ULLMANN'S

Energy: Resources, Processes, Products

Volume 3

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Volume 2

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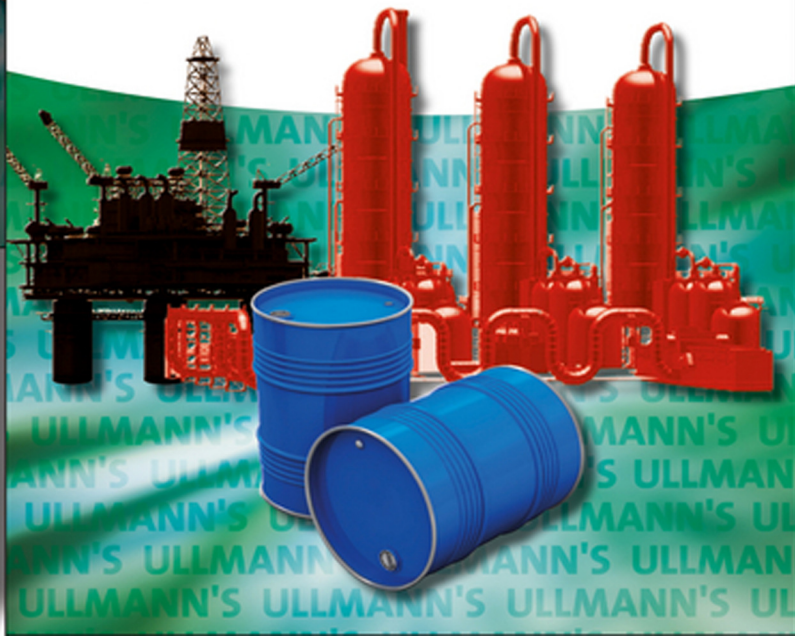
Energy: Resources, Processes, Products

Volume 1

Ullmann's Energy: Resources, Processes, Products

Ullmann's Energy: Resources, Processes, Products

Preface

This handbook features selected articles from the 7th edition of *ULLMANN'S Encyclopedia of Industrial Chemistry*, including newly written articles that have not been published in a printed edition before. True to the tradition of the ULLMANN'S Encyclopedia, products and processes are addressed from an industrial perspective, including production figures, quality standards and patent protection issues where appropriate. Safety and environmental aspects which are a key concern for modern process industries are likewise considered.

More content on related topics can be found in the complete edition of the ULLMANN'S Encyclopedia.

About ULLMANN'S

ULLMANN'S Encyclopedia is the world's largest reference in applied chemistry, industrial chemistry, and chemical engineering. In its current edition, the Encyclopedia contains more than 30,000 pages, 15,000 tables, 25,000 figures, and innumerable literature sources and cross-references, offering a wealth of comprehensive and well-structured information on all facets of industrial chemistry.

1,100 major articles cover the following main areas:

- Agrochemicals
- Analytical Techniques
- Biochemistry and Biotechnology
- Chemical Reactions
- Dyes and Pigments
- Energy
- Environmental Protection and Industrial Safety
- Fat, Oil, Food and Feed, Cosmetics
- Inorganic Chemicals
- Materials
- Metals and Alloys
- Organic Chemicals
- Pharmaceuticals
- Polymers and Plastics
- Processes and Process Engineering
- Renewable Resources
- Special Topics

First published in 1914 by Professor Fritz Ullmann in Berlin, the *Enzyklopädie der Technischen Chemie* (as the German title read) quickly became the standard reference work in industrial chemistry. Generations of chemists have since relied on ULLMANN'S as their prime reference source. Three further German editions followed in 1928–1932, 1951–1970, and in 1972–1984. From 1985 to 1996, the 5th edition of ULLMANN'S Encyclopedia of Industrial Chemistry was the first edition to be published in English rather than German language. So far, two more complete English editions have been published; the 6th edition of 40 volumes in 2002, and the 7th edition in 2011, again comprising 40 volumes. In addition, a number of smaller topic-oriented editions have been published.

Since 1997, *ULLMANN'S Encyclopedia of Industrial Chemistry* has also been available in electronic format, first in a CD-ROM edition and, since 2000, in an enhanced online edition. Both electronic editions feature powerful search and navigation functions as well as regular content updates.

Contents

Symbols and Units

Symbols and units agree with SI standards (for conversion factors see page XI). The following list gives the most important symbols used in the encyclopedia. Articles with many specific units and symbols have a similar list as front matter.

Symbol	Unit	Physical Quantity
a_B		activity of substance B
A_r		relative atomic mass (atomic weight)
A	m^2	area
c_B	mol/m^3, mol/L (M)	concentration of substance B
C	C/V	electric capacity
c_p, c_v	$J\,kg^{-1}\,K^{-1}$	specific heat capacity
d	cm, m	diameter
d		relative density ($\varrho/\varrho water$)
D	m^2/s	diffusion coefficient
D	Gy (=J/kg)	absorbed dose
e	C	elementary charge
E	J	energy
E	V/m	electric field strength
E	V	electromotive force
E_A	J	activation energy
f		activity coefficient
F	C/mol	Faraday constant
F	N	force
g	m/s^2	acceleration due to gravity
G	J	Gibbs free energy
h	m	height
$\hbar$	$W{\cdot}s^2$	Planck constant
H	J	enthalpy
I	A	electric current
I	cd	luminous intensity
k	(variable)	rate constant of a chemical reaction
k	J/K	Boltzmann constant
K	(variable)	equilibrium constant
l	m	length
m	g, kg, t	mass
M_r		relative molecular mass (molecular weight)
n_D^{20}		refractive index (sodium D-line, 20 °C)
n	mol	amount of substance
N_A	mol^{-1}	Avogadro constant ($6.023 \times 10^{23}\,mol^{-1}$)
P	Pa, bar[*]	pressure
Q	J	quantity of heat
r	m	radius
R	$J K^{-1}\,mol^{-1}$	gas constant
R	Ω	electric resistance
S	J/K	entropy
t	s, min, h, d, month, a	time
t	°C	temperature
T	K	absolute temperature
u	m/s	velocity
U	V	electric potential

