the nuclear reaction. Chemical separations, even if rapid enough, are not definitive without some independent positive determination of atomic number, since the unknown chemistry of a new element cannot be used to prove its atomic number. The U. S. and Russian groups proposed different names for these elements, and the controversy was not resolved until the compromise set of names shown in Table 1 was finally approved by IUPAC in 1997. Element 106 was produced and identified at the SuperHILAC by the Berkeley group in 1974 and confirmed by an independent group in 1994. The name seaborgium (Sg) in honor of Professor Glenn T. Seaborg was then proposed by the discovery group. After initially being rejected because Seaborg was still alive, the name was approved.

In the 1970s the Separator for Heavy Ion Reactions (SHIP) was constructed by a group at the Universal Linear Accelerator (UNILAC) at the Gesellschaft für Schwerionenforschung (GSI) in Darmstadt, Germany. The researchers hoped that SHIP might take them to the long-sought island of SuperHeavy Elements (SHEs) in the predicted region of extra stability around the "magic" numbers of 112 to 114 protons and 184 neutrons. SHIP was designed to separate the "slow" **fusion** products created in the nuclear reactions from the "fast" heavy-ion beams that produced them by using a combination of electric and magnetic fields. The reaction products were then implanted in a detector system some distance away from the target. The time, energy, and position of the implant and all subsequent decays and other information were recorded by a computer system. The original event was then correlated unambiguously with its decay to already known properties of many generations of known daughter isotopes, and its atomic number and mass were unequivocally determined.

fusion: process of combining atomic nuclei

Discovery of elements 107 through 109 was reported by the SHIP group between 1981 and 1984. After some improvements were made in SHIP, elements 110 through 112 were produced and identified in 1995 and 1996. However, the most neutron-rich of the isotopes first reported for elements 110 through 112 contain only 165 neutrons or fewer, far from the predicted SHE region. Their half-lives are milliseconds or shorter, and most scientists do not consider them to be SHEs. Even though the attempt to produce element 113 was unsuccessful, these results gave researchers new hope that the SHEs might yet be reached, sparking a renaissance of interest in their production. Between 2000 and 2002, the production of element 114 with 174 neutrons and a half-life of about 3 seconds and element 116 with 176 neutrons and a half-life of 50 milliseconds was reported by a Dubna/LLNL collaboration using the on-line separator at the Dubna cyclotron. The group used beams of the heaviest stable calcium isotope (mass 48) and either ^{244}Pu or ^{248}Cm targets, to make element 114 or 116, respectively. They have proposed that these should be called SHEs, although they are still far from the 184-neutron shell. The element 112 and 110 daughters resulting from the element 116 and 114 alpha-decay chains were reported to have half-lives on the order of 10 seconds. It is extremely im-

The Stanford Linear Accelerator Center has three giant particle spectrometers, which are used to detect subatomic particles of different energies. This is the largest linear accelerator in the world.

portant to confirm these results, as investigations of their chemical properties could then be considered.

Chemical Studies

A primary goal of the chemical studies of the transactinides is to determine their placement in the Periodic Table by comparing their properties with those of their lighter **homologues** and with theoretical predictions. These studies seek to probe the uppermost region of the Periodic Table, where the influence of relativistic effects on chemical properties should be strongest and where deviations from simple extrapolation of known trends within chemical groups in the Periodic Table have been observed. There are many challenges for chemical studies in addition to those already outlined for physical separation techniques: An isotope with a half-life of at least a second must be known. Its decay characteristics must be well established and must furnish a positive "signature" so that it can be shown that the desired element is actually being studied. Again, the method of measuring time-correlated "mother-daughter" alpha-decay chains is most definitive. Because the production rates are so low, the results of many separate identical experiments must often be combined. Very efficient separation methods must be devised that reach equilibrium rapidly and can be conducted in a length of time that is short compared to the half-life. These separations should give the same results on an "atom-at-a-time" basis as they would for the usual macro-scale laboratory experiments conducted with milligram quantities. Both aqueous- and gas-phase **chromatographic** methods have been shown

homologues: members of a group of organic compounds that have the same functional group and a regular structural pattern so that a member of the group differs from the next member by a fixed number of atoms

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 which the components are absorbed by the stationary phase to meet these criteria. A rapid and efficient method for transporting these atoms from the production site to a suitable chemical separation system is needed. Computer-controlled automated systems have been developed for these studies.

Typically, the isotope with the longest half-life and largest production rate is chosen. This is not necessarily the first isotope discovered. The half-lives of the isotopes used in the first definitive chemical studies of the transactinides were: 75-second ^{261}Rf; 34-second ^{262}Db; 21-second ^{266}Sg; 17-second ^{267}Bh; and approximately 14-second ^{269}Hs. Their well-known alpha-decay properties were used for positive identification. As of 2003, 0.04-second ^{268}Mt was the longest-known isotope of Mt, and studies of its chemical properties awaited discovery of a longer-lived isotope.

From 1969 to 1976 researchers at Dubna reported studies of the volatilities of the halides of elements 104 and 105, suggesting that the halides of these elements behaved similarly to those of their lighter group-4 and group-5 homologues. Because only spontaneous fission was detected, the identity of the species being measured could not be positively attributed to element 104 or 105.

The first study of the solution chemistry of Rf was performed at Berkeley in 1970 and showed that Rf had a stable tetravalent state with properties similar to the group-4 elements Zr and Hf and different from Lr and the other trivalent actinides. This established that Rf should be placed in the Periodic Table as the heaviest member of group 4 and the first member of a new 6d transition series. It also confirmed the 1945 prediction of Seaborg that the actinide series should end with element 103. The first studies of the solution chemistry of element 105, conducted at the 88-Inch Cyclotron at Berkeley, were reported in 1988 and showed that the element behaved similarly to the group-5 elements Nb and Ta in its sorption properties, but differently from the group-4 elements. However, in extractions into certain organic solvents, Db(Ha) and Ta extracted but Nb did not, creating a renaissance of interest in more detailed studies of the behavior of element 105.

Subsequently, extensive studies of both the aqueous- and gas-phase chemistry of elements 104 and 105 were conducted using manual and sophisticated computer-controlled automated systems. Although in general these studies confirmed that the elements' chemical properties are similar to those of the group-4 and group-5 elements, respectively, unexpected deviations from simple extrapolation of known trends within the groups were found. Theoretical investigations based on molecular relativistic calculations can explain these results and provide guidance for experimentalists in designing the sophisticated and resource-intensive experiments required for future experiments. With this guidance and further improvement in experimental techniques, chemical studies were extended to Sg, Bh, and Hs. Aqueous- and gas-phase studies of Sg were conducted between 1995 and 1998 by an international team of researchers working at the UNILAC at GSI. Gas-phase studies of an oxychloride of Bh were reported in 2000, and separation of Hs as a volatile oxide similar to that of osmium tetroxide was reported in 2002. It appears that all of these elements should be placed in the Periodic Table as members of the 6d transition series under groups 4 through 8 of the Periodic Table and that the trends in properties within the groups can be described by relativistic calculations. No investigations of the solution chemistry of Bh and Hs has been conducted as of mid-2003 because the aqueous chemistry and preparation of samples suitable for measuring alpha-particles or fission fragments is too slow. Very fast liquid-liquid extraction systems followed by direct incorporation of the activity in a flowing liquid scintillation detection system have been used for elements 104 and 105 and may prove applicable.

The improvement in experimental techniques for atom-at-a-time studies of elements with both short half-lives and small production rates has permitted chemical studies of both aqueous- and gas-phase chemistry of the transactinides through Sg, and gas-phase studies of Bh and Hs have been conducted. Extending the solution-chemistry studies will depend on the development of faster systems. Studies of elements beyond Hs await discovery of longer-lived isotopes with definitive decay properties and production rates that are larger than a few atoms per week. If isotopes with half-lives of years or more are discovered, then techniques for "stockpiling" them might be envisioned. The synergistic interactions between theory and experiment are leading to a better understanding of the chemistry of the transactinides and the role and magnitude of relativistic effects. SEE ALSO ACTINIDES; ACTINIUM; AMERICIUM; BERKELIUM; CALIFORNIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; NUCLEAR CHEMISTRY; NUCLEAR FISSION; PLUTONIUM; PROTACTINIUM; RADIOACTIVITY; RUTHERFORDIUM; SEABORG, GLENN THEODORE; THORIUM; TRANSMUTATION; URANIUM.

Darleane C. Hoffman

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Transmembrane Protein

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

The membrane of a cell is not only a border; it is also an interface. The most critical molecules involved in interface functioning are proteins that are embedded within the membrane. Many of these proteins span the distance from the outside to the inside of the cell (in part because they are much larger than the **lipids** that make up the membrane) and are referred to as transmembrane proteins. Transmembrane proteins are a class of integral proteins (i.e., proteins that penetrate into or through the membrane bilayer).

The lipid molecules of the membrane bilayer are predominantly **hydrophobic** (i.e., they do not interact strongly with polar water molecules). The portion of the transmembrane protein that is embedded in the bilayer must therefore have residues that are not polar. Commonly, these residues form a coil, or **helix**, that is hydrophobic and therefore stable within the bilayer.

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

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

Transmembrane proteins have three regions or domains that can be defined: the domain in the bilayer, the domain outside the cell (called the extracellular domain), and the domain inside the cell (called the intercellular domain). Even though a cell membrane is somewhat fluid, the orientation of transmembrane proteins does not change. The proteins are so large that the rate for them to change orientation is extremely small. Thus, the extracellular part of the transmembrane protein is always outside the cell and the intercellular portion is always inside.

Transmembrane proteins play several roles in the functioning of cells. Communication is one of the most important roles: The proteins are useful for signaling to the cell what the external environment contains. **Receptors** are capable of interacting with specific substrate molecules on the extracellular domain. Once a protein binds to substrate, a change in the geometry near the binding site results in subsequent changes in the structure of the intercellular domain. These changes result in a cascade effect—another protein in the cell changes, affecting the next protein, and so on. Thus, transmembrane proteins are capable of initiating signals that are responsive to the external environment of the cell but ultimately lead to actions that take place in other structures of the cell.

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

In addition to serving as a way for the cell to gather information about the external environment, transmembrane proteins are associated with controlling the exchange of materials across the membrane. The proteins most involved in this process are called porins. These molecules appear in clusters that create pores (or channels) within the membrane. In many cases the pores are controlled (or regulated) by other proteins so that they are open under some circumstances and closed under others.

Nerve cell signaling provides a good example of this functionality. Nerve cells propagate electrical signals called action potentials by using the flow of ions across the membrane. The channels that allow the flow of ions are usually closed in their resting state but open when a signal occurs. These proteins form voltage-gated channels. When one nerve cell interacts with another, a different mechanism opens the channels. In this case, a receptor protein binds a neurotransmitter; this interaction affects the channel proteins so that they are opened for ion flow. This structure is referred to as a ligand-gated channel. The ligand is the neurotransmitter in this case, but other ligand-gated channels also exist and all use transmembrane proteins. SEE ALSO PROTEINS; NEUROTRANSMITTERS.

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Transmutation

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

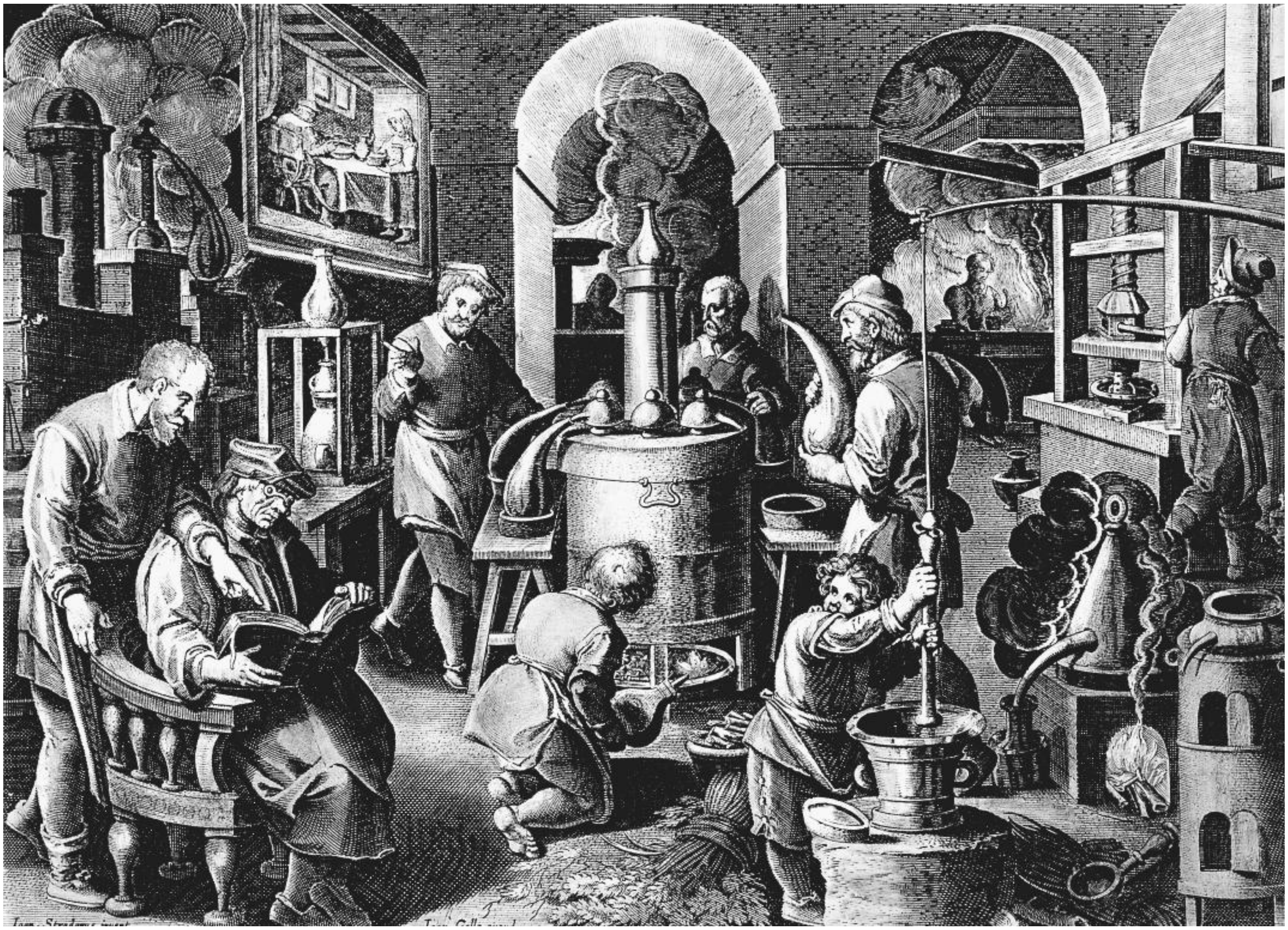
Transmutation is the act of changing a substance, tangible or intangible, from one form or state into another. To the alchemists of old, this meant the conversion of one physical substance into another, particularly base **metals** such as lead into valuable silver and gold. To the modern scientists, this means the transformation of one element into another by one or a series of **nuclear** decays or reactions.

Although people worked with gold, silver, copper, iron, tin, lead, carbon, sulfur, and mercury in ancient times, they had little understanding of chemistry and could write little about it. At this time chemistry was an art, not a science. The Egyptians were the first to produce extensive written documentation of chemical procedures, at the beginning of the Christian era, and Egypt is generally identified as the birthplace of chemistry. These writings indicate that the development of methods for transmuting one substance into another was one of the principal early goals of their investigations. During the several hundred years that followed these writings, the alchemists attempted to develop schemes to transmute base metals into gold and silver through various chemical manipulations of mixtures and distillations. The alchemists were spurred on by what appeared to be some success—for example, production of very small amounts of gold from lead ore by their chemical procedures. (This gold was undoubtedly present in trace amounts in the original ores and was not produced by transmutation.) The ultimate folly of the alchemists turned up during the Middle Ages with the search for the philosopher's stone, a substance that could be mixed with base metals and, through purification, convert them into gold. It was never found.

Because each element has a different but fixed number of protons in the nucleus of the atom, which is the atomic number, the transmutation of one chemical element into another involves changing that number. Such a nuclear reaction requires millions of times more energy than was available through chemical reactions. Thus, the alchemist's dream of transmuting lead into gold was never chemically achievable.

Although the alchemists failed to find a method for the transmutation of base metals into precious metals, a number of important chemical processes resulted from their efforts. For example, they extracted metals from ores; produced a number of inorganic acids and bases that later became commercially important; and developed the techniques of fusion, calcination, solution, filtration, crystallization, sublimation, and, most importantly, distillation. During the Middle Ages, they began to try to systematize the results of their primitive experiments and their fragments of information in order to explain or predict chemical reactions between substances. Thus the idea of chemical elements and the first primitive forms of the chemical Periodic Table appeared.

Ironically, nuclear transmutations were taking place virtually under the noses of the alchemists (or under their feet), but they had neither the methods to detect nor the knowledge to use these happenings. The discovery of the nuclear transmutation process was closely linked to the discovery of radioactivity by Henri Becquerel in 1896. Nuclear transmutations occur during the spontaneous radioactive decay of naturally occurring thorium and uranium (atomic numbers 90 and 92, respectively) and the radioactive



Alchemists considered transmutation as the conversion of one physical substance to another, such as base metals into valuable metals.

daughter products of their decay, namely the natural decay series. As an example, the ^{232}Th decay series is shown in Figure 1. The superscript 232 represents the atomic mass, which is the total number of protons and neutrons in the nucleus of the atom. In this decay series, a ^{232}Th nucleus starts the process by spontaneously emitting an α-particle (a He nucleus containing two protons and two neutrons). This reaction transmutes the Th nucleus into a nucleus with two fewer protons and two fewer neutrons, namely ^{228}Ra. Then the ^{228}Ra nucleus spontaneously emits a β-particle (an electron), which converts a neutron in the nucleus into a proton, raising the atomic number of the resultant nucleus by one with no change in atomic mass, yielding ^{228}Ac. This sequence of successive α and β decays continues from one element to another until the stable ^{208}Pb nucleus is produced (see Figure 1). There exist two other naturally occurring decay chains as well, one starting with ^{235}U (the actinium series) and one starting with ^{238}U (the uranium series). In addition to these three decay series, fourteen other radioactive **isotopes** exist in nature, ranging from ^{40}K to ^{190}Pt, which transmute by decay into stable elements.