Symbols and Units (Continued from p. IX)

Symbol	Unit	Physical Quantity
U	J	internal energy
V	m^3, L, mL, µL	volume
w		mass fraction
W	J	work
x_B		mole fraction of substance B
Z		proton number, atomic number
α		cubic expansion coefficient
α	$Wm^{-2}K^{-1}$	heat-transfer coefficient (heat-transfer number)
α		degree of dissociation of electrolyte
$[\alpha]$	10^{-2}deg cm^2g^{-1}	specific rotation
η	Pa·s	dynamic viscosity
θ	°C	temperature
$\varkappa$		c_p/c_v
λ	$Wm^{-1}K^{-1}$	thermal conductivity
λ	nm, m	wavelength
μ		chemical potential
ν	Hz, s^{-1}	frequency
ν	m^2/s	kinematic viscosity (η/ϱ)
π	Pa	osmotic pressure
ϱ	g/cm^3	density
σ	N/m	surface tension
τ	Pa (N/m^2)	shear stress
φ		volume fraction
χ	Pa^{-1} (m^2/N)	compressibility

[*]The official unit of pressure is the pascal (Pa).

Conversion Factors

SI unit	Non-SI unit	From SI to non-SI multiply by
Mass		
kg	pound (avoirdupois)	2.205
kg	ton (long)	9.842×10^{-4}
kg	ton (short)	1.102×10^{-3}
Volume		
m^3	cubic inch	6.102×10^4
m^3	cubic foot	35.315
m^3	gallon (U.S., liquid)	2.642×10^2
m^3	gallon (Imperial)	2.200×10^2
Temperature		
°C	°F	$°C \times 1.8 + 32$
Force		
N	dyne	1.0×10^5
Energy, Work		
J	Btu (int.)	9.480×10^{-4}
J	cal (int.)	2.389×10^{-1}
J	eV	6.242×10^{18}
J	erg	1.0×10^7
J	kW·h	2.778×10^{-7}
J	kp·m	1.020×10^{-1}
Pressure		
MPa	at	10.20
MPa	atm	9.869
MPa	bar	10
kPa	mbar	10
kPa	mm Hg	7.502
kPa	psi	0.145
kPa	torr	7.502

Powers of Ten

E (exa)	10^{18}	d (deci)	10^{-1}
P (peta)	10^{15}	c (centi)	10^{-2}
T (tera)	10^{12}	m (milli)	10^{-3}
G (giga)	10^{9}	μ (micro)	10^{-6}
M (mega)	10^{6}	n (nano)	10^{-9}
k (kilo)	10^{3}	p (pico)	10^{-12}
h (hecto)	10^{2}	f (femto)	10^{-15}
da (deca)	10	a (atto)	10^{-18}

Abbreviations

The following is a list of the abbreviations used in the text. Common terms, the names of publications and institutions, and legal agreements are included along with their full identities. Other abbreviations will be defined wherever they first occur in an article. For further abbreviations, see page IX, Symbols and Units; page XVII, Frequently Cited Companies (Abbreviations), and page XVIII, Country Codes in patent references. The names of periodical publications are abbreviated exactly as done by Chemical Abstracts Service.

abs.	absolute	BGA	Bundesgesundheitsamt (Federal Republic of Germany)
a.c.	alternating current		
ACGIH	American Conference of Governmental Industrial Hygienists	BGB1.	Bundesgesetzblatt (Federal Republic of Germany)
ACS	American Chemical Society	BIOS	British Intelligence Objectives Subcommittee Report (see also FIAT)
ADI	acceptable daily intake		
ADN	accord européen relatif au transport international des marchandises dangereuses par voie de navigation interieure (European agreement concerning the international transportation of dangerous goods by inland waterways)	BOD	biological oxygen demand
		bp	boiling point
		B.P.	British Pharmacopeia
		BS	British Standard
		ca.	circa
		calcd.	calculated
ADNR	ADN par le Rhin (regulation concerning the transportation of dangerous goods on the Rhine and all national waterways of the countries concerned)	CAS	Chemical Abstracts Service
		cat.	catalyst, catalyzed
		CEN	Comité Européen de Normalisation
		cf.	compare
ADP	adenosine 5′-diphosphate	CFR	Code of Federal Regulations (United States)
ADR	accord européen relatif au transport international des marchandises dangereuses par route (European agreement concerning the international transportation of dangerous goods by road)		
		cfu	colony forming units
		Chap.	chapter
		ChemG	Chemikaliengesetz (Federal Republic of Germany)
AEC	Atomic Energy Commission (United States)	C.I.	Colour Index
		CIOS	Combined Intelligence Objectives Subcommitee Report (see also FIAT)
a.i.	active ingredient		
AIChE	American Institute of Chemical Engineers	CLP	Classification, Labelling and Packaging
		CNS	central nervous system
AIME	American Institute of Mining, Metallurgical, and Petroleum Engineers	Co.	Company
		COD	chemical oxygen demand
ANSI	American National Standards Institute	conc.	concentrated
AMP	adenosine 5′-monophosphate	const.	constant
APhA	American Pharmaceutical Association	Corp.	Corporation
API	American Petroleum Institute	crit.	critical
ASTM	American Society for Testing and Materials	CSA	Chemical Safety Assessment according to REACH
ATP	adenosine 5′-triphosphate	CSR	Chemical Safety Report according to REACH
BAM	Bundesanstalt für Materialprüfung (Federal Republic of Germany)		
		CTFA	The Cosmetic, Toiletry and Fragrance Association (United States)
BAT	Biologischer Arbeitsstofftoleranzwert (biological tolerance value for a working material, established by MAK Commission, see MAK)		
		DAB	Deutsches Arzneibuch, Deutscher Apotheker-Verlag, Stuttgart
		d.c.	direct current
		decomp.	decompose, decomposition
Beilstein	Beilstein's Handbook of Organic Chemistry, Springer, Berlin – Heidelberg – New York	DFG	Deutsche Forschungsgemeinschaft (German Science Foundation)
BET	Brunauer – Emmett – Teller	dil.	dilute, diluted

DIN	Deutsche Industrienorm (Federal Republic of Germany)
DMF	dimethylformamide
DNA	deoxyribonucleic acid
DOE	Department of Energy (United States)
DOT	Department of Transportation – Materials Transportation Bureau (United States)
DTA	differential thermal analysis
EC	effective concentration
EC	European Community
ed.	editor, edition, edited
e.g.	for example
emf	electromotive force
EmS	Emergency Schedule
EN	European Standard (European Community)
EPA	Environmental Protection Agency (United States)
EPR	electron paramagnetic resonance
Eq.	equation
ESCA	electron spectroscopy for chemical analysis
esp.	especially
ESR	electron spin resonance
Et	ethyl substituent ($-C_2H_5$)
et al.	and others
etc.	et cetera
EVO	Eisenbahnverkehrsordnung (Federal Republic of Germany)
exp (. . .)	$e^{(. . .)}$, mathematical exponent
FAO	Food and Agriculture Organization (United Nations)
FDA	Food and Drug Administration (United States)
FD&C	Food, Drug and Cosmetic Act (United States)
FHSA	Federal Hazardous Substances Act (United States)
FIAT	Field Information Agency, Technical (United States reports on the chemical industry in Germany, 1945)
Fig.	figure
fp	freezing point
Friedländer	P. Friedländer, Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige Vol. 1–25, Springer, Berlin 1888–1942
FT	Fourier transform
(g)	gas, gaseous
GC	gas chromatography
GefStoffV	Gefahrstoffverordnung (regulations in the Federal Republic of Germany concerning hazardous substances)
GGVE	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit der Eisenbahn

	(regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by rail)
GGVS	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter auf der Straße (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by road)
GGVSee	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit Seeschiffen (regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by sea-going vessels)
GHS	Globally Harmonised System of Chemicals (internationally agreed-upon system, created by theUN, designed to replace the various classification and labeling standards used in different countries by using consistent criteria for classification and labeling on a global level)
GLC	gas-liquid chromatography
Gmelin	Gmelin's Handbook of Inorganic Chemistry, 8th ed., Springer, Berlin – Heidelberg –New York
GRAS	generally recognized as safe
Hal	halogen substituent ($-F$, $-Cl$, $-Br$, $-I$)
Houben-Weyl	Methoden der organischen Chemie, 4th ed., Georg Thieme Verlag, Stuttgart
HPLC	high performance liquid chromatography
H statement	hazard statement in GHS
IAEA	International Atomic Energy Agency
IARC	International Agency for Research on Cancer, Lyon, France
IATA-DGR	International Air Transport Association, Dangerous Goods Regulations
ICAO	International Civil Aviation Organization
i.e.	that is
i.m.	intramuscular
IMDG	International Maritime Dangerous Goods Code
IMO	Inter-Governmental Maritime Consultive Organization (in the past: IMCO)
Inst.	Institute
i.p.	intraperitoneal
IR	infrared
ISO	International Organization for Standardization
IUPAC	International Union of Pure and Applied Chemistry
i.v.	intravenous

Kirk-Othmer	Encyclopedia of Chemical Technology, 3rd ed., 1991–1998, 5th ed., 2004–2007, John Wiley & Sons, Hoboken	no.	number
(l)	liquid	NOEL	no observed effect level
Landolt-Börnstein	Zahlenwerte u. Funktionen aus Physik, Chemie, Astronomie, Geophysik u. Technik, Springer, Heidelberg 1950–1980; Zahlenwerte und Funktionen aus Naturwissenschaften und Technik, Neue Serie, Springer, Heidelberg, since 1961	NRC	Nuclear Regulatory Commission (United States)
		NRDC	National Research Development Corporation (United States)
		NSC	National Service Center (United States)
		NSF	National Science Foundation (United States)
		NTSB	National Transportation Safety Board (United States)
LC_{50}	lethal concentration for 50 % of the test animals	OECD	Organization for Economic Cooperation and Development
LCLo	lowest published lethal concentration	OSHA	Occupational Safety and Health Administration (United States)
LD_{50}	lethal dose for 50 % of the test animals	p., pp.	page, pages
LDLo	lowest published lethal dose	Patty	G.D. Clayton, F.E. Clayton (eds.): Patty's Industrial Hygiene and Toxicology, 3rd ed., Wiley Interscience, New York
ln	logarithm (base e)		
LNG	liquefied natural gas		
log	logarithm (base 10)		
LPG	liquefied petroleum gas		
M	mol/L	PB report	Publication Board Report (U.S. Department of Commerce, Scientific and Industrial Reports)
M	metal (in chemical formulas)		
MAK	Maximale Arbeitsplatzkonzentration (maximum concentration at the workplace in the Federal Republic of Germany); cf. Deutsche Forschungsgemeinschaft (ed.): Maximale Arbeitsplatzkonzentrationen (MAK) und Biologische Arbeitsstofftoleranzwerte (BAT), WILEY-VCH Verlag, Weinheim (published annually)	PEL	permitted exposure limit
		Ph	phenyl substituent ($-C_6H_5$)
		Ph. Eur.	European Pharmacopoeia, Council of Europe, Strasbourg
		phr	part per hundred rubber (resin)
		PNS	peripheral nervous system
		ppm	parts per million
		P statement	precautionary statement in GHS
max.	maximum	q.v.	which see (quod vide)
MCA	Manufacturing Chemists Association (United States)	REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (EU regulation addressing the production and use of chemical substances, and their potential impacts on both human health and the environment)
Me	methyl substituent ($-CH_3$)		
Methodicum Chimicum	Methodicum Chimicum, Georg Thieme Verlag, Stuttgart		
MFAG	Medical First Aid Guide for Use in Accidents Involving Dangerous Goods		
MIK	maximale Immissionskonzentration (maximum immission concentration)	ref.	refer, reference
		resp.	respectively
min.	minimum	R_f	retention factor (TLC)
mp	melting point	R.H.	relative humidity
MS	mass spectrum, mass spectrometry	RID	réglement international concernant le transport des marchandises dangereuses par chemin de fer (international convention concerning the transportation of dangerous goods by rail)
NAS	National Academy of Sciences (United States)		
NASA	National Aeronautics and Space Administration (United States)		
NBS	National Bureau of Standards (United States)	RNA	ribonucleic acid
		R phrase (R-Satz)	risk phrase according to ChemG and GefStoffV (Federal Republic of Germany)
NCTC	National Collection of Type Cultures (United States)		
NIH	National Institutes of Health (United States)	rpm	revolutions per minute
NIOSH	National Institute for Occupational Safety and Health (United States)	RTECS	Registry of Toxic Effects of Chemical Substances, edited by the National Institute of Occupational Safety and Health (United States)
NMR	nuclear magnetic resonance	(s)	solid