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

The idea of transmutation of elements in the natural decay chains did not accompany the discovery of radioactivity by Becquerel. However, Marie and Pierre Curie extended the investigations of Becquerel using a variety of

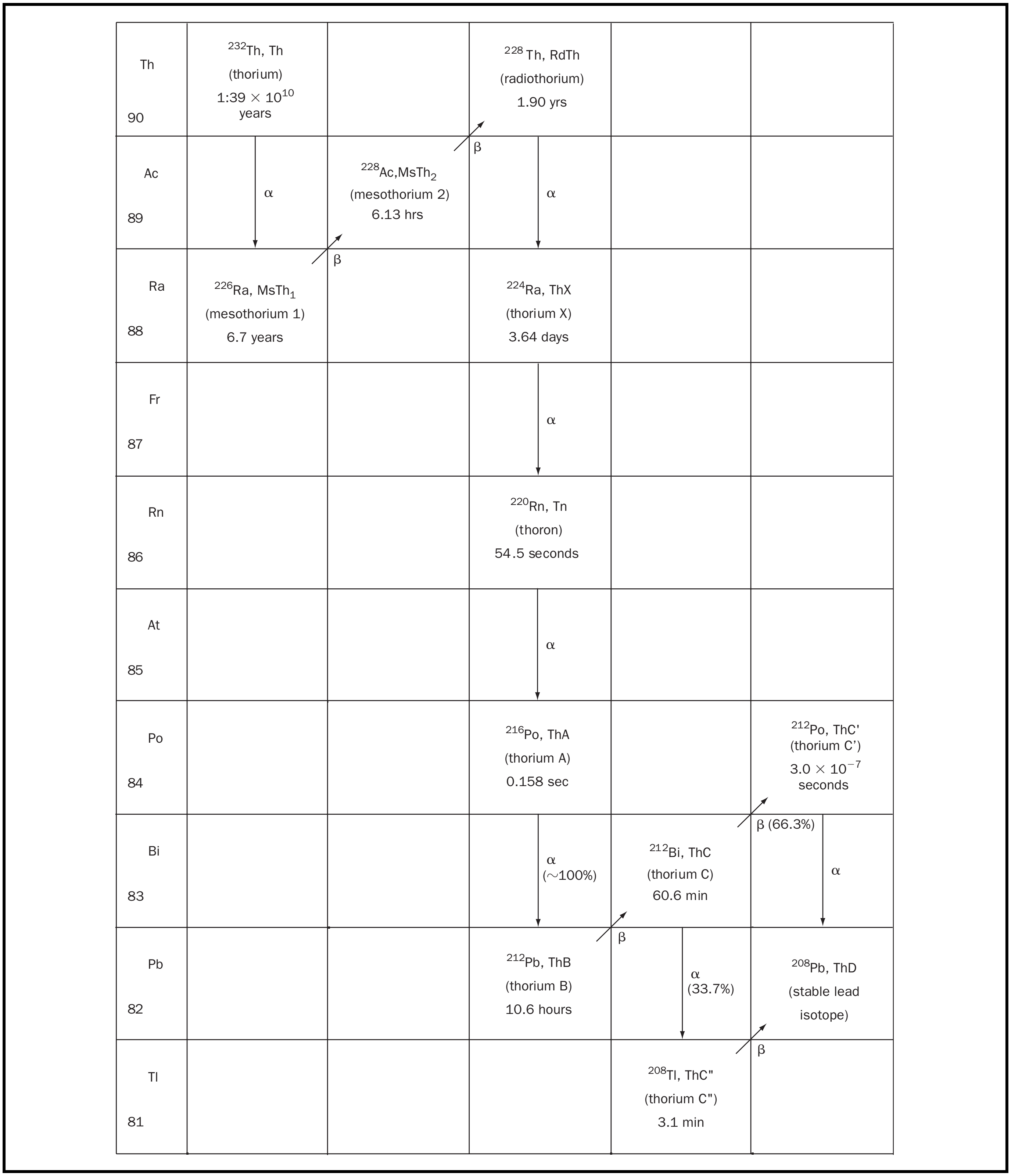

Th
90
Ac
89
Ra
88
Fr
87
Rn
86
At
85
Po
84
Bi
83
Pb
82
Tl
81
^{232}Th, Th
(thorium)
1:39 × 10^{10} years
^{228} Th, RdTh
(radiothorium)
1.90 yrs
α
β
^{228}Ac,MsTh$_2$
(mesothorium 2)
6.13 hrs
α
β
^{226}Ra, MsTh$_1$
(mesothorium 1)
6.7 years
^{224}Ra, ThX
(thorium X)
3.64 days
α
^{220}Rn, Tn
(thoron)
54.5 seconds
α
^{216}Po, ThA
(thorium A)
0.158 sec
^{212}Po, ThC'
(thorium C')
3.0 × 10^{-7} seconds
β (66.3%)
α (~100%)
^{212}Bi, ThC
(thorium C)
60.6 min
α
β
^{212}Pb, ThB
(thorium B)
10.6 hours
α (33.7%)
^{208}Pb, ThD
(stable lead isotope)
β
^{208}Tl, ThC"
(thorium C")
3.1 min

Figure 1.

U minerals and found the radioactive properties to be *not* a function of the physical or chemical forms of the uranium, but properties of the element itself. Using chemical separation methods, they isolated two new radioactive substances associated with the U minerals in 1898 and named them polonium and radium. In 1902 Ernest Rutherford and Frederick Soddy explained the nature of the process occurring in the natural decay chains as the radioactive decays of U and Th to produce new substances by transmutation.

Lord Rutherford and his group of scientists were the first persons to produce and detect artificial nuclear transmutations in 1919. He bombarded nitrogen in the air with the α-particles emitted in the decay of ^{214}Po. The transmutation reaction involved the absorption of an α-particle by the ^{14}N nuclei to produce ^{17}O and a proton (a hydrogen nucleus). This reaction can be written as

$$^{14}\mathrm{N} + {}^{4}\mathrm{He} \rightarrow {}^{17}\mathrm{O} + {}^{1}\mathrm{H}$$

Lord Rutherford was able to detect and identify the protons produced in this nuclear reaction and thereby demonstrate the transmutation process.

Until 1934, only naturally occurring radioactive elements were available for study. However, in January of that year, Irene Curie (daughter of Marie Curie) and Frederic Joliot reported that boron and aluminum samples were made radioactive by bombarding them with α-particles from polonium to produce the two new radioactive products, ^{13}N and ^{30}P respectively. This discovery established the new fields of nuclear chemistry and radiochemistry and sparked their rapid growth.

With the development of nuclear reactors and charged particle accelerators (commonly referred to as "atom smashers") over the second half of the twentieth century, the transmutation of one element into another has become commonplace. In fact some two dozen synthetic elements with atomic numbers higher than naturally occurring uranium have been produced by nuclear transmutation reactions. Thus, in principle, it is possible to achieve the alchemist's dream of transmuting lead into gold, but the cost of production via nuclear transmutation reactions would far exceed the value of the gold. SEE ALSO ALCHEMY; NUCLEAR CHEMISTRY; NUCLEAR FISSION; RADIOACTIVITY; TRANSACTINIDES.

Robert J. Silva

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A computer-generated representation of a molecule of the hemoglobin-carrier of oxygen in blood, a transport protein.

Transport Protein

There are two different types of transport proteins: those that carry molecules to "distant" locations (within a cell or an organism), and those that serve as gateways, carrying molecules across otherwise impermeable membranes.

In order for vast numbers of multicellular organisms to exist, they must have a system for delivering oxygen to all their cells, especially those cells that are not in direct contact with the organism's external environment. Hemoglobin is an example of an oxygen-transport protein and is a part of these oxygen delivery systems.

A single human hemoglobin molecule consists of four **polypeptide** chains. Each of these chains contains a tightly bound prosthetic group called heme. A prosthetic group is a small organic molecule (non-amino acid) that is bound tightly to a protein. At the heart of each **heme group** is a tightly bound iron atom, to which oxygen binds. The function of hemoglobin is to bind oxygen in the oxygen-rich environment of the lungs, then to release that oxygen to oxygen-poor tissues elsewhere. The polypeptide chains are wrapped around the heme groups in such a way that the affinity between the iron and oxygen is strong enough for hemoglobin to bind oxygen in the lungs, but the resulting bond is weak enough such that hemoglobin will release the oxygen when it encounters organs or tissues that need oxygen. Hemoglobin also performs the complementary function of accepting carbon dioxide from the peripheral tissues and releasing it in the lungs.

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

heme group: functional group formed by an iron atom interacting with a heterocyclic ligand called a porphyrin

Cell membranes are impermeable to charged and polar molecules, meaning that these molecules cannot cross them spontaneously. Some transport proteins are intrinsic to cell membranes and facilitate the transport of polar molecules across the membranes. Each cell of the human body needs **glucose**, a very polar molecule, and human beings have five different glucose transport proteins (known as GLUT1 through GLUT5) that all serve a similar function: They carry glucose molecules across membranes and into cells. Without these transport proteins, the rate of glucose entry into cells would be very low indeed. Other membrane-linked transport proteins carry other molecules across membranes, including amino acids, ions, and **vitamins**. SEE ALSO PROTEINS.

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

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

Paul A. Craig

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Travers, Morris

ENGLISH CHEMIST
1872–1961

The discovery of a new chemical element is a rare event; therefore, it is amazing that, in the space of only forty-two days, Morris Travers was involved in the discovery of not one but three new elements—krypton, neon, and xenon.

Morris William Travers was born on January 24, 1872, in Kensington, London, England. His father was an eminent surgeon who was an early champion of antiseptic medicine. Young Morris was well schooled and showed an early interest in science. He entered University College, London, in 1889, and there came under the influence of Sir William Ramsay. Travers received his B.S. in 1893, and, like most of his contemporaries, he planned to specialize in organic chemistry. He began his studies in this field at the University of Nancy in France, but finding both the subject and his adviser disagreeable, he returned to University College, where he began work on his doctorate.

During this time, Ramsay was conducting the research that led to the discovery of argon in 1894 and then helium in 1895. He asked Travers to join him in identifying the properties of these new elements, and the young researcher never again returned to the study of organic chemistry. From 1895 until 1900 Travers worked with Ramsay to find the missing rare gases that the Periodic Table indicated should exist. The two isolated krypton in May 1898, and then a few days later, while examining a large volume of argon, they separated a small quantity of another new element, which they named neon. On further examination of the liquefied air residues from which they had isolated these new elements, they discovered yet another heavier gas, which was named xenon. Because of the chemical inertness of these gases, they were identified by passing an electric current through tubes containing the gases and measuring the characteristic frequencies at which they emitted light. Travers obtained his Ph.D. in 1898 and continued to work on cryogenic research at University College until 1903, when he accepted a position at University College in Bristol.

In 1906 Travers traveled to India to help found the Indian Institute of Science in Bangalore. He returned to England in 1915 and aided the World War I effort by applying his expertise to the production of scientific glassware and munitions. He remained in the chemical industry in various capacities until 1927, when he returned to Bristol as an honorary professor and research fellow. He retired in 1937 but remained active as a consultant and, in his eighties, wrote a vivid and erudite biography of Ramsay, his early mentor. He died on August 25, 1961, at his home in Stroud, Gloucestershire. SEE ALSO Krypton; Neon; Ramsay; William; Xenon.

Bartow Culp

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Triglycerides

Triglycerides are the most common storage form of fat in many organisms. They are neutral **lipid** molecules created via the **esterification** of three fatty acids to a single glycerol molecule. Triglycerides are an efficient storage

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

esterification: chemical reaction in which esters (RCO_2R') are formed from alcohols (R_1OH) and carboxylic acids (RCO_2H)

hydrophobic: water repelling

medium because their highly **hydrophobic** nature allows them to be stored as part of droplets (in which they have little or no contact with water molecules).

synthesis: combination of starting materials to form a desired product

Triglycerides vary in molecular composition according to the identities of the fatty acids used in their **synthesis**. Fatty acids that have been esterified to the glycerol moiety of the triglyceride may be unsaturated (containing double bonds) or saturated (containing no double bonds). The number of double bonds in the fatty acids affects the melting temperature of the triglyceride. Saturated fats have higher melting points and are often solids at room temperature. Unsaturated fats have lower melting points and are often liquids at room temperature. Although all triglycerides are correctly identified as fats, triglycerides with melting points below room temperature are also known as oils. Animal triglycerides generally have more saturated fatty acyl groups than plant triglycerides. Beef triglycerides (lard) have a saturated to unsaturated fatty acyl group ratio of 50:50, whereas the ratio for olive oil is about 20:80. Hydrogenation (removal of the double bonds in the fatty acids) will convert an oil, such as vegetable oil, from a liquid to a solid.

adipose tissue: connective tissue in which fat is stored

In animals, triglycerides are either ingested as part of the diet or synthesized in the liver. Triglycerides are transported in blood as part of lipoprotein particles. Dietary triglycerides are transported as part of lipoprotein particles called chylomicrons. Triglycerides synthesized in the liver are transported as part of lipoprotein particles called very low density lipoproteins or VLDLs. Triglycerides are then removed from lipoprotein particles as they move through the circulatory system. Tissues either utilize this transported triglyceride immediately, or it is stored in **adipose tissue**.

hormonal signaling: collective processes by which hormones circulate in the blood stream to their target organs and trigger the desired responses

Triglyceride is stored within cells that make up adipose tissue (fat). Triglycerides are the most abundant form of stored potential fuel in the human body. A typical 70-kilogram (154-pound) man will have approximately 15 kilograms (33 pounds) of stored triglyceride, representing several months of stored fuel. When physiologic conditions necessitate the use of triglycerides stored in adipose tissue, a hormone or neurotransmitter signals their release. Exercise or stress triggers the release of the neurotransmitter norepinephrine from nerve terminals in the adipose tissue, thereby stimulating triglyceride release. Fasting also initiates the release of triglycerides. Insulin and glucagon, two hormones produced by the pancreas, control this release of triglycerides. During fasting, blood glucagon levels increase and insulin levels decrease. The combination of increased glucagon and decreased insulin levels in the blood is the hormonal signal that triggers the release of triglycerides from the adipose tissue. However, triglycerides do not exit adipose tissue intact. **Hormonal signaling** activates an enzyme called a lipase that hydrolyzes a triglyceride molecule into a glycerol molecule and three fatty acids. The glycerol and fatty acids are then transported within the circulatory system to tissues that will utilize them as fuel. Fatty acids are transported in the blood bound to the serum protein albumin, as their hydrophobic natures would otherwise make them insoluble in the blood. SEE ALSO FATS AND FATTY ACIDS; LIPIDS.

Robert Noiva

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Tungsten

MELTING POINT: 3,422 ±15°C
BOILING POINT: 5,700 ±200°C
DENSITY: 19.3 g/cm^3
MOST COMMON IONS: WO_4^{2-}

74
W
TUNGSTEN
183.85 ±0.03

Tungsten is a metallic transition element in Period 6, Group 6 of the Periodic Table. It was first described in 1783 by Spanish brothers Juan Jose and Fausto de Elhuyar. They named the element *Wolfram* after a term used by the ancient tin miners in Saxony-Bohemia, describing a still unknown mineral. The name was later changed to tungsten, derived from the Swedish words *tung* and *sten* (meaning "heavy stone").

Tungsten has a silvery-white luster and is brittle at room temperature. At elevated temperatures (100°–500°C [212°–932°F]), it is transformed into the **ductile** state. Tungsten **metal** is stable in air only at moderate temperatures; all high-temperature applications are therefore limited to a protective atmosphere or vacuum.

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

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

Thirty-five **isotopes** of tungsten are known; five of them are naturally occurring (180, 182, 183, 184, and 186). In nature, tungsten occurs only in a chemically combined state, mainly as tungstate. The most important tungsten minerals are: scheelite ($CaWO_4$), wolframite ($Fe,MnWO_4$), ferberite ($FeWO_4$), and huebnerite ($MnWO_4$). The average abundance in Earth's crust is 1.3 μg/g [1.3 ppm].

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

Tungsten and tungsten **alloy** products are used in lighting (in the form of wires, coils, and coiled coils in incandescent lamps, and as electrodes in discharge lamps), electrical engineering (high-performance switches), electronics (integrated circuits), medical engineering (x-ray targets), sport equipment (golf club components), aviation and military components (tank ammunition), and steel technology (high-speed steels). Tungsten carbide (WC) forms the main constituent in cemented carbides (also known as hardmetals); these very hard and tough materials are used for metal cutting, machining of wood, plastics and composites, mining tools, construction and wear parts, and military components. Oxides are used as phosphors, pigments, catalysts (oil industry, **combustion** plants), and electrochromic devices (smart windows).

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

combustion: burning, the reaction with oxygen

Wolf-Dieter Schubert
Burghard Zeiler

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Uracil *See Nucleotide.*

Uranium

MELTING POINT: 1,408°C
BOILING POINT: 4,404°C
DENSITY: 19.04 g/cm^3
MOST COMMON IONS: U^{3+}, U^{4+}, UO_2^{+}, UO_2^{2+}

92
U
URANIUM
238.03

Uranium is a very dense, highly reactive, metallic element that has the highest atomic mass of the naturally occurring elements. Natural uranium consists of two long-lived radioactive **isotopes**: ^{238}U (99.28%) and ^{235}U (0.72%). A very small amount of ^{234}U (0.005%) occurs in secular **equilibrium** with ^{238}U. Uranium was discovered in 1789 by Martin Klaproth, who named it after the planet Uranus (which had just been discovered). In 1841 Eugène Melchior Péligot prepared uranium **metal** and proved that Klaproth had actually isolated uranium dioxide.

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

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

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

Uranium is found in Earth's crust at an average concentration of about 2 ppm, and is more abundant than silver or mercury. The most common uranium-containing mineral is uraninite, a complex uranium oxide. Other uranium-containing minerals are autunite, a hydrated calcium uranium phosphate, and carnotite, a hydrated potassium uranium vanadate.

The most prevalent form of uranium in **aqueous solution** is the light yellow, fluorescent uranyl ion UO_2^{2+}. The U^{4+} cation (green in solution) can be obtained by strong reduction of U(VI), but readily oxidizes back to UO_2^{2+} in air. The pentavalent ion UO_2^{+} can be reversibly formed by reduction of UO_2^{2+}, but it readily disproportionates into U(IV) and U(VI). The trivalent U^{3+} can be formed by reduction of U(IV) but is unstable to **oxidation** in aqueous solution.