SAE	Society of Automotive Engineers (United States)
SAICM	Strategic Approach on International Chemicals Management (international framework to foster the sound management of chemicals)
s.c.	subcutaneous
SI	International System of Units
SIMS	secondary ion mass spectrometry
S phrase (S-Satz)	safety phrase according to ChemG and GefStoffV (Federal Republic of Germany)
STEL	Short Term Exposure Limit (see TLV)
STP	standard temperature and pressure (0°C, 101.325 kPa)
T_g	glass transition temperature
TA Luft	Technische Anleitung zur Reinhaltung der Luft (clean air regulation in Federal Republic of Germany)
TA Lärm	Technische Anleitung zum Schutz gegen Lärm (low noise regulation in Federal Republic of Germany)
TDLo	lowest published toxic dose
THF	tetrahydrofuran
TLC	thin layer chromatography
TLV	Threshold Limit Value (TWA and STEL); published annually by the American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, Ohio
TOD	total oxygen demand
TRK	Technische Richtkonzentration (lowest technically feasible level)
TSCA	Toxic Substances Control Act (United States)
TÜV	Technischer Überwachungsverein (Technical Control Board of the Federal Republic of Germany)
TWA	Time Weighted Average
UBA	Umweltbundesamt (Federal Environmental Agency)
Ullmann	Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., Wiley-VCH, Weinheim 2002; Ullmann's Encyclopedia of Industrial Chemistry, 5th ed., VCH Verlagsgesellschaft, Weinheim 1985–1996; Ullmanns Encyklopädie
	der Technischen Chemie, 4th ed., Verlag Chemie, Weinheim 1972–1984; 3rd ed., Urban und Schwarzenberg, München 1951–1970
USAEC	United States Atomic Energy Commission
USAN	United States Adopted Names
USD	United States Dispensatory
USDA	United States Department of Agriculture
U.S.P.	United States Pharmacopeia
UV	ultraviolet
UVV	Unfallverhütungsvorschriften der Berufsgenossenschaft (workplace safety regulations in the Federal Republic of Germany)
VbF	Verordnung in der Bundesrepublik Deutschland über die Errichtung und den Betrieb von Anlagen zur Lagerung, Abfüllung und Beförderung brennbarer Flüssigkeiten (regulation in the Federal Republic of Germany concerning the construction and operation of plants for storage, filling, and transportation of flammable liquids; classification according to the flash point of liquids, in accordance with the classification in the United States)
VDE	Verband Deutscher Elektroingenieure (Federal Republic of Germany)
VDI	Verein Deutscher Ingenieure (Federal Republic of Germany)
vol	volume
vol.	volume (of a series of books)
vs.	versus
WGK	Wassergefährdungsklasse (water hazard class)
WHO	World Health Organization (United Nations)
Winnacker-Küchler	Chemische Technologie, 4th ed., Carl Hanser Verlag, München, 1982-1986; Winnacker-Küchler, Chemische Technik: Prozesse und Produkte, Wiley-VCH, Weinheim, 2003–2006
wt	weight
$	U.S. dollar, unless otherwise stated

Frequently Cited Companies (Abbreviations)

Air Products	Air Products and Chemicals	IFP	Institut Français du Pétrole
Akzo	Algemene Koninklijke Zout Organon	INCO	International Nickel Company
Alcoa	Aluminum Company of America	3M	Minnesota Mining and Manufacturing Company
Allied	Allied Corporation	Mitsubishi Chemical	Mitsubishi Chemical Industries
Amer. Cyanamid	American Cyanamid Company	Monsanto	Monsanto Company
BASF	BASF Aktiengesellschaft	Nippon Shokubai	Nippon Shokubai Kagaku Kogyo
Bayer	Bayer AG	PCUK	Pechiney Ugine Kuhlmann
BP	British Petroleum Company	PPG	Pittsburg Plate Glass Industries
Celanese	Celanese Corporation	Searle	G.D. Searle & Company
Daicel	Daicel Chemical Industries	SKF	Smith Kline & French Laboratories
Dainippon	Dainippon Ink and Chemicals Inc.	SNAM	Societá Nazionale Metandotti
Dow Chemical	The Dow Chemical Company	Sohio	Standard Oil of Ohio
DSM	Dutch Staats Mijnen	Stauffer	Stauffer Chemical Company
Du Pont	E.I. du Pont de Nemours & Company	Sumitomo	Sumitomo Chemical Company
Exxon	Exxon Corporation	Toray	Toray Industries Inc.
FMC	Food Machinery & Chemical Corporation	UCB	Union Chimique Belge
GAF	General Aniline & Film Corporation	Union Carbide	Union Carbide Corporation
W.R. Grace	W.R. Grace & Company	UOP	Universal Oil Products Company
Hoechst	Hoechst Aktiengesellschaft	VEBA	Vereinigte Elektrizitäts- und Bergwerks-AG
IBM	International Business Machines Corporation	Wacker	Wacker Chemie GmbH
ICI	Imperial Chemical Industries		

Country Codes

The following list contains a selection of standard country codes used in the patent references.

AT	Austria	IL	Israel
AU	Australia	IT	Italy
BE	Belgium	JP	Japan[*]
BG	Bulgaria	LU	Luxembourg
BR	Brazil	MA	Morocco
CA	Canada	NL	Netherlands[*]
CH	Switzerland	NO	Norway
CS	Czechoslovakia	NZ	New Zealand
DD	German Democratic Republic	PL	Poland
DE	Federal Republic of Germany	PT	Portugal
	(and Germany before 1949)[*]	SE	Sweden
DK	Denmark	SU	Soviet Union
ES	Spain	US	United States of America
FI	Finland	YU	Yugoslavia
FR	France	ZA	South Africa
GB	United Kingdom	EP	European Patent Office[*]
GR	Greece	WO	World Intellectual Property
HU	Hungary		Organization
ID	Indonesia		

[*]For Europe, Federal Republic of Germany, Japan, and the Netherlands, the type of patent is specified: EP (patent), EP-A (application), DE (patent), DE-OS (Offenlegungsschrift), DE-AS (Auslegeschrift), JP (patent), JP-Kokai (Kokai tokkyo koho), NL (patent), and NL-A (application).

Periodic Table of Elements

element symbol, atomic number, and relative atomic mass (atomic weight)

1A	"European" group designation and old IUPAC recommendation	0
1	group designation to 1986 IUPAC proposal	18
IA	"American" group designation, also used by the Chemical Abstracts Service until the end of 1986	VIIIA

1	2A											3B	4B	5B	6B	7B	2
H	2											13	14	15	16	17	**He**
1.0079	IIA											IIIA	IVA	VA	VIA	VIA	4.0026
3	4											5	6	7	8	9	10
Li	**Be**											**B**	**C**	**N**	**O**	**F**	**Ne**
6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
11	12	3A	4A	5A	6A	7A	8	8	8	1B	2B	13	14	15	16	17	18
Na	**Mg**	3	4	5	6	7	8	9	10	11	12	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
22.990	24.305	IIIB	IVB	VB	VIB	VIIB	VIII	VIII	VIII	IB	IIB	26.982	28.086	30.974	32.066	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**	**Kr**
39.098	40.078	44.956	47.867	50.942	51.996	54.938	55.845	58.933	58.693	63.546	65.409	69.723	72.61	74.922	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc***	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	**Xe**
85.468	87.62	88.906	91.224	92.906	95.94	98.906	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	**Ba**		**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po***	**At***	**Rn***
132.91	137.33		178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	208.98	209.99	222.02
87	88		104	105	106	107	108	109	110	111	112	113	114	115	116		118
Fr*	**Ra***		**Rf***	**Db***	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Cn**	**Uut**ᵃ	**Fl**	**Uup**ᵃ	**Lv**		**Uuo**ᵃ
223.02	226.03		261.11	262.11													

ᵃ provisional IUPAC symbol

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	**Ce**	**Pr**	**Nd**	**Pm***	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
138.91	140.12	140.91	144.24	146.92	150.36	151.97	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac*	**Th***	**Pa***	**U***	**Np***	**Pu***	**Am***	**Cm***	**Bk***	**Cf***	**Es***	**Fm***	**Md***	**No***	**Lr***
227.03	232.04	231.04	238.03	237.05	244.06	243.06	247.07	247.07	251.08	252.08	257.10	258.10	259.10	260.11

* radioactive element; mass of most important isotope given.

Part 1

Energy Resources, Generation and Storage

Batteries, 1. General

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1. Introduction

Batteries and fuel cells are electrochemical energy converters that directly convert chemical into electrical energy. In batteries the energy is generally stored within the electrodes. But there are exceptions, e.g., the air–zinc system, where one of the reacting substances is continuously supplied from outside, or the zinc–bromine system, where the active material is stored in separate tanks. *Fuel cells* receive their chemical energy from outside sources ($\rightarrow$ Fuel Cells).

Batteries can be recharged, if they represent reversible systems. This, however, often is restricted, since not only the system's electrochemical reactions must be reversible, but also the structure of its electrodes. As a consequence,

two basically different battery systems exist, i.e., primary and secondary batteries:

1. *Primary batteries* are designed to convert their chemical energy into electrical energy only once.
2. *Secondary batteries* are reversible energy converters and designed for many cycles, i.e., repeated discharges and charges.

The border between both types is blurred, since some primary battery systems permit charging under certain, but usually limited conditions. In general, the efficiency of their recharging process is poor and often results in early failure. The IEC therefore does not recommend the charging of any primary system [1, 2].