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

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

After the discovery of uranium radioactivity by Henri Becquerel in 1896, uranium ores were used primarily as a source of **radioactive decay** products such as ^{226}Ra. With the discovery of **nuclear fission** by Otto Hahn and Fritz Strassman in 1938, uranium became extremely important as a source of nuclear energy. Hahn and Strassman made the experimental discovery; Lise Meitner and Otto Frisch provided the theoretical explanation. Enrichment of the spontaneous fissioning isotope ^{235}U in uranium targets led to the development of the atomic bomb, and subsequently to the production of nuclear-generated electrical power. There are considerable amounts of uranium in nuclear waste throughout the world. SEE ALSO ACTINIUM; BERKELIUM; EINSTEINIUM; FERMIUM; LAWRENCIUM; MENDELEVIUM; NEPTUNIUM; NOBELIUM; PLUTONIUM; PROTACTINIUM; RUTHERFORDIUM; THORIUM.

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

nuclear: having to do with the nucleus of an atom

fission: process of splitting an atom into smaller pieces

W. Frank Kinard

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Urey, Harold

AMERICAN PHYSICAL CHEMIST
1893–1981

American chemist Harold Clayton Urey, recipient of the 1934 Nobel Prize in chemistry, "for his discovery of heavy hydrogen."

Harold Urey was a prolific scientist whose research interests included chemistry, astronomy, geology, and biology. Although he did important work on **isotope** applications and cosmochemistry, Urey is best remembered for his discovery of heavy hydrogen, or deuterium, for which he received the 1934 Nobel Prize in chemistry.

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

Urey was born in Walkerton, Indiana, on April 29, 1883. When he was six, his father died. His mother remarried and the family later moved to Montana. After graduating from high school in 1911, Urey taught in country schools in Indiana and Montana. In 1914 Urey entered the University of Montana and graduated three years later with a B.S. in biology and a minor in chemistry. During World War I he worked for a chemical company in Philadelphia, and after the war, Urey returned to the University of Montana as an instructor in chemistry. He enrolled in the chemistry department at the University of California at Berkeley in 1921 and only two years later received his Ph.D. in physical chemistry. After a year in Copenhagen, Denmark, Urey joined the chemistry faculty at Johns Hopkins University. He would later move to Columbia University, the University of Chicago, and finally the University of California at San Diego.

In July 1931 Urey read a paper that proposed the existence of a stable isotope of hydrogen of mass 2, or heavy hydrogen. He decided to look for the isotope and designed an experimental plan with his lab assistant George Murphy. As a detection method, they chose to examine the lines in the **atomic spectrum** of hydrogen. Since the predicted natural abundance of the heavy hydrogen was only 0.05 percent, Urey hoped to detect the rare isotope by analyzing a sample of hydrogen enriched in heavy hydrogen prepared by Ferdinand G. Brickwedde, a physicist working at the National Bureau of Standards in Washington, D.C.

atomic spectrum: electromagnetic array resulting from excitement of a gaseous atom

While waiting for the enriched sample to arrive, Urey and Murphy analyzed a sample of regular hydrogen and were surprised to see evidence of heavy hydrogen (which Urey later called deuterium). Believing that it was an artifact of their detection method, Urey and Murphy decided to keep their results secret until they obtained further proof using the enriched sample. On Thanksgiving Day of 1931, Urey analyzed the sample of enriched hydrogen and observed the lines confirming the existence of deuterium. Urey received the 1934 Nobel Prize in chemistry for his discovery. He publicly acknowledged Brickwedde and Murphy's role by giving each of them one-quarter of the Nobel Prize money.

Since 1913 scientists had accepted the existence of isotopes, but conventional wisdom claimed that isotopes of a given element could not be differentiated or separated by a chemical process. Urey challenged and overturned this thinking in 1932 by showing that deuterium (D_2) could be concentrated in the form of deuterium oxide, or heavy water (D_2O), and then converted back into pure deuterium by electrolysis of the D_2O. Deuterium and deuterium oxide are convenient sources of deuterium-labeled compounds that today are used routinely in medicine and science.

After World War II Urey moved to the University of Chicago. While there, Urey perfected a method, also based on oxygen isotope ratios, that accurately measured the temperatures of ancient oceans.

Urey additionally developed an interest in the chemistry of the solar system. In his 1952 book, *The Planets*, he argued that what we needed to understand the origins of the solar system was a thorough understanding of the Moon. Urey's work on the chemical composition of meteorites set the stage for later studies that explained the origins of chemicals in stars.

Urey left Chicago in 1958 to become professor-at-large at the newly formed University of California at San Diego. He retired from that institute in 1970 and died in 1981. SEE ALSO HYDROGEN.

Thomas M. Zydowsky

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V

Valence Bond Theory

The valence bond (VB) theory of bonding was mainly developed by Walter Heitler and Fritz London in 1927, and later modified by Linus Pauling to take bond direction into account. The VB approach concentrates on forming bonds in localized orbitals between pairs of atoms, and hence retains the simple idea of Lewis structures and electron pairs. The wave function for the bonding electrons is described as the overlap of atomic orbitals. Thus, in the H_2 molecule, the spherical s orbitals of the two H atoms simply overlap, so that the electrons in the bond sense the nuclei of both atoms. This method also works well for simple molecules like H_2O, CH_4, and NH_3. First the appropriate hybrid orbitals are constructed on the central atom to give the correct molecular geometry (e.g., four sp^3 tetrahedral orbitals on the C atom in CH_4). The bonding picture is then constructed by simple overlap of the atomic orbitals, (e.g., one 1s orbital of a H atom with each sp^3 lobe of the C atom in CH_4 to give four C—H bonds).

Bonding in BF_3

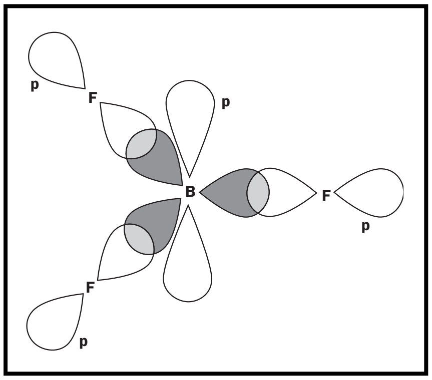
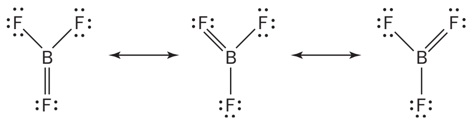


Figure 1. The bonding in the BF_3 molecule: Three sp^2 hybrid orbitals on the boron atom overlap a p orbital from each of the three fluorine atoms.

The electron configuration of the boron atom is $2s^2 2p^1$, with one unpaired electron. This electron is excited to the higher energy configuration $2s^1 2p^2$, with three unpaired electrons. These three orbitals are now hybridised to give three equivalent sp^2 hybrid orbitals, coplanar, and lying 120° apart, each containing one electron. These hybrid orbitals then overlap the half-filled p orbitals of the three fluorine atoms, thus forming three coplanar B—F electron-pair bonds. (See Figure 1.)

All seems well, except that the boron atom does not have an octet: One perpendicular 2p orbital remains empty. This orbital can accept electron density from the F atoms to a maximum of one electron pair. On average, each F atom donates one-third of an electron pair to the empty p orbital on boron. One model for BF_3 is a resonance hybrid of three structures, each having one double bond and two single bonds. The B−F bond is said to have a bond order of $1\frac{1}{3}$.



Some Shortcomings

The valence bond approach is especially useful in organic chemistry where so many molecules are built of tetrahedral C atoms, sp^3 hybridised. The concept of hybrids is intuitively very satisfying because they fit visually with our perceived picture of the shape of a molecule with its directed bonds between pairs of atoms. Unfortunately, the VB approach is not satisfactory for species like $CO_3^{=}$, NO_3^{-}, and benzene because the VB picture does not reflect the known chemical structure. A new concept of resonance hybrids must be introduced, and $CO_3^{=}$ must now be represented by a combination of three Lewis-octet structures. Worse still, the VB approach cannot easily give a satisfactory bonding picture for either of the important molecules O_2 or CO.

In cases where the VB approach does not work well, the molecular orbital (MO) method is often more successful. The situation is best summarized by using the strengths of the VB approach where they are appropriate, as in CH_4, and using the MO approach where it is best suited, as in O_2 and benzene. After all, each approach is an approximation, incomplete and imperfect. SEE ALSO Bonding; Lewis Structures; Molecular Orbital Theory.

Michael Laing

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Vanadium

MELTING POINT: **1,910 ±10°C**
BOILING POINT: **3,047°C**
DENSITY: **6.11 g/cm³**
MOST COMMON IONS: **V^{2+}, V^{3+}, VO^{+}, VO_2^{+}**

23
V
VANADIUM
50.9415

Vanadium is a soft silver **metal** in group 5B of the Periodic Table. It was discovered in Mexican lead ore by Andreas Manuel del Rio in 1801. Because of the red color of its salts, he named it erythronium (the Greek word *erythro* means "red"). Upon challenge by H. V. Colett-Desotils, del Rio withdrew his claim. In 1830 the element was rediscovered by Nils Selfstöm in iron ore. Since the element is found in compounds of many different col-

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

ors, he named it "vanadium" after the Scandinavian goddess of beauty, Vanadis.

Vanadium is the nineteenth element in abundance (136 ppm) and the fifth most abundant transition element in Earth's crust. It is found in approximately sixty-five different minerals (such as roscoelite and vanadinite), phosphate rock, iron ores, and some crude oils as organic complexes. Since there are few concentrated deposits of vanadium compounds, it is obtained as a coproduct of refining. The element has two naturally occurring **isotopes**: ^{50}V (0.25%) and ^{51}V (99.75%).

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

Although vanadium is an essential **trace element**, its exact role has not been determined. It is found in the blood of the ascidian seaworm. A related species has vanadium concentrations of up to 1.45 percent in its blood cells. The metal may play a role in the oxygen transport system.

trace element: element occurring only in a minute amount

Vanadium reacts with most nonmetals at high reaction temperatures (660°C; 1,220°F). The compounds of vanadium reflect the varied **oxidation** states possible for this element. Formal oxidation states of +5 to -1 have been found, with the +4 state being the most stable. The element has good corrosion resistance to alkali, acid, and salt water. For this reason it is used in rust resistant springs and high speed tools. Approximately 80 percent of the vanadium produced yearly is used as an additive to produce steel that has a resistance to wear. Vanadium oxide is used in ceramics and as a **catalyst**. SEE ALSO Corrosion; Steel.

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

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

Catherine H. Banks

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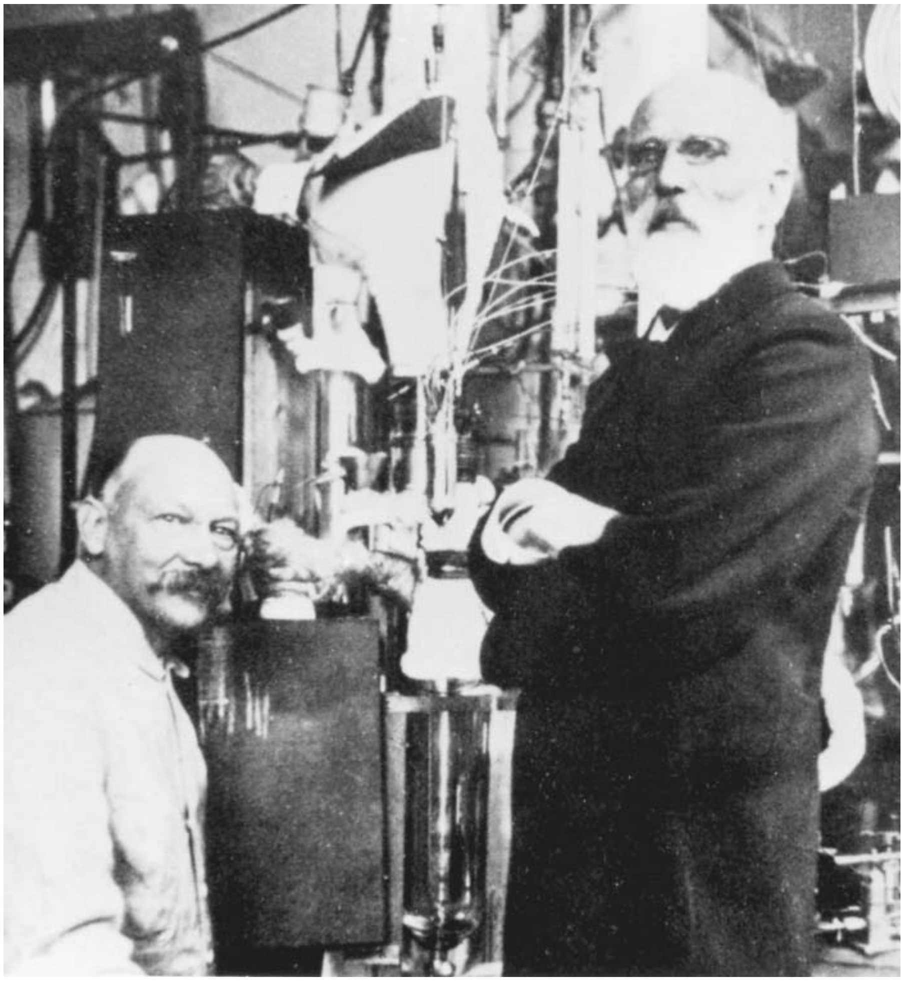
van der Waals, Johannes

DUTCH PHYSICIST
1837–1923

That atoms exist is a fact seemingly indisputable, but such was not always the case. In the early eighteenth century, when English chemist and physicist John Dalton made a case for his **atomic theory**, it was met with skepticism and spawned a vigorous debate that continued well into the twentieth century about whether or not atoms were real. Coming down squarely on the side of real atoms was van der Waals, the father of modern molecular science.

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

Johannes Diderik van der Waals was born in Leiden, the Netherlands, in 1837. The son of a carpenter, he was not afforded the advantages that some of his contemporaries enjoyed. Lacking knowledge of classical languages, he was barred from taking his academic examinations at the University of Leiden. Instead, he continued his studies in his spare time between



Dutch physicist Johannes Diderik van der Waals (right), recipient of the 1910 Nobel Prize in physics, "for his work on the equation of state for gases and liquids."

1862 and 1865, eventually obtaining teaching certificates in both mathematics and physics. In 1864 he was appointed as a teacher at a secondary school in Deventer. In 1866 he moved to the Hague, first as a teacher and then as a director of one of the secondary schools there.

When new legislation was introduced exempting science students from a classical education, van der Waals was finally allowed to sit for his university examinations. In 1873 he obtained his doctorate with a thesis titled, "On the Continuity of the Gas and Liquid State." His thesis proposed a correction to the **equation of state for ideal gases** that would allow the equation to be applied to real gases. That is, he proposed a modification of the formula $PV = nRT$ to account for the fact that atoms are real and that they interact.

equation of state for ideal gases: mathematical statement relating conditions of pressure, volume, absolute temperature, and amount of substance; $PV = nRT$

In his own words, his incentive to his life's work "came to me when, after my studies at university, I learned of a treatise by Clausius (1857) on the nature of the motion which we call heat. In this treatise . . . he showed how Boyle's law can very readily be derived on the assumption that a gas consists of material points which move at high velocity" (van der Waals, "The Equation of State of Gases and Liquids"). This treatise was a revelation, as it derived the ideal gas law from first principles and framed it in terms of atoms and molecules. Here was a theoretical rationalization for experimentally obtained data. But it also occurred to van der Waals that this treatise might not be complete. If the atoms of gases are in constant motion when a gas is dilute, then this must also be the case as the gas is compressed and, indeed, must still be the case down to maximum compression as the gas condenses to a liquid. This led to the idea of the continuity of matter and the notion that both the liquid and gaseous states can be described by a similar mathematical theory.

Further, van der Waals recognized that real gases take up volume and atoms do interact with one another. For the German mathematical physicist Rudolf Clausius to obtain his results, he had to ignore both of these factors. Van der Waals found experimentally derived constants that allowed him to modify the ideal gas law to take into account real atoms. His equation of state,

$$(P + a/V^2)(V - b) = RT$$

has subsequently been modified to include Avogadro's number, but it was critical to scientists' first steps in understanding atoms and molecules. *a* arises from considering interatomic forces (collectively called "van der Waals forces" in his honor), and *b* recognizes that atoms have a real volume—that they actually exist. SEE ALSO BOYLE, ROBERT; DALTON, JOHN.

Todd W. Whitcombe

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van Helmont, Johann Baptista

FLEMISH RELIGIOUS SCHOLAR, PHYSICIAN, AND CHEMIST
1579–1644

Johann Baptista van Helmont was a contemporary of the English philosopher Francis Bacon and the Italian astronomer Galileo Galilei. As with Galileo and his work, van Helmont's work in science brought him into conflict with religious authorities. He also spent about sixteen years under house arrest while an Inquisition court prosecuted its legal case against him. His use of chemistry to understand medicine made him a leading iatrochemist (physician-chemist, *iatro* being Greek for "physician") of his time.

Van Helmont was the first to use the term "gas" to describe an airlike substance that was distinct from ordinary atmospheric air. His approach to chemistry included both mysticism and the use of the new experimental philosophy (science). He believed in astrology and the **philosopher's stone**. His study of the written works of Paracelsus led to his criticism of established medical practice and his adoption of experimental testing. He tested Paracelsus's notion that all substance was made of "earth" by conducting his "willow tree experiment." In the experiment he weighed a pot that contained dry soil and a willow sapling cleansed of soil. After planting the sapling in the soil, he added no soil, and watered the sapling with pure rainwater

philosopher's stone: the substance thought by the alchemists to have the power to transmute base metals into gold

Flemish physician and chemist Johann van Helmont, the first person to distinguish gas from atmospheric air.

or distilled water (and not with mineral water or well water, which might contain dissolved earth). At the end of five years he removed the tree from the soil, weighed it, and weighed the dried pot of soil. The soil had lost nearly none of its weight, whereas the tree had gained a great deal of weight. Van Helmont concluded that a tree was not composed mostly of "earth," as avowed by Paracelsus, but was composed mostly of "water," somehow transformed into tree substance.

Van Helmont offered another experiment as a proof of the existence of vacuums. He positioned a lighted candle upright in a wide tray of water. He used a glass dome to enclose the candle, with the edge of the glass immersed in the water. The candle soon went out, and the level of the water enclosed by the glass rose. Van Helmont claimed there was something in the air that was annihilated by the fire. The water rose due to suction that had been created by a vacuum that resulted from the annihilation of a part of the air.

This description is essentially correct. The experiment would continue to be investigated by chemists for another 150 years, ultimately becoming a model experiment in the chemical revolution. SEE ALSO Alchemy; Paracelsus; Transmutation.

David A. Bassett

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Dutch chemist Jacobus Hendricus van't Hoff, recipient of the 1901 Nobel Prize in chemistry, "in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions."

van't Hoff, Jacobus Hendricus

COFOUNDER OF MODERN STEREOCHEMISTRY AND PHYSICAL CHEMISTRY

1852–1911

Jacobus Hendricus van't Hoff, born in Rotterdam, Netherlands, was in his youth, along with the French chemist Joseph Achille Le Bel, the cofounder of modern stereochemistry. He then became one of the fathers of modern physical chemistry. In 1901 he was awarded the first Nobel Prize in chemistry for his work on chemical dynamics and the osmotic pressure in solutions.

As is the case with many creative minds, van't Hoff's career initially encountered many roadblocks, mostly related to the ignorance of the scientific establishment. Unemployed for two years after receiving his doctorate, he eventually took a teaching job in physics at the veterinary school in Utrecht. Success finally came in 1877 when the newly founded University of Amsterdam offered him a lectureship; the next year he became a professor of chemistry at the same institute. Although his international reputation led to the formation of a new chemical laboratory at the Amsterdam school, which was completed in 1891, he moved to Berlin in 1896 as both a university professor and member of the prestigious Prussian Academy of Science.

isomer: molecules with identical compositions but different structural formulas

Shortly before he submitted an only average doctoral thesis in synthetic organic chemistry to the University of Utrecht, the twenty-two-year-old van't Hoff had printed and distributed a twelve-page pamphlet at his own expense that, although ignored for many years, essentially outlined the foundation of modern stereochemistry. Inspired by the earlier ideas of the German chemist Johannes Wislicenus to extend chemical structure theory from constitutional chemical formulas to representations in three-dimensional space, van't Hoff suggested a structural distinction between optical **isomers** that had been represented up until that time by the same formula. By screening known substances for optical activity (i.e., the rotation of the plane of polarized light), he found that all their constitutional formulas contained at least one carbon atom that combined with four different atomic groups. If the latter were placed at the corners of a tetrahedron in three-dimensional space, with the carbon atom at its center, there were exactly two possible tetrahedra with asymmetric carbon atoms, each being the mirror image of the other, that could account for the pairs of optical isomers. This structural theory was further supported by his observation that for every known chemical transformation where the optical activity of a reactant disappeared, there was no more asymmetric carbon atom in the structural representation of the reaction product. Independently and virtually simultaneously, Le Bel arrived at the same theory in Paris.

Due to his early interest in philosophy, particularly the ideas of French philosopher Auguste Comte, van't Hoff's chemical research strove for general and theoretical insight into chemistry and thus gradually shifted from organic to physical chemistry. In 1884 he published his well-known *Études de dynamique chimique* (Studies in chemical dynamics); it contained many important ideas on chemical kinetics and thermodynamics that confirm van't Hoff's status as a true pioneer in the field. Based on numerous measurements of organic reaction rates, he classified chemical reactions according to different orders and molecularities and formulated the temperature dependence of reaction rates, now known as the "Arrhenius equation." Following through on earlier ideas, he interpreted chemical equilibria as dynamic states where backward and forward reaction rates were equal, which he represented by a double arrow. He further formulated the temperature dependence of the **equilibrium** constant, known as the "van't Hoff isochore," and suggested what later came to be known as "Le Chatelier's principle." Most important, he established the foundation of chemical thermodynamics by expressing the relationship between what is now called the free energy of a reaction and its equilibrium constant.

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

During the late 1880s van't Hoff turned the seemingly exotic phenomenon of osmotic pressure into a crucial part of the new physical chemistry of solutions. He discovered that the osmotic pressure π increased with the concentration of the solute, $c = n/V$, and the absolute temperature T according to the equation

$$\pi = \frac{nRT}{V}$$

which is equivalent to the ideal gas law if one replaces the osmotic pressure, π, with the gas pressure, p:

$$p = \frac{nRT}{V}$$

with R being the gas constant in both cases. The surprising correspondence between the two suggested that the osmotic pressure depended only on the number of solute molecules and not their chemical nature, like other so-called colligative properties such as vapor pressure lowering and freezing point depression. Van't Hoff did not simply advance all these phenomena on a common thermodynamic basis; he also successfully explained apparent anomalies with the Arrhenius theory of electrolytic dissociation.

In his later years, van't Hoff applied chemical thermodynamics to the formation of marine salt deposits, which made him one of the pioneers in the science of petrology. SEE ALSO THERMODYNAMICS.

Joachim Schummer

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Vasoconstrictors ***See Norepinephrine.***

Venom

It may be tempting to equate the concept of venom with poison, but to do so would be inaccurate. Many plants, for example, are poisonous but present no harm to humans because they have learned not to eat them. By contrast, one can be quite careful on a walk through the southwestern United States or Australian outback and still have an unfortunate accident involving the venom of a snake. In any given year, around 40,000 people die as a result of snakebites. To be more accurate with the definition of venom, therefore, it must be noted that venom is not just a poison, but one that is injected under the skin of the victim.

Snakes are not the only animals that use venom. Spiders, scorpions, bees, and wasps are also venomous animals. The specific venom used by these animals varies not only with its type (spider venom is different from bee venom, for example), but also within a species. Thus, some spiders are venomous but not actually a threat to adult humans, whereas the bite of other spiders is lethal unless treated with appropriate medicines.

The differences in venoms have important medical implications, but there are also similarities among many venoms. Most are rather complicated mixtures of chemicals, each of which plays some role in the action that the venom takes. Many involve some mechanism designed to immobilize the victim and are therefore targeted at nerve cells that control muscles.

enzyme: protein that controls a reaction in a cell

Thus, snake venoms typically contain neurotoxins, but they also often include **enzymes** that promote various hydrolysis reactions. The neurotoxins carry out the task of immobilizing the victim by interrupting the ability

The gila monster is a venemous animal. Venom is a poison injected under the skin.

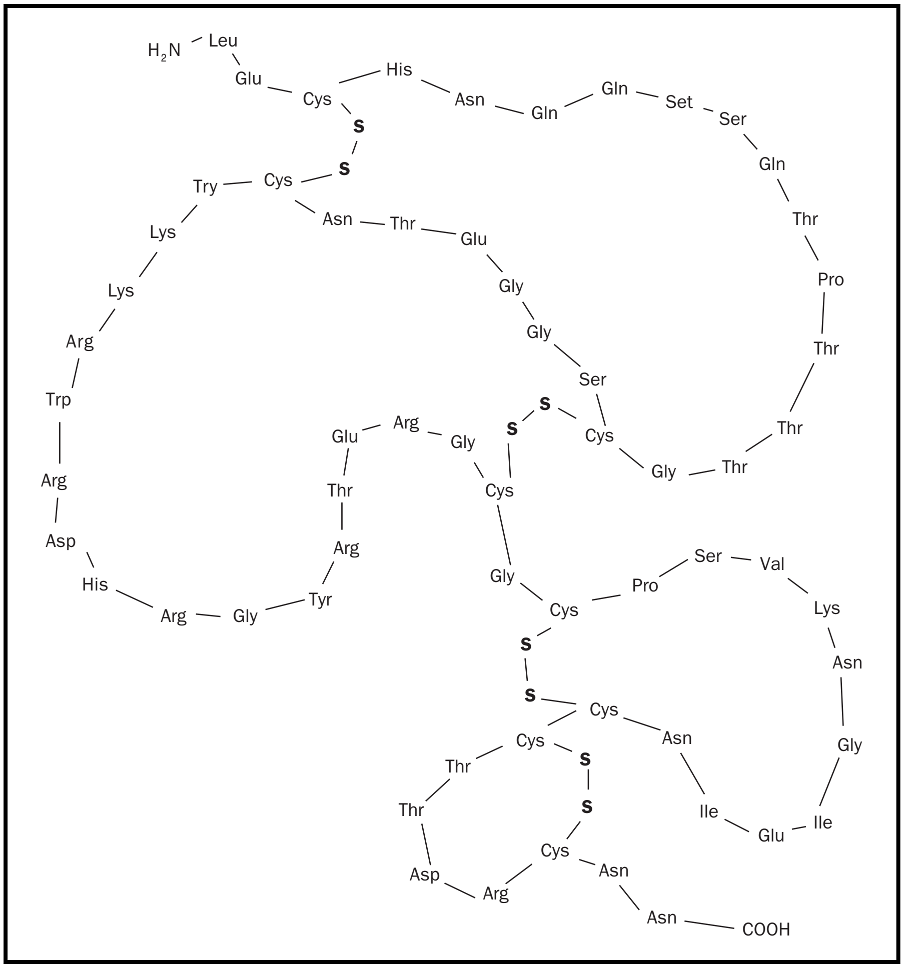

Figure 1. Primary structure of cobrotoxin.

of the nerve cells to stimulate muscle movement. Hydrolysis helps make the tissues of the victim easier for the snake to digest if it is eaten. These hydrolytic enzymes may include molecules capable of breaking down collagen and phospholipids as well as other enzymes.

For many who study the chemistry of venoms, the neurotoxins hold particular interest. One example would be the **polypeptide toxin cobrotoxin** that was isolated from the Formosan cobra and analyzed in 1965 by Chen-Chung Yang, a distinguished chair professor at Tsing Hua University in Taiwan. The primary structure of this neurotoxin is indicated in Figure 1, along with some components of its secondary structure. There are sixty-two residues in the primary structure and four di-sulfide bonds in the secondary structure. If even one of these di-sulfide bonds is somehow disrupted, the polypeptide is rendered nontoxic. This points to the fact that secondary structure is important even in small polypeptides, not only full-size proteins.

The action of cobrotoxin arises from its ability to bind strongly to the **receptors** in postsynaptic neurons. In order for one nerve cell to signal a neighbor, it releases neurotransmitters that diffuse across a small gap called the synapse. The nerve on the other side of the synapse (the **postsynaptic neuron**) has proteins that are specifically geared to sense the presence of these neurotransmitters. If these receptors are blocked, the signal is not passed on, and the nerve cell function is disrupted. Cobrotoxin is able to

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

toxin: poisonous substance produced during bacterial growth

cobrotoxin: polypeptide toxin containing 62 residues that is found in the venom of cobras

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

postsynaptic neuron: receptor nerve cell

acetylcholine: neurotransmitter with the chemical forumula $C_7H_{17}NO_3$; it assists in communication between nerve cells in the brain and central nervous system

disrupt a specific type of receptor that is sensitive to **acetylcholine**. Once this polypeptide binds to the receptor, it is not released, so the nerve cell loses its ability to signal and the muscles it is supposed to trigger do not function. If the muscle that stops working is the diaphragm, the animal will not be able to breathe and it essentially suffocates. Cobrotoxin is very toxic, with an LD_{50} of 65 nanograms per kilogram in mice. SEE ALSO Globular Protein; Neurotoxin; Proteins; Toxicity.

Thomas A. Holme

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Vitamins ***See Ascorbic Acid; Cholecalciferol; Retinol; Riboflavin; Thiamin.***

Volta, Alessandro

ITALIAN PHYSICIST
1745–1827

Until the late 1700s static electricity was the only known form of electricity. Alessandro Volta, born in Como, Italy, is best known for discovering current electricity and for developing the voltaic pile, which became an invaluable tool in electrochemistry.

Volta was interested in electricity early in his career. He published his first book on static electricity at the age of twenty-four. In 1775, Volta announced the discovery of the electrophorus, a new sort of instrument that could store static electricity. And in 1782, Volta invented another instrument, the condensing electroscope that was an extremely sensitive measuring device capable of detecting the existence of negative charge in water vapor and in the smoke of burning coals.

By this time, Volta was a professor at the University of Pavia in Italy, where he was to teach for forty years. He had a very good reputation among chemists and scientists throughout Europe. Among his correspondents was Luigi Galvani (1737–1798), a fellow Italian scientist. Galvani sent Volta a copy of a pamphlet he had written detailing his latest experiments in 1792. Galvani reported that when a partially dissected frog came into contact with two different **metals** that were grounded, its muscles flexed and legs twitched. He further reported that there was a relationship between the muscular **contraction** and the electrical stimulus, which he believed to be proof of the existence of "animal electricity."

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

contraction: the shortening and thickening of a functioning muscle or muscle fiber

Volta at first accepted Galvani's explanation of animal electricity as the reason for the frog's involuntary movements. But after carefully repeating Galvani's experiments, Volta became convinced that the contractions of the frog's legs did not result from animal electricity but were due to some external electricity caused by the two different metals in an arc coming into contact with the moist frog. He believed that the frog merely assumed the role of a simple and sensitive electroscope.

Italian physicist Alessandro Volta, who discovered current electricity.

In addition to repeating Galvani's experiments, Volta noticed some other effects involving dissimilar metals when they come into contact with moist substances. He found that if two different metals touched the tongue and were brought into contact, a bitter taste resulted. And when two metals touched the eye, contact between them created the sensation of light. After all these experiments, Volta was soon convinced that the metals not only served as conductors but also generated electricity when they were brought into contact.

By 1794 Volta had completely abandoned Galvani's theories of animal electricity. Instead, he advanced the notion of "metallic electricity" or, in modern terms, current electricity. Through further experimentation, he noticed that the electrical effects between select dissimilar substances became stronger the farther apart they were from one another in the following series: tin, lead, iron, copper, platinum, gold, silver, graphite, and charcoal. Volta also determined that an electrical force was generated when a metal was in contact with a fluid. By putting together these two findings, Volta created the first battery.

Volta found that a current was produced when two different metal disks such as silver and zinc were separated by a moist conductor, such as paper soaked in salt water, and brought into contact by a wire. By stacking a collection of silver-moist paper-zinc units, in effect forming a pile, Volta determined that the current intensified. If someone touched the top of such a "voltaic pile" (as this early battery was called) and put his or her other hand in a dish of salt water that was connected to the bottom metal disk by a strip of metal, that person would feel a continuous, if weak, shock.

Volta made his discovery of the current electricity–generating voltaic pile known to the scientific community by 1800. His invention gave rise to new fields of scientific inquiry, including electrochemistry, electromagnetism, and the modern applications of electricity. The first chemists to use the voltaic pile were William Nicholson and Anthony Carlisle, who built a pile and used it to decompose water. Humphry Davy (1778–1829) used the voltaic pile to decompose many substances, such as **potash** and soda. Davy was also able to isolate for the first time several elements, including calcium and magnesium, using the voltaic pile.

potash: the compound potassium oxide, K_2O

The voltaic pile also had applications in other fields of science. William Cruikshank discovered the process of electroplating while working with a voltaic pile. Davy constructed the first crude electric light with the pile in 1820. SEE ALSO DAVY, HUMPHRY; ELECTROCHEMISTRY; ZINC.

Lydia S. Scratch

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Waksman, Selman Abraham

RUSSIAN MICROBIOLOGIST
1888–1973

Selman Waksman changed the course of medical history while investigating how soil microbes defended themselves against invaders. He and coworkers isolated twenty-two new defensive compounds produced by soil microbes and in the process discovered **streptomycin**, the first antibiotic effective against tuberculosis. For his discovery of streptomycin, Waksman received the 1952 Nobel Prize in physiology or medicine.

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

Selman Abraham Waksman was born on July 22, 1888, in Priluka, near Kiev, Russia (now the Ukraine). After graduating from the Fifth Gymnasium in Odessa, Russia, in 1910, Waksman immediately immigrated to the United States. In 1911 he enrolled at Rutgers University, where he received a B.S. in 1915 and an M.S. in 1916, both in agriculture. While at Rutgers, Waksman worked with Jacob G. Lipman, another Russian immigrant, whose primary research interest was soil microbiology. After receiving his Ph.D. in biochemistry from the University of California, Berkeley, in 1918, Waks-

American biochemist Selman Waksman, recipient of the 1952 Nobel Prize in physiology or medicine for his discovery of streptomycin.

man returned to New Jersey to begin work as a microbiologist and as a part-time instructor at Rutgers. He was appointed professor of soil microbiology at Rutgers in 1930, a position he held until his retirement in 1958. He also established a lab to study marine microbiology at the Woods Hole Oceanographic Institute in Woods Hole, Massachusetts, in 1931.

Although Waksman was involved in many areas of soil microbiology, it was his interest and expertise in the life-and-death struggles between soil microbes that eventually led to a cure for tuberculosis. In 1932 the American National Association against Tuberculosis asked Waksman to investigate earlier reports that the tubercle bacillus, or the bacteria that cause tuberculosis, was rapidly destroyed in soil. Waksman confirmed those reports and concluded that the tubercle bacillus was probably killed by other bacteria present in the soil. He proposed that the soil bacteria defended themselves by producing an unknown substance that destroyed the tubercle bacillus. He also coined the term “antibiotic” for substances produced by one microorganism that suppress the growth of another.

screen: process of comparing multiple reagents simultaneously to provide information on reaction of one reagent with another

Waksman and his collaborators grew a batch of a soil microorganism called *Actinomyces griseus* and isolated their first antibiotic from the brew in 1940. They called it actinomycin, after the species of microorganism from which it was isolated. In 1942 they isolated streptothricin. Like actinomycin, it was too toxic to use in humans, but unlike actinomycin, it destroyed the tubercle bacillus. Encouraged by these discoveries, Waksman continued to test, or **screen**, other soil microbes for their ability to produce antibiotics with activity against the bacteria that caused tuberculosis (now known as *Mycobacterium tuberculosis*).

Waksman and his colleagues screened more than 10,000 different soil microbes before they isolated streptomycin in 1943. Streptomycin was what they were looking for: It destroyed the tubercle bacillus and was safe enough to test in humans. Subsequent clinical trials proved that streptomycin cured several types of tuberculosis and that it was safe enough to prescribe for a variety of gram-negative bacterial infections. Even after sixty years, streptomycin continues to be used in the battle against tuberculosis and other life-threatening infections.

Waksman died on August 16, 1973, and is buried in a churchyard in Woods Hole, Massachusetts. SEE ALSO ANTIOBIOTICS.

Thomas M. Zydowsky

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Water

If a person knows nothing else about chemistry, he or she will likely know that water is H_2O. The chemical formula for water is common knowledge, used in advertisements, elementary school science classes, and casual conversation. But more than just a conversation piece, the formula H_2O can tell a chemist a great deal of information.

For starters, H_2O indicates that water is composed of two hydrogen atoms and one oxygen atom. That this is so can be demonstrated using very simple apparatus—a couple of pieces of wire, a battery, and some tap water. Electrolysis—the decomposition of water molecules with electricity—will result when the wires are connected to the ends of the battery and the other ends are immersed in the water with a small gap between them. One electrode releases bubbles of pure oxygen and the other pure hydrogen. Measuring the volume of gases released reveals that twice as much hydrogen is produced as oxygen. Twice as much gas means two hydrogen atoms for every one oxygen atom. Of course, this is our modern understanding of water. When these experiments were first tried, around 1800, an explanation for the results was not available. But the experiments did force scientists to think about the nature of water.