Batteries are of increasing importance in all areas of our daily life. They are fabricated in very large ranges of system, volume, weight, and construction. Batteries may be purchased as small button cells, that may have volumes of well below $1\,cm^3$ to operate a wrist watch, a pocket calculator, a hearing aid, or another small electronic device. Other types of batteries power large electric vehicles including trains and ships, and may have a volume of the order of cubic meters and a weight of several tons. In between a huge variety of batteries exists, designed for all kinds of applications. To meet all needs of the market, batteries offer a large range of optimized properties regarding electric energy, voltage, power output, self-discharge, environmental compatibility, and price.

The term "direct energy conversion" indicates that also nondirect energy conversion systems exist. A famous example is the combustion engine, which converts chemical into mechanical energy via a thermal process (Carnot process) and which may serve for a simplified comparison. Both systems are characterized by a reducing agent and an oxidizing agent. In the case of the combustion engine the reducing agent is the fuel and the oxidizing agent usually atmospheric oxygen. A battery is also characterized by a reducing agent ("fuel") and an oxidizing agent, that serve as energy storage. A well known fuel of this kind is metallic zinc (representing the negative electrode of, e.g., a flashlight battery), and the corresponding oxidant is manganese dioxide, constituting the positive electrode of that battery.

In principle, direct and nondirect chemical energy conversion are comparable: In both cases the reductant is oxidized under consumption of the oxidant, the latter being stored inside or outside the system (e.g., air). However, the direct energy conversion is not restricted by the limited efficiency of the Carnot process of the combustion engine. In the battery the reaction is split up into one that releases electrons (which means oxidation), and another one that absorbs electrons (which means reduction) (see Fig. 1). The electron exchange that is connected with these reactions, can so be transformed directly into a current that flows through the electrical appliance (or the charging device).
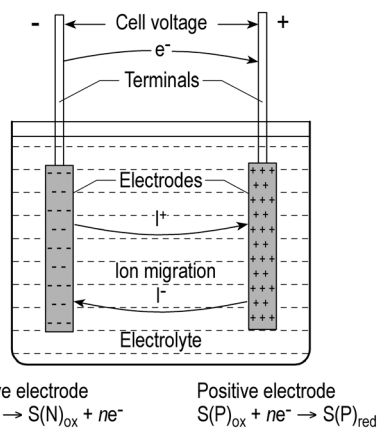
Figure 1. Electrochemical cell and the split-up of the cell reaction
$S(N)_{red}$ and $S(P)_{ox}$ are the reacting components of the negative and the positive electrode, respectively. The shown reactions apply when the battery is discharged.

In principle, a large range of "fuels" and "oxidants" exists for electrochemical energy storage and conversion, each combination representing a new battery system. However, not all combinations are meaningful. A careful selection has to be made, also with respect to the type of electrolyte being employed.

2. History

The history of batteries is usually traced back to LUIGI GALVANI (1737–1798), who detected electrical phenomena between different metals in his famous experiments with frog legs. ALLESSANDRO VOLTA (1745–1827) built the first primary battery, the so-called Volta pile. The scientific foundation of electrochemical energy storage was derived by MICHAEL FARADAY (1791–1867).

The early development of *secondary batteries* is connected to names like GASTON PLANTÉ (1834–1899), CAMILLE ALFONS FAURE (1840–1898), and HENRY OWEN TUDOR (1859–1928) in the field of the lead–acid battery, while THOMAS ALVA EDISON (1847–1931) and VALDEMAR JUNGNER (1869–1924) are the two important names in connection with nickel–iron and nickel–cadmium batteries.

In the decades following these discoveries the lead–acid and the nickel–cadmium system

were constantly improved. Today's motor cars would be unthinkable without their reliable batteries. Sealed nickel–cadmium batteries supply the energy for many of our portable electronic devices, and valve-regulated lead–acid batteries have gained a large share of the market for standby batteries.

In the 1990s new rechargeable systems appeared on the market. Of special importance are the nickel–metal hydride and the lithium-ion system.

Primary batteries for practical use emerged in the middle of the 19th century. Special reference is made to GEORGE LECLANCHÉ, who pioneered the 1.5 V manganese dioxide–zinc system with aqueous ammonium chloride as electrolyte. This system was described first by him in 1866 [3]. It is still produced, technically much more advanced by now, of course, but still known as Leclanché or zinc-carbon battery.

Over the years another 1.5 V system became most successful. It is the alkaline version of the manganese dioxide–zinc system, first proposed in 1882. Its development was taken up again by W. S. HERBERT [4, 5] about 70 years later. It took, however, another 20 years before the system became commercially available.

Further to be mentioned is the alkaline silver oxide–zinc system. First patents date back to 1883–1910 [6]. This 1.5 V battery is an expensive system, which, however, exhibits very favorable electrochemical properties. To become successful it needed a market for small batteries which opened up in 1975 with the introduction of microelectronics (e.g., wrist watches).

Another primary system that deserves mentioning is the air–zinc system. H. COHEN [7] was the first to develop a practical carbon–zinc element with aqueous ammonium chloride as electrolyte and air as oxidant in 1891. The system is still in use. Its main application is in the area of low power output over a long period of time (e.g., electric fence controllers).

Special future promise has the alkaline air–zinc version. C. FÉRY was obviously the first [8] to realize this system in 1925. Owing to further development the alkaline zinc–air element offers the highest energy density of all currently available battery systems. Since the alkaline air–zinc battery is also an environmentally benign system, it has replaced the mercuric oxide–zinc

system in important application areas, e.g., hearing aids. After activation, however, its storage behavior is limited, depending on construction (e.g., air access) and environment (e.g., humidity).