From our modern understanding of both the formula of water and the Periodic Table, we also know that the hydrogen atoms in water are bound to the oxygen. That is, water is "HOH" and not "HHO." We know that atoms can form either covalent or ionic bonds to give molecules. In water, the interaction of hydrogen and oxygen is a polar covalent bond, meaning that the two elements share a pair of electrons and that each atom contributes one of the electrons in the pair. Since hydrogen is the first element of the Periodic Table, it has only one electron and can form just one covalent bonding interaction. In the case of water, hydrogen bonds by sharing its electron with the oxygen. If hydrogen shared its electron with the other hydrogen atom in this instance, there would be no electron available to interact with the oxygen. Indeed, hydrogen gas, H_2, results when two hydrogen atoms form a covalent bond, and hydrogen gas is very different from water.

A molecular graphic of water molecules evaporating from a solution.

In a pure (nonpolar) covalent bond, both atoms have possession of the electron pair exactly the same amount of time. In a polar covalent bond, there is unequal sharing that results from an inequity in the distribution of the electrons due to the effective nuclear charge on the atoms. This polarization of the O-H interaction is critical to explaining all of the properties of water. It results in water having a dipole with the hydrogens having a slight positive charge and the oxygen having a slight negative charge. (More precisely, the advanced explanation is that the molecular orbital that describes the oxygen-hydrogen interaction has more oxygen character, resulting in a skewed electron distribution.)

If we consider oxygen's position in the Periodic Table, we know that it starts with six valence electrons, and since it has two bonds with hydrogen, two of its electrons are involved in bonding pairs. This means that the oxygen has four electrons remaining. These electrons are organized into two "non-bonding" pairs. That is, the oxygen of water has four pairs of electrons around it—two that are interacting in polar covalent bonds with hydrogen and two that are not interacting when water is in the gaseous state. Four electron pairs means that the atoms adopt a tetrahedral arrangement with the two hydrogens occupying two corners and the electron pairs occupying the other two.

In a perfect tetrahedron, the angle between the hydrogens would be 109.5°, but because the lone pairs occupy a little more space, the experimentally measured angle in water is actually 104.5°.

The presence of two lone pairs plays a very important role in "hydrogen bonding," which is one of the most critical properties of water. The positively charged hydrogen of one water molecule can be attracted to the lone pair of an adjacent molecule, resulting in a weak hydrogen bonding interaction. This bonding is much weaker than the polar covalent bond that holds a water molecule together, but it is a substantial inter-molecular interaction resulting in two water molecules being attracted to one another. Water forms an extended network of hydrogen bonding interactions, with each water molecule capable of both creating and accepting two hydrogen bonds. As a result each and every water molecule in the liquid or solid state is surrounded by four hydrogen bonded neighbors. The presence of hydrogen bonding interactions means:

- that water has an anomalously high melting and boiling point;
- that solid water or ice is less dense than liquid; and
- that water has a high surface tension.

Melting and Boiling Point of Water

Phase changes in matter result because of a change in the translational motion of molecules. A solid is a solid because its molecules are stuck in place. In a liquid, molecules can move past one another but are still closely associated. In a gas, molecules move independent of one another and only occasionally collide. It would make sense then that lighter molecules would shift from a solid to a liquid to a gas at lower temperatures than heavy molecules because they require less energy to get moving. Consider the molecular substances in Table 1.

Hydrogen gas, being the lightest and smallest molecule in the list, has the lowest melting point (−259°C or 14.15 K or −434°F) and boiling point (−253°C or 20.15 K or −423°F). Similarly, of the second row compounds with hydrogen, methane (CH_4) has the lowest melting and boiling points. However, water does not follow this trend. Its melting point is 0°C or 32°F. Its boiling point is 100°C or 212°F. Compared to the other molecules around it or its heavier cousin, hydrogen sulphide (H_2S), water has melting and boiling points that are anomalously high. This is due to the fact that the hydrogen bonds between water molecules must be broken for a phase transition to occur. The extra energy required results in more heat being necessary and a higher temperature.

Density of Ice

Hydrogen bonding interactions between water molecules hold the molecules in place in the solid state. The O-H····O interaction spaces all of the water molecules in an orderly array, much like students sitting in rows of desks. This spacing provides an open structure. When water is in the liquid state, the water molecules hold on to each other through hydrogen bonding interactions, but individual molecules can occupy the space between rows. The result is that at a molecular level, more liquid water molecules can occupy a given volume than when water is in the solid state. More students will fit in a classroom if they are allowed to stand than if they are arranged in nice neat rows. More molecules or more mass in a given volume means a higher density.

PHASE CHANGES FOR SOME COMMON MOLECULAR SUBSTANCES

Substance	Molecular Weight (g/mol)	Melting Point °C	Boiling Point °C
H_2	2.016	−259	−253
N_2	28.01	−210	−196
O_2	32.00	−218	−183
CH_4	16.04	−182	−162
NH_3	17.03	−78	−33
H_2O	18.02	0	100
HF	20.01	−93	20
H_2S	34.08	−86	−60

SOURCE: Adapted from Jones, Loretta, and Atkins, Peter (1999). *Chemistry: Molecules, Matter, and Change.* New York: W. H. Freeman.

Table 1.

The decrease in density between water and ice has a number of important implications for the world around us. Ice floats because it is less dense than liquid water. This is not true of any other liquid/solid equilibrium. Solid methane sinks in liquid methane and solid ammonia sinks in liquid ammonia. Floating ice means that ponds and lakes freeze from the top down, allowing fish and other biota to live protected from the cold weather of winter. If water froze from the bottom up, life as we know it would not have evolved on Earth.

Surface Tension

Surface tension is a bulk property of matter and results in liquid water trying to contract to the smallest possible surface area for a given volume. Surface tension explains why water beads up on the surface of a freshly waxed car and droplets of water in a fog are spherical. The sphere is the shape with the minimum area for a given volume. Surface tension results because of the asymmetry of forces at the surface of liquid water. Water molecules at the surface are missing their hydrogen bonding interactions on one side. They are being "tugged" back into the bulk of solution.

Of course, occasionally water molecules have sufficient energy to leave the surface, resulting in evaporation. Conversely, sometimes water molecules in the gaseous state strike the surface of a drop of water and have insufficient energy to leave again. The result is condensation. The competing rates of evaporation and condensation lead to the formation of clouds and fog, to cloudy mirrors after a shower and iced-up windows on a winter's day.

Surface tension is also critical to capillary action. A surface that is covered in suitable molecules or functional groups, such as a glass surface or the cellulose of paper, will interact with water molecules and can actually draw the molecules out of the bulk. In this case, the interaction with the surface is stronger than the hydrogen bonding interaction between adjacent water molecules. As a result, water will creep up a glass tube or adsorb into paper. The latter is critically important in mopping up a spill or mess.

Universal Solvent

Water is often called the "universal solvent," as it is capable of dissolving a wide range of compounds—from sugars to salt, from DNA to hydrogen. Again, hydrogen bonding interactions play a role. For example, sugar dissolves because of the hydrogen bonding interactions between the hydroxyl groups on the sugar molecules (-OH groups) and the water molecules. But of equal importance to the dissolution of substances in water is water's capacity to act as a dipole. Water's negatively charged oxygen binds to sodium ions in salt while the positively charged hydrogens interact with the chloride ions. The result is that sodium chloride or table salt dissolves into ionic species that are more energetically stable with the sodium and chloride ions surrounded by water.

The ability of water to dissolve a wide variety of substances makes it the ideal medium for living organisms. Water's great solvency is also the reason that water pollution is so pervasive. Almost any substance will dissolve in water, including pesticides, herbicides, industrial waste, household byproducts, and a wide variety of other potentially harmful compounds. Indeed, we rely on the dissolving properties of water to get our clothes clean.

Table 2. Most of the water we use is obtained from rivers and ground water.

Water Source	Water Volume (cubic miles)	Mass (kg)	Percent of Total Water
Oceans	317,000,000	1.335×10^{21}	97.24%
Icecaps, glaciers	7,000,000	2.949×10^{19}	2.14%
Ground water	2,000,000	8.424×10^{18}	0.61%
Fresh-water lakes	30,000	1.264×10^{17}	0.009%
Saline lakes and inland seas	25,000	1.053×10^{17}	0.008%
Soil moisture	16,000	6.740×10^{16}	0.005%
Atmosphere	3,100	1.306×10^{16}	0.001%
Rivers and streams	300	$1{,}264 \times 10^{15}$	0.0001%

SOURCE: Adapted from the U.S. Geological Survey at http://ga.water.usgs.gov/edu/waterdistribution.html.

But the dirt and grime from our clothes must end up somewhere, and that somewhere is in the water that we discharge from our homes. The Law of Conservation of Matter says that matter can be neither created nor destroyed. The atoms and molecules that we dissolve into the water in our washing machines are only being removed to another location.

Dealing with the pollution of water is a huge task, and for too long the philosophy was "the solution to pollution is dilution." Dilution is no longer an acceptable approach, as it just shifts the problem instead of addressing it. Significant effort is being spent in both addressing the real problems of water pollution and in ensuring that we have access to clean water sources. There are many techniques for purifying water, with distillation providing the cleanest and purest water. Unfortunately, distillation requires a lot of energy as it is difficult to overcome the hydrogen bonds between water molecules. Distillation also leaves behind the polluting material, which must be disposed of in a manner that does not allow it to come in contact with water and thus simply dissolve again. The difficulties of maintaining clean water is one of the major challenges facing us in the twenty-first century. For without water, life as we know it would not exist. It is because of the shape and the interactions of that very simple molecule, H_2O, that water is the most essential of all chemical compounds. SEE ALSO GREEN CHEMISTRY; MOLECULAR GEOMETRY; VALENCE BOND THEORY; WATER POLLUTION; WATER QUALITY.

Todd W. Whitcombe

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Water Pollution

Water pollution occurs when undesirable foreign substances are introduced into natural water. The substances may be chemical or biological in nature. Common pollutants include human or animal waste; disease-producing organisms; radioactive materials; toxic **metals** such as lead or mercury; agricultural chemicals such as pesticides, herbicides, or fertilizers; **acid rain**; and high-temperature water discharged from power plants, often called "thermal pollution." Pollutants in water are dangerous for human or animal consumption and harm crops. High temperatures may cause algae to grow rapidly, rendering water unfit for consumption.

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

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

Point sources of pollution, such as an oil leak from a pipeline or chemical waste from a factory, can often be controlled. Nonpoint sources, such as runoff sediment and nitrate-rich water from feedlots represent larger amounts of pollution and are difficult to identify and remedy. Pollution from nonpoint sources may pass into streams or aquifers, covering a wide area.

Although water has been identified on several planets, none has as much water as Earth, of which 70 percent is covered with water. Approximately 97.4 percent of the water on Earth is found in oceans and is too salty for human consumption. An additional 2.6 percent is freshwater found in underground bodies of water called aquifers or frozen in glaciers or polar ice caps. Less than 0.02 percent of Earth's water is present in lakes, rivers, or the atmosphere.

In a few places, water is pure enough to drink directly from wells or springs, but increasingly water must be treated to remove dangerous contaminants, and substances such as chlorine, chloramines, or ozone must be added to kill harmful bacteria.

Pollutants in water are commonly measured and reported as parts per million (ppm) or parts per billion (ppb). A solution that contains 2 grams (0.071 ounces) of lead in 1 million grams (2,205 pounds) of water (1,000 liters, or 264.2 gallons) is a 2 ppm solution. A 1 ppb solution of calcium contains 1 gram (0.036 ounces) of calcium in 1 billion grams (2,205,000 pounds) of water. A concentration of 1 ppm is the same as 1 milligram (3.6×10^{-5} ounces) per liter.

While it is impractical to remove all impurities from water, the Safe Drinking Water Act, passed by the U.S. Congress in 1974, gives the Environmental Protection Agency (EPA) the authority to set limits for harmful contaminants in water. For each substance, the EPA establishes Maximum Contaminant Level Goals (MCLGs), levels at which the substance can be consumed over a long period of time with no known adverse effects. This level is defined as the amount of impurity that could be present in two liters of water drunk by a person weighing 70 kilograms (154 pounds), each day for seventy years, without ill effects. In addition, the EPA sets Maximum Contaminant Levels (MCLs) of substances for exposure at any single time. A single exposure to concentrations of pollutants below the MCL is considered to be harmless. The MCLG of lead is 0; continuous exposure to lead in any concentration is considered hazardous. The MCL of lead is 0.015 ppm. Both the MCLG and MCL of mercury are set at 0.002 ppm.

Specialized analytical equipment allows technicians to monitor pollutants. In the field, pH meters are used to measure acidity and turbidometers measure the presence of suspended solids. Samples taken to laboratories are analyzed by gas **chromatography** to determine the presence of organic

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

These fish were killed as a result of living in polluted water.

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

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

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

compounds such as vinyl chloride, by emission **spectroscopy** to detect **heavy metals**, and by high performance liquid chromatography (HPLC) to detect pesticide residues. Such instruments are capable of detecting as little as one part per trillion of pollutants in water.

For much of history, humans used waterways and bodies of water as waste dumps. When the human population was low, fewer people were exposed to the effects of pollution, and the sources were fewer and produced less pollution. During the **Industrial Revolution** of the nineteenth century, water pollution was recognized as a danger to public health.

Even early settlers were concerned with water quality. Two hundred years before laws were written to protect consumers from lead poisoning, Benjamin Franklin wrote of a family that suffered gastrointestinal pains after drinking water collected from their lead roof. During the trek west, members of wagon trains avoided drinking from stagnant pools, some of which contained large amounts of alkali.

As populations and production grew, industrial and household refuse accumulated, and it became clear that many discarded materials did not simply disappear, but were spread through the water table, absorbed by lower forms of life and passed up the food chain, causing deaths, birth defects, and mental problems. Now, many beaches are closed occasionally or permanently due to pollution, and at a time when populations of fish have decreased, many areas are unsafe for fishing. Water pollution represents an especially dangerous problem in developing nations, which have high populations and manufacturing facilities that do not meet safety standards.

The most dangerous forms of water pollutants include sewage, which frequently contains dangerous pathogenic organisms; oil and hydrocarbons;

heavy metals; radioactive substances; pesticides and herbicides; and corrosive substances such as acids and bases.

In developed countries, few direct sources of water pollution should exist, but homeowners still discharge motor oil, antifreeze, pet waste, and paint into storm sewers, and small manufacturers sometimes ignore proper disposal procedures. In developing countries, businesses and households often discharge wastes directly into streams or ponds that are also used for water supplies. Many sources contaminate water supplies indirectly. Indirect sources of pollution include runoff of waste from feedlots or runoff of agricultural chemicals from farmlands; leaking oil from pipelines, wells, or platforms; and large amounts of sediment from streets and parking lots.

Most industrial operations are required to treat wastewater before discharging it into rivers. Wastes from feedlots are collected in lagoons, settled, collected, and used for fertilizer. Heavy metals and organic compounds from industry are often reclaimed from wastewater and recycled, decreasing manufacturing costs. Sewage from homes undergoes at least two stages of treatment. Primary treatment consists of sedimentation and dyeing of solids, which may be used as fertilizer. Secondary treatment consists of aeration of the remaining liquid, through a process of stirring, trickling over filters, and spraying; aerobic bacteria oxidize much of the remaining organic matter. Tertiary treatment, using antibacterial agents such as chlorine or ozone, may be used to produce effluent water that is safe for further use. SEE ALSO NEUROTOXINS; TOXICITY; WATER; WATER QUALITY.

Dan M. Sullivan

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Water Quality

Next to a supply of air, nothing is so essential to life as a supply of high-quality water. We drink it, cook our food in it, use it as a source of energy, and lift a hundred pounds or so of it each time we stand up. Water carries nutrients in and removes waste materials from our bodies. Contaminated water also spreads numerous diseases.

We judge the quality of water by taste, smell, color, and lack of pathogenic organisms or harmful contaminants. Often bad taste, odor, or color indicates contamination. Most of the water we drink has been treated to remove harmful substances and has had chlorine, ozone, or chloramines added to kill bacteria. Ordinary water contains dissolved gases such as oxygen, nitrogen, carbon dioxide, and other atmospheric components, as well as harmless minerals.

Pollutants are usually present at very low concentrations, commonly measured and reported as parts per million (ppm) or parts per billion (ppb). A solution containing 2 grams (0.071 ounces) of lead in 1 million grams of water (1,000 liters, or 264.2 gallons) is a 2 ppm solution of lead in water. A

1 ppb solution of calcium in water contains 1 gram (0.036 ounces) of calcium in 1 billion grams (2,205,000 pounds) of water. A concentration of 1 ppm is the same as 1 milligram (3.6×10^{-5} ounces) per liter.

It would be impractical and expensive to remove all impurities from water. The Safe Drinking Water Act of 1974 gives the Environmental Protection Agency (EPA) authority to set limits for dangerous contaminants. For each substance, the EPA sets Maximum Contaminant Level Goals (MCLGs), levels at which the substance could be consumed over a long period of time with no known adverse effects. The MCLG is the amount of contaminant that can safely be present in two liters of water drunk each day for seventy years by a person weighing 70 kilograms (154 pounds). In addition, the EPA sets Maximum Contaminant Levels (MCLs), the maximum permissible level of a contaminant in drinking water.

Removing all pollutants from water would be difficult and expensive, but concentrations below the MCL and MCLG are considered harmless. Lead damages kidneys, and chronic exposure to even tiny amounts may cause damage to the nervous system. The MCLG of lead is 0; the EPA maintains that no amount of lead should be consumed for an extended time. The MCL of lead is 0.015 ppm, but consumption of even low levels of lead in water is not recommended. Both the MCLG and MCL of mercury are set at 0.002 ppm.

Technicians use specialized analytical equipment to monitor pollutants. In the field, pH meters are used to measure acidity; very acidic or basic water may be corrosive. Turbidometers measure suspended solids, which may be harmless but often carry or hide pathogenic organisms. In laboratories, samples are subjected to gas **chromatography** to determine the presence of organic compounds such as vinyl chloride, high pressure liquid chromatographs measure pesticide traces, and absorption and emission **spectroscopy** are used to detect **heavy metals**. Such instruments are capable of detecting as little as one part per trillion of pollutants.

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

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

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

Biological tests are also commonly performed on drinking water. Biochemical oxidative demand (BOD) is a measure of the concentration of biodegradable organic matter. While coliform bacteria such as *Eschericia coli* are seldom dangerous themselves, they act as indicator bacteria. Water containing coliforms is likely to contain other, more dangerous pathogens.

The acceptable level of pollutants depends on the use intended. We need not flush toilets or water lawns with water pure enough to drink. River water commonly contains traces of animal wastes that are acceptable for irrigation but must be removed before human consumption. Ocean water too salty for consumption can be used for industrial cooling and may be purified by distillation or reverse osmosis to render it suitable for drinking.

Common pollutants include traces of human or animal waste; disease organisms; radioactive materials; toxic **metals** such as lead or mercury; agricultural chemicals such as pesticides, herbicides, or fertilizers; and high-temperature water discharged from industrial plants. Polluted water may be dangerous to drink, may harm crops, and may cause eutrophication.

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

Metals such as lead, cadmium, chromium, and mercury are toxic even at low concentrations (the MCL for cadmium is 0.005 ppm). Aquatic microorganisms often concentrate toxic materials from soil or water and may

Newly treated water in the Orange County Water Treatment Works, Florida.

convert inorganic substances such as mercury to organic forms such as methylmercury. These organisms may be consumed by fish, which in turn are eaten by animals higher on the food chain, and eventually the toxic materials can find their way into human diets. Organic mercury is sometimes absorbed by the central nervous system. Mercurial wastes discharged into the bay at Minimata, Japan, resulted in birth defects and **neurological** disorders among many children. Even small amounts of lead or mercury may be converted by aquatic microorganisms into toxic organic mercury compounds such as methyl- or dimethylmercury, which, acting as neurotoxins, may be passed up the food chain, eventually causing damage to the central nervous system of humans.

neurologic: of or pertaining to the nervous system

Lead and copper ions in water pose health risks and contribute to the corrosion of pipes and fittings, as does water that is at a high or low pH. Lead solder was banned from pipes in 1986, but much old plumbing still contains a mixture of 50 percent lead and 50 percent tin solder in joints. In plumbing systems having pipes and fittings of two different metals, corrosion may lead to the failure of joints.

Hot water discharged by industries, such as at power plants, and nitrates and phosphates from feedlot runoff cause algae to grow rapidly, rendering water unfit for consumption by humans or farm animals. High-BOD organic matter in sewage, feedlot runoff, or excess fertilizer from farm fields accumulates in ponds and lakes. Oxidative processes then consume so much oxygen that fish and aquatic plants die.

Organic contaminants such as vinyl chloride or hydrocarbons, hormones from animal feed, and pesticides and herbicides often find their way into streams or aquifers. From these sources, the contaminants may make their way into water supplies.

Hard water contains metallic ions, such as magnesium or calcium ions, that interact with soap to form insoluble films or scum. Hardness is not hazardous to health but may form scale in boilers and clog water pipes. Excess calcium and magnesium can be removed by ion exchange water softeners. SEE ALSO GREEN CHEMISTRY; NEUROTOXINS; TOXICITY; WATER; WATER POLLUTION.

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Watson, James Dewey

AMERICAN BIOCHEMIST
1928–

The American biochemist James Dewey Watson was a discoverer of the double-**helical** structure of the deoxyribonucleic acid molecule.

helical: in the form of a helix—a spiral or coil, such as a corkscrew

James D. Watson was born April 6, 1928, in Chicago, Illinois. At age fifteen he entered the University of Chicago. He graduated in 1947 and went on to pursue graduate study in the biological sciences at Indiana University. There he came under the influence of some distinguished scientists, including Nobel laureate Hermann J. Muller, who were instrumental in shifting his interests from natural history toward genetics and biochemistry. In 1950 Watson successfully completed his doctoral research project on the effect of x rays upon the multiplication of **bacteriophages**.

bacteriophages: viruses that attack bacterial cells

Watson spent 1950 and 1951 as a National Research Council fellow in Copenhagen doing postdoctoral work with biochemist Herman Kalckar. Watson had hoped to learn more about the biochemistry of the genetic material deoxyribonucleic acid (**DNA**). These studies proved unproductive. It was not until the spring of 1951, when he heard the English biophysicist

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

Maurice Wilkins speak in Naples on the structure of the DNA molecule, that Watson enthusiastically turned his full attention to the DNA problem.

Watson's next research post at Cavendish Laboratory, Cambridge, England, brought him into contact with the physicist turned biologist Francis Crick. Together they shared an interest in DNA. Thus began the partnership between Watson and Crick that resulted in their joint proposal of the double-helical model of the DNA in 1953. Watson, Crick, and Wilkins shared the 1962 Nobel Prize in physiology or medicine for their DNA studies.

The structure of the giant and complex DNA molecule reveals the physical and chemical basis of heredity. Watson and Crick were convinced that the molecular subunits which made up DNA were arranged in a relatively simple pattern that could be discovered by them. Their mode of operation stressed the conception and construction of large-scale models that would account for the known chemical and physical properties of DNA. To this model-building endeavor Watson contributed the double-helical structure, along with other fruitful, intuitive suggestions, while Crick provided the necessary mathematical and theoretical knowledge. After their work on DNA was completed, Watson and Crick collaborated again in 1957, this time in clarifying the structure of viruses.

After a two-year stay at the California Institute of Technology, Watson accepted a position as professor of biology at Harvard University in 1956 and remained on the faculty until 1976. In 1968 he became the director of the Cold Spring Biological Laboratories but retained his research and teaching position at Harvard. That same year he published The Double Helix, revealing the human story behind the discovery of the DNA structure, including the rivalries and deceits that were practiced by all.

In l989 Watson was appointed the director of the Human Genome Project of the National Institutes of Health. He resigned in 1992 in protest over policy differences in the operation of this massive project. He continued to speak out on various issues concerning scientific research and upheld his strong presence concerning federal policies in supporting research. In addition to sharing the Nobel Prize, Watson received numerous honorary degrees from institutions, including one from the University of Chicago (1961) when Watson was still in his early thirties. He was also awarded the Presidential Medal of Freedom in 1977 by President Jimmy Carter. On July 4, 2000, Watson and Crick were awarded the Philadelphia Liberty Medal. The Liberty Medal was established in 1988 to honor individuals or organizations whose actions represent the founding principles of the United States.

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American biochemist James Dewey Watson, corecipient, with Francis Harry Compton Crick and Maurice Hugh Frederick Wilkins, of the 1962 Nobel Prize in physiology or medicine, "for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material."

FRANCIS CRICK (1916–)

Starting in his childhood in England, Francis Crick developed a fascination with science. After his collaborative work on DNA with James Watson, for which the two received a Nobel Prize, Crick unraveled the mystery of how DNA bases code for the primary sequence of a protein, and in 1957 he introduced its central dogma. Since 1976 Crick has been studying the functions of the human brain.

—Valerie Borek

Weizmann, Chaim

RUSSIAN-BORN BRITISH CHEMIST, PRESIDENT OF ISRAEL
1874–1952

One of the few who have achieved success in two disparate fields, chemist and statesman Chaim Weizmann was born on November 17, 1874, in the small town of Motol, Russia—part of what was known as the Pale of Settlement, an area where Jewish families were allowed to live. Beginning at age four he attended a religious school in which classes were conducted in Yiddish. (He did not learn Russian until he was eleven.) In 1885 he migrated to Pinsk to attend a Russian high school, where he studied chemistry and devoted much of his spare time to Zionist activities. He later became president of the World Zionist Organization (from 1921), president of the Hebrew University in Palestine (from 1932), and the first president, a largely ceremonial position, of the new State of Israel (from its establishment in 1948 until his death).

After university studies in Germany and Switzerland (he earned a Ph.D. in 1899 for research on dyestuffs), he taught as a privatdocent (unsalaried lecturer) at the University of Geneva. He subsequently carried out basic and applied research at the University of Manchester in England. His academic research was supplemented by industrial research. In 1904 he was awarded the first of his 110 patents. He became a British citizen in 1910.

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

During World War I, a search for synthetic rubber in England led to Weizmann's classic work on the fermentation of **glucose**, a sugar containing six carbon atoms, as a source of acetone (1915), urgently needed by the British government for the manufacture of cordite (smokeless powder). Weizmann's use of a fermenting agent to produce acetone followed his discovery of the acid-resistant microorganism *Clostridium acetobutylicum*; this method of acetone production became known as the Weizmann process. At the request of Winston Churchill, then first lord of the admiralty, the Weizmann process was put into operation on an enormous scale in England, Canada, and the United States. The rapid wartime expansion of this process (from a laboratory to an industrial scale) was not only unique among microbiological processes used in industry, but was also the forerunner of the rapid expansion of penicillin production during World War II, as well as of the breadth of operations of many of today's biotechnological processes.

Weizmann knew that his fermentation process yielded chemical compounds containing three and four carbon atoms and predicted that the same process could produce the substances on which modern petrochemical industries are based. He often enunciated the need for countries (especially those poor in natural oil) to replace a petroleum-based chemical industry with one based on fermentation.

The Balfour Declaration (1917), the first formal international recognition of Zionism, was, to some extent, a culmination of Weizmann's scientific and political efforts. His fermentation process, which contributed to the Allies' victory in World War I, was not a direct cause of the declaration but was certainly an indirect one.

During the two decades following World War I, politics replaced chemistry as Weizmann's main pursuit. However, he did pursue scientific research, alongside his political activities, until the end of his life. In his later years (and while president of Israel), he worked at the Weizmann Institute of Science in Rehovot, Israel, where he died on November 9, 1952. In Israel his grave is a place of national pilgrimage. SEE ALSO Starch.

George B. Kauffman

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Werner, Alfred

FRENCH-BORN SWISS CHEMIST
1866–1919

Alfred Werner, the founder of **coordination chemistry**, was born on December 12, 1866, in Mulhouse, Alsace, France (in 1870 annexed to Germany). He was the fourth and last child of Jean-Adam Werner, a foundry worker and locksmith, and his second wife, Salomé Jeanette Tesché, the dominant figure in the Werner household and a member of the wealthy Tesché family. Although most of Werner's articles were published in the German language and in German journals, his cultural and political sympathies remained with France. The spirit of rebellion and resistance to authority that characterized his childhood and adolescence may have contributed to the development of his revolutionary coordination theory.

Swiss chemist Alfred Werner, recipient of the 1913 Nobel Prize in chemistry, "in recognition of his work on the linkage of atoms in molecules by which he has thrown new light on earlier investigations and opened up new fields of research especially in inorganic chemistry."

coordination chemistry: chemistry involving complexes of metal ions surrounded by covalently bonded ligands

Werner attended the École Libre des Frères (1872–1878), and then the École Professionelle (1878–1885), a technical school where he studied chemistry. During his compulsory year of military service in the German army (1885–1886), he audited chemistry lectures at the Technische Hochschule (Technical University) in Karlsruhe. He then attended the Eidgenössisches Polytechnikum, now the Eidgenössische Technische Hochschule (Federal Polytechnic University), in Zurich, Switzerland, from which he received a degree in technical chemistry in 1889. He received his Ph.D. from the University of Zurich in 1890.

Between 1890 and 1893, Werner produced the three most important theoretical papers of his career. His doctoral dissertation (1890, cowritten with his teacher Arthur Hantzsch), a true classic of science writing on the topic of stereochemistry, extended Joseph Achille Le Bel and Jacobus Henricus van't Hoff's concept of the tetrahedral carbon compound (1874) to the nitrogen compound. It explained many puzzling paradoxes of geometrically isomeric, trivalent nitrogen compounds and placed nitrogen compound stereochemistry on a firm theoretical basis.

Werner's second theoretical paper (1891)—his Habilitationsschrift (an original article that was a requirement for teaching at a university)—took a stand against August Kekulé, the supreme architect of structural organic chemistry: It replaced Kekulé's focus on rigidly directed valences with a more flexible theory that viewed affinity as a somewhat cloudlike, attractive force emanating from the center of an atom and acting equally in all directions. During the winter of 1891–1892 Werner worked on thermochemical studies at the Collège de France in Paris with Marcellin Berthelot, but then returned to Zurich to become a privatdocent (unsalaried lecturer) at the Polytechnikum.

In 1893, at age twenty-six, Werner was appointed associate professor at the University of Zurich, largely owing to the almost overnight fame that resulted from his third article—the one that set forth his revolutionary, controversial coordination theory (which had occurred to him in a dream). Although his knowledge of inorganic chemistry was limited, he awoke at 2 A.M. with the solution of a long-standing puzzle centered on what were then called "molecular compounds." An enthralling lecturer and gifted researcher, he was promoted to full professor in 1895.

valence: combining capacity

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

octahedral: relating to a geometric arrangement of six ligands equally distributed around a Lewis acid; literally, eight faces

Werner discarded Kekulé's distinction between **"valence"** compounds, which are eminently explainable using classical valence theory, and "molecular compounds," which are not. Werner proposed a new approach in which the configurations of some compounds—**metal**-ammines (now sometimes called "Werner complexes"), double salts, and metal salt hydrates—were logical consequences of their coordination numbers (a new concept) and two types of valence, primary and secondary. For compounds having coordination number six he postulated an **octahedral** configuration; for those having coordination number four he proposed a square planar or tetrahedral configuration.

Werner's "ionogenic and nonionogenic" bonding concepts predated the currently used models of electrostatic and covalent bonding by a full generation. His ideas encompassed almost the entire field of inorganic chemistry and even found application in organic chemistry, analytical chemistry, and physical chemistry, as well as in biochemistry, geochemistry, and mineralogy. He was one of the first scientists to recognize that stereochemistry was not limited to organic chemistry, but is a general phenomenon. His coordination theory exercised an influence over inorganic chemistry comparable to that of the ideas of Kekulé, Archibald Scott Couper, Le Bel, and van't Hoff over organic chemistry.

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

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

Although today it is known that electronic configuration is the underlying basis for chemical periodicity and the periodic system, Werner (in 1905), relying only on intuition, his vast knowledge of chemistry, and his recognition of analogies among elements, devised a "long form" of the Periodic Table, in which the **lanthanide** elements (inner transition elements or **"rare earths,"** having atomic numbers 58 through 71), occupied a separate place in the table—a characteristic of all modern tables.

In 1913 Werner became the first Swiss chemist to win the Nobel Prize in chemistry, the prize given "in recognition of his work on the linkage of atoms in molecules, by which he has thrown fresh light on old problems and opened new fields of research, particularly in inorganic chemistry."

Shortly thereafter, his health was declining. He died in a Zurich psychiatric hospital, on November 15, 1919. He was not only the founder of modern inorganic stereochemistry, but also one of the most brilliantly innovative chemists of all time. SEE ALSO Coordination Compounds.

George B. Kauffman

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Willstätter, Richard Martin

GERMAN CHEMIST
1872–1942

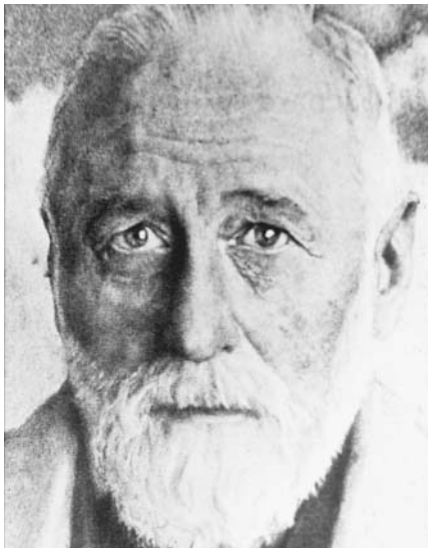
As a boy, Willstätter proved to be a gifted student and tried to attend the best schools in Germany. But since he was a Jew, he was denied admission and was forced to attend public school. After graduation he entered the University of Munich, where he established himself in the scientific community.

He studied the structure of cocaine, the subject of his 1894 doctoral thesis, and analyzed and synthesized such similar plant extracts as *atropine* and *tropine*. One of his teachers greatly disapproved of this line of work, and Willstätter soon turned his attention to quinone chemicals, which are the basis for many dyes, including aniline black. After spending several years as a research assistant in Germany, Willstätter joined the teaching staff of the University of Zurich as a professor in 1905. He became intrigued by chlorophyll and other pigments because of their extreme complexity and their intimate role in plant and animal life. To study these pigments, Willstätter revived the technique of **chromatography**, which had been introduced by Mikhail Tsvett (1872–1920) in 1906.

Before Willstätter began studying **chlorophyll**, scientists thought that each different shade of green in plants was created by a unique chlorophyll molecule. Working with the dried leaves from more than two hundred plants, Willstätter showed that there are two major types of chlorophyll found in land plants—the blue-green, or *a type*, and the yellow-green, or *b type*. Willstätter also discovered a similarity between chlorophyll and hemoglobin—the red pigment that carries oxygen through blood. Both chlorophyll and hemoglobin contain a ring-like structure surrounding a single

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

chlorophyll: active molecules in plants undergoing photosynthesis



German chemist Richard Martin Willstätter, recipient of the 1915 Nobel Prize in chemistry, "for his researches on plant pigments, especially chlorophyll."

atom, but chlorophyll contains a magnesium atom, while the hemoglobin molecule holds an atom of iron. This discovery was the first clue to magnesium's importance as a plant nutrient. Since then, agricultural fertilizers for magnesium-deficient soils have greatly increased crop yields. Willstätter also studied the chemistry of nongreen plant pigments, which give flowers and fruits their bright colors. As a result of Willstätter's research on plant pigments, he was awarded the Nobel Prize in chemistry in 1915.

In 1911 Willstätter had returned to Germany where his work was interrupted by World War I. His friend Fritz Haber (1868–1934) convinced him to help design an effective gas mask for German troops. In 1916 he succeeded his mentor Adolf von Baeyer as chemistry professor at the University of Munich, where he became interested in **enzymes**, a class of biological **catalysts**. Although he succeeded in obtaining pure enzyme samples, he tried to prove, incorrectly, that enzymes were not proteins.

enzyme: protein that controls the reaction in a cell

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

In 1925 prejudice again interfered with Willstätter's career. When his university rejected a qualified Jewish scientist for a professorship, Willstätter resigned in protest. Willstätter was offered many industrial and university positions outside of Germany, but he preferred to live in Germany. He was forced into hiding when the Nazis targeted him for arrest. He was caught when he tried to escape to Switzerland, but was turned over to the Swiss authorities. Willstätter died in Switzerland in 1942.

Wöhler, Friedrich

GERMAN CHEMIST
1800–1882

German chemist Friedrich Wöhler, who isolated the element aluminum.

Friedrich Wöhler was born on July 31, 1800, at Eschersheim, near Frankfurt-am-Main, Hesse. The son of a veterinary surgeon, young Wöhler attended public schools in Frankfurt and passed exams qualifying him for admission to a university in 1820. During his earlier school years Wöhler had acquired an all-consuming interest in practical chemistry and mineralogy. He chose to study medicine at Heidelberg University and obtained an M.D. degree from that institution in 1823.