Finally there are primary battery systems using nonaqueous electrolytes, i.e., lithium batteries. Research activities to develop high energy lithium systems started in about 1960, especially in the USA and soon spread worldwide. Of the many lithium systems developed since the 1960s, about ten systems have attained market relevance (see → Batteries, 2. Primary Batteries, Chap. 3. Batteries with Nonaqueous Electrolyte).

For a more detailed description of the history of batteries, see, e.g., [9–11].

3. Fundamental Laws

Direct conversion of chemical into electrical energy requires the split-up of the electrochemical reactions into reactions of reductants that deliver electrons and reactions of oxidants that accept electrons. Such a split-up is achieved in the electrochemical cell, shown in Figure 1. A positive and a negative electrode are immersed in the electrolyte and the reacting substances (the active materials) are usually stored in the electrodes and the electrolyte, if it participates in the overall reaction.

During discharge, oxidation of $S(N)_{red}$ occurs at the negative electrode according to

$$S(N)_{red} \rightarrow S(N)_{ox} + n \cdot e^-$$
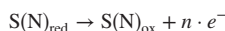
while $S(P)_{ox}$ is reduced at the positive electrode:

$$S(P)_{ox} + n \cdot e^- \rightarrow S(P)_{red}$$
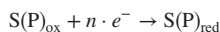
Both together form the cell reaction

$$S(N)_{red} + S(P)_{ox} \rightarrow S(N)_{ox} + S(P)_{red} + energy$$

When the battery is charged, this reaction is reversed and energy has to be supplied to the cell.

The arrangement shown in Figure 1 resembles an electrolytic capacitor where also two electrodes are separated by the electrolyte.

However, charging and discharging of such a capacitor involves only charge shifting within the double layer at the electrode–electrolyte interface. Chemical reactions do not occur and the physical structure of the electrodes is not affected. For this reason, a nearly unlimited number of charge–discharge cycles are possible. Since mass transport does not occur, charge and discharge of a capacitor occur extremely fast, but the amount of stored energy per weight or volume is comparatively small.

In batteries, such a double layer also exists, and the large surface area of the active material gives rise to a high double-layer capacitance that is observed when impedance measurements are made. The double-layer capacitance is caused by charge shifting and is given in the unit Farad, i.e., As/V. The real battery capacity, however, is based on chemical reactions and measured as As or Ah. (Actually, the double-layer capacity is always involved when a battery is charged or discharged). Each charge–discharge cycle changes the physical structure of the electrodes, and these changes inevitably cause an aging processes. Thus, with a battery the number of possible charge–discharge cycles is inevitably limited, and performance changes during service live are unavoidable.

The *cell reaction* characterizes each battery system and its components that represent the charged and discharged states determine the amount of energy that can be stored. As a consequence, the parameters of its cell reaction are of paramount importance for the battery system. While for primary batteries only reactions are relevant that describe the open circuit voltage and the discharge behavior, for rechargeable batteries these reactions must be reversible.

In the following, a brief survey is given of the most important rules. For details and derivations, see textbooks of electrochemistry or fundamental books on batteries, e.g., [12–17].

3.1. Equilibrium or Thermodynamic Parameters

The laws of thermodynamics generally apply to the state of equilibrium, which means that all reactions are balanced. In the electrochemical cell, equilibrium data can only be measured when no current flows through the cell or its electrodes. On account of this balance, the thermodynamic parameters do not depend on the reaction path but only on the difference in energy levels between the final and initial components of the system (the products and the reactants of the electrochemical reaction). The thermodynamic parameters describe the maximally achievable performance data. As soon as current flows through the cell, these values are lowered, owing to kinetic parameters.

The main thermodynamic parameters of an electrochemical reaction are:

1. The *enthalpy of reaction* ΔH which represents the amount of energy released or absorbed. ΔH describes the heat that is generated, provided that 100% of the chemical energy is converted into heat.
2. The *free enthalpy of reaction* ΔG, also called *change of Gibbs free energy* ΔG, which describes the (maximum) amount of chemical energy that, under equilibrium conditions, can be converted into electrical or mechanical energy and vice versa.
3. *The entropy of reaction* ΔS which characterizes the reversible heat effect $T \cdot \Delta S$ (where T = temperature in kelvins) which describes the energy loss or gain connected with any chemical or electrochemical process under equilibrium conditions.

Important relations between the three parameters are:

$$\Delta G = \Delta H - T \cdot \Delta S \text{ or } \Delta H - \Delta G = T \cdot \Delta S \qquad (1)$$

The difference between ΔH and ΔG, the product $T \cdot \Delta S$, is the aforementioned reversible heat effect. $T \cdot \Delta S$ can be positive or negative. In the first case, additional energy is generated by cooling of the environment (Peltier or heat pump effect). Otherwise, $T \cdot \Delta S$ constitutes an additional heat increment.

The equilibrium voltage U^{o} is given by

$$U^{\mathrm{o}} = -\frac{\Delta G}{n \cdot F} \qquad (2)$$

where n is the number of exchanged electronic charges; F the Faraday constant (96 485 As/equivalent; i.e., 26.802 Ah/equivalent); $n \cdot F$

denotes the amount of electrical charge connected with the reaction; and $n \cdot F \cdot U^{\mathrm{o}}$ describes the generated electrical energy (kJ). Thermodynamic quantities like ΔH and ΔG depend on the concentrations (or, more accurately, activities) of the reacting components, as far as these components are in solution. The corresponding relation is:

$$\Delta G = \Delta G^{\mathrm{o,s}} + R \cdot T \cdot$$
$$\left(\sum \ln[(a_i)^{j_i}]_{\mathrm{prod}} - \sum \ln[(a_i)^{j_i}]_{\mathrm{react}} \right) \qquad (3)$$

where a_i is the activity of the reacting component i (approximately its concentration; in mol/cm^3); j_i is the number of equivalents of this component that take part in the reaction; R is the molar gas constant for an ideal gas ($R = 8.3145$ JK^{-1} mol^{-1}); $\Delta G^{\mathrm{o,s}}$ is the standard free enthalpy value when all activities are unity. The terms "reac" and "prod" designate in the formula reactants and products for the forward (spontaneous) reaction.