As a student at Heidelberg Wöhler attended the chemistry lectures of Leopold Gmelin, and the experience prompted Wöhler to choose chemistry over medicine. On the advice of Gmelin, Wöhler spent a year at the laboratory of Jöns Jakob Berzelius in Stockholm, where he honed his experimenter's skills. Wöhler developed a lifelong friendship with Berzelius and acted as the translator into German of Berzelius's influential *Textbook of Chemistry* (1808–1818, published in six parts over ten years) as well as of his annual reports of new developments in chemistry. Wöhler himself was a prolific writer of textbooks; his organic and inorganic chemistry texts went through thirteen and fifteen editions, respectively, in his lifetime.

Returning to Germany in 1825 Wöhler held positions in technical schools in Berlin and Kassel. In 1832 he was offered the professorship of chemistry of the medical faculty at the University of Göttingen, where he stayed until his death (on September 23, 1882). Wöhler is best known for his **synthesis** of urea and the isolation of aluminum. He is also known

synthesis: combination of starting materials to form a desired product for his important studies of the elements boron, silicon, beryllium, and titanium.

Wöhler's synthesis of urea was the result of experiments begun in 1823, in which he investigated the salts of cyanic acid, known as cyanates. In 1824 Wöhler showed that the empirical formula of silver cyanate was AgNCO. Justus von Liebig, who had studied the compound silver fulminate, had come up with the same formula for an entirely different compound. (These two compounds were structural **isomers**.) Isomerism was a novel idea at that time, as it was believed that each compound had a unique formula: No two compounds could have the same formula. (Berzelius had first described the phenomenon of isomerism in 1831.)

isomer: molecules with identical compositions but different structural formulas

In 1828 Wöhler attempted to synthesize ammonium cyanate via the treatment of silver cyanate with aqueous ammonium chloride. The reaction produced a white crystalline solid that did not possess the properties of ammonium cyanate. Wöhler then attempted to synthesize ammonium cyanate using lead cyanate and ammonium hydroxide. This produced the same white powder, but with fewer contaminants so that it could be analyzed. Upon analysis this white powder proved to have the composition and properties of urea, a compound that had been isolated from urine.

$$Pb(OCN)_2 + 2\ NH_3 + H_2O \rightarrow PbO + NH_4OCN \rightarrow H_2NCONH_2$$

Wöhler recognized in the urea he had synthesized the phenomenon of isomerism, and, incidentally, that he had prepared an organic compound outside a living system. At that time it was believed that all organic (carbon-based) compounds could be made within living organisms only. Vitalism was a theory that developed as a reaction to mechanistic explanations of physical phenomena, which were viewed as a threat to belief in the unique nature of life. It held that living processes could not be understood according to totally mechanistic models, and that it was a material invisible force in organisms that made life possible. August W. von Hofmann, in his obituary notice for Wöhler, alleged that it was Wöhler's synthesis of urea that led to the demise of the theory of vitalism.

Wöhler's other major achievement was his isolation of the element aluminum in 1827. Attempts by chemists Humphry Davy and Berzelius to prepare aluminum from alumina (Al_2O_3) via electrolytic decomposition had all failed. Wöhler employed a chemical approach that included the reduction of anhydrous aluminum chloride by potassium **amalgam**, followed by treatment with water. It produced a gray powder that Wöhler was able to identify as the element aluminum.

amalgam: metallic alloy of mercury and one or more metals

$$3K + AlCl_3 \rightarrow Al + 3KCl$$

SEE ALSO ALUMINUM; BERZELIUS, JÖNS JAKOB.

Martin D. Saltzman

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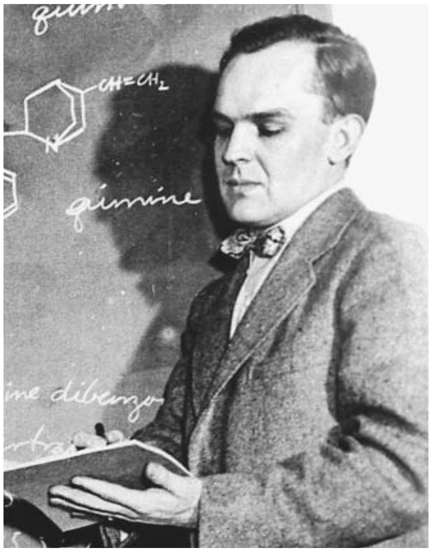
Woodward, Robert Burns

AMERICAN CHEMIST
1917–1979



American chemist Robert Woodward, recipient of the 1965 Nobel Prize in chemistry, "for his outstanding achievements in the art of organic synthesis."

Robert Burns Woodward is generally recognized as the leading organic chemist of the twentieth century. He and his coworkers determined the structures of biologically active natural products, developed theoretical rules for predicting the outcomes of organic reactions, and synthesized some of the most complex molecules known to humans. In 1965 Woodward received the Nobel Prize in chemistry for his "outstanding achievements in the art of organic synthesis."

Woodward was born on April 10, 1917, in Boston, Massachusetts. His father, Arthur Woodward, died of influenza eighteen months later. His mother, Margaret Burns Woodward, remarried, and the family eventually settled in Quincy, Massachusetts. Young Woodward fell in love with chemistry while doing experiments with his boyhood pals in Quincy: He ate, drank, and slept chemistry and dreamed up ways to synthesize the antimalarial drug quinine.

At age sixteen Woodward entered the Massachusetts Institute of Technology (MIT) and raced through their chemistry studies in record time: It took him three years to get his B.S. degree (in 1936), and only one to get his Ph.D. (in 1937). After a summer stint at the University of Illinois, Woodward joined the chemistry department at Harvard University, where, for the next forty-two years, he urged chemists worldwide to accept the creative challenges that organic synthesis had introduced.

Woodward was always attracted to molecules with novel structures or interesting biological activities. He attacked the synthesis of steroids during his years at MIT, and with American chemist Bill Doering in 1944, he published the paper that described the fulfillment of his boyhood dreams: the synthesis of quinine. What Woodward and Doering actually reported was the twenty-step synthesis of a quinotoxine, a molecule whose conversion into quinine had been reported by the German chemist Paul Rabe in 1918. Rabe's reported synthesis of quinine was later discredited, but that in no way diminished the impact of Woodward's beautifully planned synthesis of quinotoxine.

After quinine, Woodward and his coworkers synthesized a series of increasingly complex natural products, such as **reserpine**, **lysergic acid**, **chlorophyll**, **cephalosporin C**, **vitamin B_{12}**, and **erythromycin**. Each synthesis had its own unique set of challenges, but Woodward's insistence on careful planning, great attention to detail, and observation shines through in all of them. He took full advantage of the latest advances in organic stereochemistry and reaction mechanisms and pushed for the use of **spectroscopic** and analytical tools to determine the structures of reaction products. Woodward used the same approach to determine the structures of natural (plant- or animal-derived) and synthetic products. During World War II he was asked to join the team of scientists that was investigating the miracle antibiotic penicillin. In characteristic Woodward fashion, he summarized all of the available chemical and spectroscopic data and was the first to propose the β-lactam structure for penicillin. After penicillin came strychnine, tetracycline, and, with its unprecedented iron-sandwich structure, ferrocene.

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

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

chlorophyll: active molecules in plants undergoing photosynthesis

cephalosporin C: family of antibiotics obtained from a fungus acting in a manner similar to penicillin

vitamin B_{12}: also known as cyanocobalamin; a complex red crystalline compound containing cyanide and cobalt and occurring in the liver; lack of it in the tissues leads to pernicious anaemia.

erythromycin: antibiotic used to treat infections

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

Woodward saw organic synthesis as a way to advance science and to solve practical problems. One need only look to his vitamin B_{12} work to illustrate this. A reaction that Woodward had planned to use as part of the early stages of the synthesis of vitamin B_{12} gave a product with unexpected stereochemistry, leading the perplexed Woodward to look for similar reactions in the organic literature. He found them, and with Roald Hoffmann, a theoretical chemist at Harvard, formulated what are now known as the Woodward-Hoffmann rules for the conservation of orbital symmetry. These rules explained the outcomes of a series of seemingly unrelated chemical reactions and correctly predicted the outcomes of many others. For his contributions to the orbital symmetry rules, Hoffmann shared the 1981 Nobel Prize in chemistry with Kenichi Fukui of Japan, who had reached similar conclusions independently. Woodward died before the 1981 Nobel Prize was awarded, and had he lived longer, he certainly would have received his second Nobel Prize.

Woodward also recognized in the drive of scientists to synthesize molecules something that spoke to the spirit of people. According to Woodward: "The structure known, but not yet accessible by synthesis, is to the chemist what the unclimbed mountain, the uncharted sea, the untilled field, the unreached planet, are to other men" (Woodward, p. 63).

Woodward died from a heart attack on July 8, 1979, but not before teaching generations of chemists the fine art of organic synthesis. SEE ALSO CHEMICAL REACTIONS; ORGANIC CHEMISTRY; PENICILLIN; SYNTHESIS, CHEMICAL.

Thomas M. Zydowsky

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X

Xenon

MELTING POINT: **−111.79°C**

BOILING POINT: **−108.12°C**

DENSITY: **No data available**

MOST COMMON IONS: $HXeO_4^-$, $HXeO_6^{3-}$

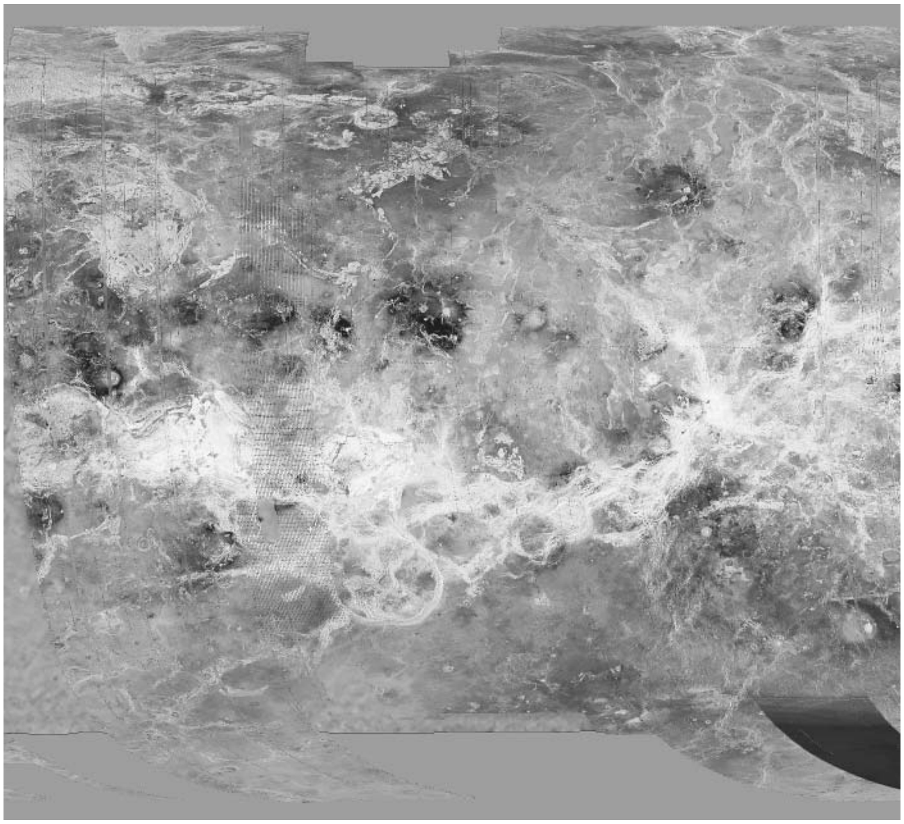
54
Xe
XENON
131.293

Xenon (its name derived from the Greek word *xenos*, meaning "strange"), is the heaviest of the **noble gases**. Discovered in 1898 in London by Sir William Ramsay and Morris Travers while engaged in their investigations of liquid air, xenon accounts for less than 1 ppm of the volume of Earth's atmosphere. It is present in the Sun and in the atmospheres of Mars, Venus, and Mercury.

At room temperature xenon is a colorless, odorless gas. Upon freezing it forms a crystal with a face-centered cubic structure. The chief application of xenon gas is its use in various kinds of lamps. In an electric discharge

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

The gas xenon is present in the atmosphere of Venus.



tube it produces a blue glow. Liquid xenon is used in some particle detectors that are used in space-based research.

nucleosynthesis: creation of heavier elements from lighter elements via fusion reactions in stars

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

fission: process of splitting an atom into smaller pieces

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

Unlike the lighter noble gases, xenon is not produced by **nucleosynthesis** within stars. It is made during supernova explosions. It is also formed on Earth through **radioactive decay** (e.g., of iodine-135) and in **fission** reactions, and it is sometimes found in gases emitted from mineral springs. It has nine stable **isotopes**, of which xenon-129 and xenon-132 are the most abundant (26.4% and 26.9%, respectively).

Also, unlike the lighter noble gases, which are inert, xenon is able to form compounds, mostly with oxygen and fluorine. SEE ALSO NOBLE GASES.

Richard Mowat

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Yalow, Rosalyn Sussman

AMERICAN PHYSICIST AND MEDICAL RESEARCHER
1921–

Rosalyn Sussman Yalow was awarded the Nobel Prize in physiology or medicine in 1977 for her pioneering work in developing the technique known as radioimmunoassay (RIA), a method first applied to the measurement of concentrations in blood of the hormone insulin. Subsequently the use of RIA was extended to include the detection and quantification of a wide range of substances of biological interest, including other hormones, serum proteins, enzymes, viruses, and tumor antigens.

Born on July 19, 1921, in the Bronx, New York, Rosalyn Sussman studied physics and chemistry at New York's Hunter College, graduating in 1941. She was awarded a Ph.D. in **nuclear** physics by the University of Illinois in 1945. Two years earlier she had married fellow physics student Aaron Yalow. For a time in the mid-1940s Rosalyn Yalow worked at the Federal Communications Laboratory in New York, but then returned to Hunter College to teach physics. Her work in medical physics began in 1947 at the Veterans Administration (VA) Hospital in the Bronx, which was then in the process of establishing a radioisotope service.

nuclear: having to do with the nucleus of an atom

American physicist and medical researcher Rosalyn Yalow, corecipient of the 1977 Nobel Prize in physiology or medicine, "for the development of radioimmunoassays of peptide hormones."

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)

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

After designing and building much of the equipment she would need to detect and quantify minute amounts of radioactive substances, Yalow devised studies in the early 1950s that used a radioactive isotope of iodine to investigate a number of physiological processes, including the **metabolism** of proteins. Similar studies monitored changes in insulin levels following the intravenous administration of foreign insulin in both diabetic and nondiabetic patients. The unexpected finding that radiolabeled insulin disappeared more slowly in patients who had received prior insulin injections led Yalow and her colleague Solomon Berson to postulate that the presence of the foreign insulin triggered **antibody** production. They further concluded that the binding of the radiolabeled insulin to these antibodies caused it to be cleared more slowly from the plasma. Yalow and Berson understood that the binding of labeled insulin to a fixed concentration of antibody depends quantitatively on the amount of insulin present. This led directly to their realization that RIA could be used to measure concentrations of the body's own insulin; insulin levels were not easily determined before the advent of RIA in 1959. Although slow to be adopted by others in the field, the technique was further developed by Yalow and Berson such that it could be used to measure concentrations of substances in body tissues and fluids in even infinitesimal concentrations. RIA is now used to identify hypothyroidism in newborn infants. It is also used in blood bank screening, for cancer detection, for the measurement of neurotransmitters, and in forensic chemistry.

Yalow received many honorary doctorates and awards in addition to her 1977 Nobel Prize (which she shared with Andrew Schally and Robert Guillemin). She was the first woman to receive the Albert Lasker Prize for Basic Medical Research (1976). She has served on several national committees, among them the President's Study Group on Careers for Women. Particularly interested in early science education, she frequently visits junior high and high schools. A strong supporter of nuclear medicine and a defender of nuclear power generation, she works to increase public awareness of the major benefits of these technologies. SEE ALSO INSULIN; NUCLEAR MEDICINE.

Mary R. S. Creese

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70
Yb
YTTERBIUM
173.04

Ytterbium

MELTING POINT: **824°C**
BOILING POINT: **1,196°C**
DENSITY: **6.98 g/cm^3**
MOST COMMON IONS: **Yb(III)**

Ytterbium was discovered by the Swiss chemist Jean Charles Galissard de Marignac in 1878 and named after the town of Ytterby, in Sweden (the site of the discovery of the ore with which de Marignac worked). Its primary source is xenotime and monazite ores, which are mixtures of rare earth orthophosphates. In the earth, ytterbium is more abundant than tin. Ytterbium has been found in meteorites, in lunar rock samples, and to a small extent in the oceans.

At room temperature the element is a silvery **metal**. Its ground state electronic configuration is Xe 6 $s^2 4f^{14}$. Ytterbium has many stable **isotopes**: ^{168}Yb, from ^{170}Yb through ^{174}Yb, and ^{176}Yb. Unstable synthetic isotopes have been produced: from ^{151}Yb through ^{167}Yb, as well as ^{169}Yb and ^{175}Yb. Yb(III) compounds, as solids and in solution, are colorless.

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

Ytterbium has no known biological function or toxicity. The metal has been used to improve the strength and mechanical properties of stainless steel. Ytterbium also finds use in fiber amplifiers and fiber optic technologies. Its single absorption band in the infrared at 985 nanometers (3.88×10^{-5} inches) has made it useful in silicon photocells that convert radiant energy directly into electrical energy. In the laboratory, chemists usually start with Yb_2O_3 to make other compounds.

Herbert B. Silber

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Yttrium

MELTING POINT: 1,522°C
BOILING POINT: 3,338°C
DENSITY: 4.469 g/cm^3
MOST COMMON IONS: Y^{3+}

39
Y
YTTRIUM
88.90585

Carl Axel Arrhenius found in 1787 in a quarry near Ytterby, Sweden, a new mineral, which he named ytterbite, and made a summary analysis of it. Further, the Finnish chemist Johan Gadolin isolated in 1794 from this mineral an impure new oxide that he named ytterbia. Friedrich Wöhler partly purified the metal yttrium in 1828, whereas Carl Gustaf Mosander separated the oxides of yttrium, erbium and terbium in 1843 from a mixture of yttria oxide.

Yttrium is trivalent and has an effective ionic radius of 0.900 angstroms. At room temperature the metal structure is hexagonal, close packed, and **diamagnetic**. The metal yttrium has a silver-metallic luster and is relatively stable in air.

One stable **isotope** ^{89}Y and thirty-seven unstable isotopes and **isomers** have been characterized. All four halides of yttrium are known and are commonly prepared by dissolving the oxide in corresponding acids.

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

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

isomer: molecules with identical compositions but different structural formulas

Main yttrium minerals are bastnäsite, kainosite, xerosime, and zinnwaldite. It is estimated that the upper continental crust contains yttrium at a concentration of 20.7 milligrams (0.00073 ounces) per kilogram and seawater contains a total amount of 1,569,000,000 kilograms (1,730,000 tons).

The Porifera *Melythoea* and the tree *Carya* sp. are considered accumulator organisms. Yttrium accumulates in bone and teeth, a phenomenon that is explained by its ability to bind to phosphorus-containing compounds, and to polysaccharides. Nucleic acids have high affinities for yttrium, which binds to phosphate at a ratio of 1:3. Yttrium has stimulatory effects on some fungi and other lower organisms. It is believed that yttrium binds to the surface of cells, without penetrating the cell membrane.

Chaim T. Horovitz

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Yukawa, Hideki

JAPANESE PHYSICIST
1907–1981

Hideki Ogawa (he changed his surname upon marrying Sumi Yukawa) was born on January 23, 1907, in Tokyo. A year thereafter his family moved to Kyoto, where he was raised and attended school. The fifth of seven children of Takuji and Koyuki Ogawa, Hideki came from a family of scholars. Although not inclined to science as he grew up, Hideki happened upon some books on modern physics while in high school and soon found quantum mechanics (which was still a rapidly developing field at the time) very intriguing. As a result of that interest, he entered Kyoto University to study physics in 1926. He received his M.S. from that institution in 1929 and a Ph.D. from Osaka University in 1938.

nuclear: having to do with the nucleus of an atom

Japanese physicist Hideki Yukawa, recipient of the 1949 Nobel Prize in physics, "for his prediction of the existence of mesons on the basis of theoretical work on nuclear forces."

In the 1930s the English physicist James Chadwick had discovered the neutron, and scientists were struggling to determine how protons and neutrons interacted inside a nucleus. A theory known as quantum electrodynamics explains electricity and magnetism by assuming that the force is caused by the interaction of photons with charged particles. Scientists tried to create a similar theory of **nuclear** forces based on the interaction of protons and neutrons with some particle analogous to photons. Yukawa developed a theory for the interaction of massive force carriers, the so-called Yukawa potential, and predicted that, since the nuclear force only acts over distances of 10^{-15} meters (3.281×10^{-14} feet), these unknown force carriers should have a mass about two hundred times as heavy as an electron. Yukawa published his theory in 1935, but since such a particle was unknown at the time, his results were largely ignored.

This situation changed in 1937 when a new particle was discovered in a cosmic-ray experiment. It had the correct mass, and Yukawa's theory was thought to be vindicated as a consequence. However, the details of the theory did not correspond with the measured properties of this particle. In a confusing cosmic coincidence, it turned out that particle was a muon (a heavier electronlike particle), and it was not until 1947 that the pion (as the force carrier came to be known) was discovered. Finally, all the pieces of the theory of nuclear force fell into place, and in 1949 Yukawa received the Nobel Prize in physics.

Yukawa had left Osaka in 1948 to work in the United States. However, in 1953 he returned home to Kyoto to become director of a new interuniversity research institute housed in an academic building named for him. He retired from this position in 1970 and died in Kyoto on September 8, 1981. see also Chadwick, James.

Michael J. Fosmire

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Zeolites

Zeolites are a large group of natural and synthetic hydrated aluminum silicates. They are characterized by complex three-dimensional structures with large, cagelike cavities that can accommodate sodium, calcium, or other cations (positively charged atoms or atomic clusters); water molecules; and even small organic molecules. Ions and molecules in the cages can be removed or exchanged without destroying the aluminosilicate framework. Zeolites find wide use as ion-exchange agents, catalysts, and molecular filters in a range of industrial processes. The word "zeolite" comes from the Greek for "boiling stone," because of the early observation that zeolites release water when heated. As their compositions are not fixed, they are examples of nonstoichiometric compounds.

The Structures of Zeolites

The atomic structures of zeolites are based on three-dimensional frameworks of silica and alumina tetrahedra, that is, silicon or aluminum ions surrounded by four oxygen ions in a tetrahedral configuration. Each oxygen is bonded to two adjacent silicon or aluminum ions, linking them together. Clusters of tetrahedra form boxlike polyhedral units that are further linked to build up the entire framework. In different zeolites the polyhedral units may be equidimensional, sheetlike, or chainlike. The aluminosilicate framework of a zeolite has a negative charge, which is balanced by the cations housed in the cagelike cavities. Zeolites have much more open, less dense structures than other silicates; between 20 and 50 percent of the volume of a zeolite structure is voids. Silicates such as zeolites that have three-dimensional frameworks of tetrahedra are termed tectosilicates. Besides the zeolites, other tectosilicates include quartz and feldspars.

Natural Zeolites

There are about forty-five natural zeolites. They form in a number of relatively low temperature geologic environments. Gas pockets in basalt and other volcanic rocks may contain dramatic crystal groups of zeolites. Economically more important are the fine-grained zeolites such as clinoptilolite $(Na, K)AlSi_5O_{12} \cdot 3H_2O$ formed by the alteration of fine-grained volcanic deposits by underground water. These are mined in the western United States and Mexico. Zeolites also form in alkaline desert lake sediments, in alkaline soils in deserts, and in marine sediments. Zeolites occur in low-temperature metamorphic rocks in geologically young regions of mountain building, such as South Island, New Zealand.

Synthetic Zeolites

Although some natural zeolites occur in large amounts, they offer only a limited range of atomic structures and properties. Synthetic zeolites have a wider range of properties and larger cavities than their natural counterparts. They were first produced in the 1950s. Today more than 100 different zeolites have been made, and the annual production of synthetic zeolites exceeds 12,000 tons. Zeolites are manufactured in a number of ways; one important technique involves mixing sodium, aluminum, and silica chemicals with steam to create a gel (an amorphous, noncrystalline, water-rich solid). The gel is aged, then heated to about 90°C (194°F). Another technique uses kaolin clay that has been heated in a furnace until it begins to melt, then chilled and ground to powder. This powder is mixed with sodium salts and water, aged, and heated. In all the **synthesis** methods, the zeolite produced depends on the compositions of the starting materials and the conditions of reaction, including acidity, temperature, and water pressure.

synthesis: combination of starting materials to form a desired product

Uses of Zeolites

The uses of zeolites derive from their special properties: They can interact with water to absorb or release ions (ion exchange); they can selectively absorb ions that fit the cavities in their structures (molecular sieves); they can hold large molecules and help them break into smaller pieces (**catalytic** cracking). Zeolites are used as water softeners, to remove calcium ions, which react with soap to form scum. The water is filtered through a sodium-bearing zeolite, which absorbs the calcium and releases sodium ions into the water. When the zeolite can absorb no more calcium, it may be recharged by flushing it with **brine** (a saturated sodium chloride solution), which forces out the calcium ions and replaces them with sodium. At the Hanford Nuclear Facility in Richland, Washington, radioactive strontium-90 (Sr^{90}) and cesium-137 (Cs^{137}) have been removed from radioactive waste solutions by passing them through tanks packed with the natural zeolite clinoptilolite. Zeolites have also been used to clean radioactive wastes from the Three Mile Island nuclear power plant site and elsewhere. In addition, clinoptilolite is used to clean ammonium ions (NH_4^+) from sewage and agricultural wastewater.

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

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

Sulfur dioxide (SO_2) is a pollutant produced by burning high-sulfur coal. It is a major cause of **acid rain**. Natural zeolites are the most effective filters yet found for absorbing sulfur dioxide from waste gases. As efforts to improve air quality continue, zeolites can be used to help purify the gases from power plants that burn high-sulfur coal from the Ohio River Valley and other regions.

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

Industrial applications make use of synthetic zeolites of high purity, which have larger cavities than the natural zeolites. These larger cavities enable synthetic zeolites to absorb or hold molecules that the natural zeolites do not. Some zeolites are used as molecular sieves to remove water and nitrogen impurities from natural gas. Because of their ability to interact with organic molecules, zeolites are important in refining and purifying natural gas and petroleum chemicals. The zeolites are not affected by these processes, so they are acting as catalysts. Zeolites are used to help break down large organic molecules found in petroleum into the smaller molecules that make up gasoline, a process called catalytic cracking. Zeolites are also used in hydrogenating vegetable oils and in many other industrial processes involving organic compounds. SEE ALSO Green Chemistry; Petroleum; Stoichiometry.

Peter B. Leavens

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Zinc

MELTING POINT: 419°C
BOILING POINT: 907°C
DENSITY: 7.14 g/cm^3
MOST COMMON IONS: Zn^{2+}

30
Zn
ZINC
65.39

Like many **transition metals**, zinc has been known in impure form since ancient times. Brass (copper and zinc) coins were used by Egyptians and Palestinians as early as 1400 B.C.E. The first purification of zinc probably occurred during India in the thirteenth century C.E. Although the origin of the name is unknown, it has been suggested that it derives from the German word *Zincke*, meaning "spike" or "tooth."

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

Zinc is a **trace element** (with an abundance of 0.0076%) in Earth's crust. Like the other elements in its family, zinc is found predominantly as a sulfide compound (ZnS). Pure zinc is a silver-white solid at room temperature. Like other **metals**, zinc conducts electricity and can be formed into wires or sheets. Some properties of zinc are quite different from those of the other transition metals—namely, its relatively low melting point, boiling point, and density. These different properties are attributed to zinc's full outermost **subshell** of electrons, which also causes it to be relatively unreactive.

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

subshell: electron energy sublevel, of which there are four: s, p, d, and f

Due to the low reactivity of zinc, its most common use is in anticorrosion coatings. Zinc is also often used to form **alloys**, including brass and commercial bronze. Pennies minted after 1983 are made of a core of zinc surrounded by copper. Historically, zinc was used by Alessandro Volta in 1800 to produce

alloy: mixture of two or more elements, at least one of which is a metal the first battery. Zinc ions, due to their low reactivity, are important biologically. In animals zinc is the most abundant metallic **cofactor**; it is used by insulin in the regulation of **glucose** consumption and by hydrolytic enzymes. An adult human body contains 2 to 3 grams (0.071–0.106 ounces) of zinc. SEE ALSO COFACTORS; VOLTA, ALESSANDRO.

Thomas B. Rauchfuss
Amanda Lawrence

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cofactor: inorganic component that combines with an apoenzyme to form a complete functioning enzyme

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

Zirconium

40
Zr
ZIRCONIUM
91.224

MELTING POINT: **185°C**
BOILING POINT: **4,375°C**
DENSITY: **6.4 g/cm^3**
MOST COMMON IONS: **Zr^{4+}**

Zirconium was discovered by the German chemist Martin H. Klaproth in 1789. The principal ore of zirconium is zircon, which is widely distributed in nature as beach sands, particularly in Australia and India. Zirconium is the nineteenth most abundant element in the earth's crust (at approximately 0.03%). Zircon is a silicate of formula $ZrSiO_4$ and occurs as the gemstones hyacinth and zirconite. Synthetic gemstones are prepared from zircon and from the oxide ZrO_2. Zirconium **metal** is difficult to produce. Its production requires treatment of the **tetrachloride** $ZrCl_4$ with magnesium metal. Zirconium metal is silvery-gray, **ductile**, and malleable.

Zirconium's major use is as **cladding** for **nuclear** reactors. It is ideal for this use, as it has a limited ability to capture neutrons, strength at elevated temperatures, considerable corrosion resistance, and satisfactory neutron damage resistance. Almost all ores of zirconium contain about 2 percent of zirconium's sister element, hafnium (Hf). Hafnium readily absorbs neutrons and therefore must be completely separated and removed from zirconium before either element can be used in nuclear reactors. A major task of the **Manhattan Project** was the separation of hafnium from zirconium. The elements are the two most chemically similar in the Periodic Table. The recovered hafnium metal is used to make the control rods of nuclear reactors, as the metal readily absorbs neutrons.

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

tetrachloride: term that implies a molecule has four chlorine atoms present

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

cladding: protective material surrounding a second material, which is frequently tubes filled with uranium dioxide pellets in a nuclear reactor

nuclear: having to do with the nucleus of an atom

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

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

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

phase: homogeneous state of matter

Zirconium oxide, or zirconia, occurs as the mineral baddeleyite, but zirconium oxide is obtained commercially mainly via its recovery from zircon. Zircon is treated with molten sodium hydroxide to dissolve the silica. Zirconia is used as a ceramic, but it must be **doped** with about 10 percent CaO or Y_2O_3 to stabilize it in its face-centered cubic form. Zirconia is **monoclinic**, meaning that it has one oblique intersection of crystallographic axes, but it undergoes a **phase** change at about 1,100°C (2,012°F), its crystal structure becoming tetragonal, and above 2,300°C (4,172°F) it becomes cubic. To

Zirconium is found in beach sand, such as on this beach in Australia.

prevent expansion and shrinkage across the 1,100°C phase change (which produces cracking), the stabilized form of zirconia is used, as it does not change phase until very high temperatures are reached. Stabilized zirconia is used to regulate the air-fuel mixtures in automobiles, as it is an **oxide ion conductor**. It generates an electric potential based on the amount of oxygen in the fuel and can adjust the mixture by electrical control of valves to ensure proper fuel burning.

The most important soluble compound of zirconium is zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, but this compound does not contain the zirconyl ion ZrO^{2+}. It is a tetramer of composition $[Zr(OH)_2 \cdot 4H_2O]_4^{8+}$, prone to polymerize to larger species as pH increases, forming hydrous zirconia, $ZrO_x(OH)_y \cdot nH_2O$. Other important soluble salts are the sulfate, $Zr(SO_4)_2 \cdot 4H_2O$, and the nitrate, $Zr(NO_3)_4 \cdot 5H_2O$, isolated from strongly acidic solutions. Both zirconium and titanium form **organometallic compounds** that are important catalysts in the conversion of ethylene to polyethylene. SEE ALSO HAFNIUM; NUCLEAR CHEMISTRY; MANHATTAN PROJECT; ORGANOMETALLIC COMPOUNDS.

oxide ion conductor: series of oxides of various compounds in perovskite structure—especially of interest in high-temperature fuel cells

organometallic compound: compound containing both a metal (transition) and one or more organic moieties

Abraham Clearfield

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Zsigmondy, Richard Adolf

AUSTRIAN CHEMIST
1865–1929

Richard Zsigmondy received the 1925 Nobel Prize in chemistry for his elucidation of the nature of colloidal suspensions. With Henry Siedentopf (1872–1940), he invented, used, and promoted the ultramicroscope. Zsigmondy and others used ultramicroscopic studies of colloidal suspensions to

Austrian chemist Richard Adolf Zsigmondy, recipient of the 1925 Nobel Prize in chemistry, "for his demonstration of the heterogeneous nature of colloid solutions and for the methods he used, which have since become fundamental in modern colloid chemistry."

convince influential skeptics that molecules are real and that matter is discontinuous at the molecular level.

Zsigmondy was born in Vienna, Austria, the fourth child of Irma von Szakmáry and Adolf Zsigmondy. Both parents encouraged chemical and physical experiments at home for their children. Young Zsigmondy studied chemistry in Vienna and Munich. Between 1883 and 1887 he worked at a glass factory in Bohemia, investigating luster and color in glasses. The University of Erlangen awarded him a doctorate degree in 1889. From 1890 to 1892 he worked in Berlin with August Kundt (1839–1894), studying the phenomenon of colors appearing on porcelain when suspensions of colloidal gold were applied before firing.

Beginning in 1893, Zsigmondy taught chemical technology and at the same time continued his own research on colloidal gold at the Technische Hochshule in Graz. He formed associations with glassmakers at the Schott Glass Company in Jena. The Schott Glass Company was famous for its making of glass scientific apparatus, including optical instruments. Zsigmondy left Graz in 1897 and became part of the Schott laboratory, where he conducted systematic investigations of colored glasses as colloidal systems.

Zsigmondy needed new types of optical instruments for his experiments. At the Schott laboratory, he had a hand in designing and constructing such instrumentation. Siedentopf joined the laboratory in 1899, and there he and Zsigmondy created the ultramicroscope. The Carl Zeiss Company, also in Jena, manufactured and sold the instruments.

Just as individual dust particles suspended in air can be seen and counted in a beam of sunlight, so individual colloidal particles can be seen and counted when a sample is illuminated in an ultramicroscope. In each case, the best viewing direction is **perpendicular** to the direction of illumination. Zsigmondy used **aqueous solutions** of colloidal gold as model systems. He prepared colloidal gold by reducing solutions of gold chloride with **formaldehyde**. Knowing the mass of gold in a known volume of solution and using the ultramicroscope to count the number of colloidal particles in that volume, he determined the molecular weight of the gold colloid.

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

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

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

Zsigmondy extended his observations to a wide range of important colloids—proteins, soaps, dyestuffs, clays, and polysaccharides. He was an influential leader in colloid physical chemistry throughout the first quarter of the twentieth century. SEE ALSO COLLOIDS; DYES; PROTEINS; SOAP.

George Fleck

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Zwitterions

Zwitterions (the word is derived from the German for "hybrid ion") are ions that are electrically neutral overall but contain nonadjacent regions of positive and negative charges; they are sometimes referred to as "dipolar ions." The best-known examples of zwitterions are the free amino acids found in cells.

An examination of the general structure of an amino acid reveals that there are two parts, or groups, of the molecule that can function as an acid/base pair, the –COOH and $–NH_2$ groups. At pH values near neutrality, a protein transfer reaction takes place that results in the –COOH becoming $–COO^-$ and the $–NH_2$ becoming $–NH_3{}^+$. A large favorable (stabilizing) **electrostatic interaction** now develops between these two parts of the molecule. This interaction is favorable enough to shift the **equilibrium** constant for the proton transfer reaction toward the formation of the charged species, by a factor of between 10- and 50-fold. In addition to the favorable electrostatic interaction between the charged regions, these same charged regions have very favorable electrostatic interactions with surrounding water molecules. Water molecules solvate these regions of the amino acid in a manner very similar to their solvation of cations and **anions**.

The physical properties of crystalline amino acids are consistent with their existence as zwitterions. Their melting points are relatively high, often above 200ºC (392°F), and they are far more soluble in water than in **nonpolar** solvents such as ether or chloroform. Measured dipole moments for crystalline amino acids are fairly large, reflecting the significant degree of charge separation. SEE ALSO AMINO ACID.

Matthew A. Fisher

electrostatic interaction: force that arises between electrically charged particles or regions of particles

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

anion: negatively charged chemical unit, like Cl^-, $CO_3{}^{2-}$, or NO^{3-}

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

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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

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