Combination of Equation 2 and Equation 3 results in the Nernst Equation:

$$U^{\mathrm{o}} = U^{\mathrm{o,s}} - \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\Pi(a_i)^j_{\mathrm{react}}}{\Pi(a_i)^j_{\mathrm{prod}}} \qquad (4)$$

which is simplified for 25°C (298.2 K) to

$$U^{\mathrm{o}} = U^{\mathrm{o,s}} - \frac{0.0592}{n} \cdot \log \frac{\Pi(a_i)^j_{\mathrm{react}}}{\Pi(a_i)^j_{\mathrm{prod}}} \qquad (5)$$

under consideration that

$\ln(..) = 2.303 \, log(..)$,

$R = 8.3145 \, \mathrm{J \, K^{-1} mol^{-1}} = 8.3145 \, \mathrm{Ws K^{-1} mol^{-1}}$

and

$F = 96485 \, \mathrm{As/equiv.}$

thus

$R \cdot T / F = 0.02569 \, \mathrm{V \cdot equiv. \cdot mol^{-1}} \, (T = 298.16 \, \mathrm{K})$

or

$2.303 \cdot R \cdot T / F = 0.0592 \, \mathrm{V \cdot equiv. \cdot mol^{-1}}$.

The thermodynamic data also determine the temperature coefficient of the equilibrium cell voltage according to:

$$\frac{\mathrm{d}U^o}{\mathrm{d}T} = -\frac{\Delta S}{n \cdot F} \qquad (6)$$

Single Electrode Potentials. Thermodynamic calculations are always based on an electrochemical cell reaction and the derived voltage and its temperature coefficient in fact concern the voltage difference between two electrodes. The voltage difference between the electrode and the electrolyte, the *absolutepotential*, cannot be determined exactly, since potential differences can only be measured between two electronic conductors [18]. Thus, single electrode potential always means the cell voltage between the electrode in question and a reference electrode. To provide a basis for the electrode-potential scale, the zero point was arbitrarily equated with the potential of the *standard hydrogenelectrode* (SHE), a hydrogen electrode under specified conditions at 25°C [19].

Hydrogen reference electrodes are not used in battery practice. They are not only impracticable to handle but also involve some risk of contamination of the battery's electrodes by the noble metals like platinum or palladium used as electrode materials in the hydrogen electrode [20]. Therefore, a number of reference electrodes are used instead, e.g., the *mercury/mercury(I) sulfate reference electrode* (Hg/Hg$_2$SO$_4$) in lead–acid batteries, and the *mercury/mercury (II) oxide reference electrode* (Hg/HgO) in alkaline solutions (cf., e.g. [21]). In lithium-ion batteries with organic electrolytes, the electrode potential is mostly referred to that of the lithium electrode.

3.2. Current Flow, Kinetic Parameters

When current flows, the cell reaction must occur at a corresponding rate. This means that electron transfer has to be forced into the desired direction, and mass transport is required to bring the reacting ions to the electrode surface or carry them away. To achieve this current flow, additional energy is required. This energy finds its expression in *overvoltages*, i.e., deviations from the equilibrium voltage (sometimes denoted as "irreversible entropy loss" $T \cdot \Delta S_{\mathrm{irr}}$).

Furthermore, current flow through conducting elements causes *ohmic voltage drops*. Both mean irreversible energy loss and a corresponding heat generation, caused by current flow.

As a result, the voltage U under current flow i is reduced (on discharge) or increased (secondary cell on charge) compared to the equilibrium value U^{o}. The difference $U - U^{\mathrm{o}}$, when measured as deviation from the cell voltage comprises:

1. The overvoltage, caused by electrochemical reactions and concentration deviations on account of transport phenomena.
2. The ohmic voltage drops, caused by the electronic as well as the ionic currents in the conducting parts including the electrolyte.
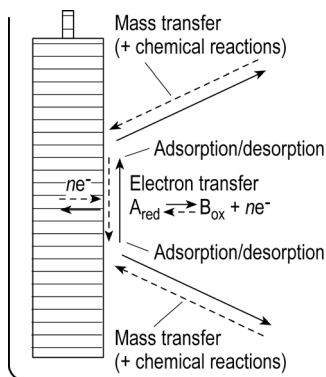
The sum of all the voltage drops caused by the current flow is called *polarization*, i.e.,

$$\text{polarization} = \text{overvoltage} + \text{ohmic voltage drops} \qquad (7)$$

The quantity determined in practice is always polarization. Overvoltage can be determined separately only by special electrochemical methods.

Usually, the reaction path consists of a number of reaction steps that precede or follow the actual charge transfer step as indicated in Figure 2.

The rate of each of these reaction steps is determined by kinetic parameters, such as exchange current density, diffusion coefficients, or transport numbers. The slowest partial step of this chain is decisive for the rate of the overall reaction. As a consequence, overvoltages, or even limitations of the reaction rate, often are not caused by the electron-transfer step itself, but by preceding or following steps.

Transport of the reacting species is achieved by two mechanisms, diffusion and migration, and, when only one-dimensional transport is assumed, is given by:

$$N_j = \frac{i_j}{n \cdot F} = -D_j \frac{\partial c_j}{\partial \zeta} + \frac{i \cdot t_j}{z_j \cdot F} \qquad (8)$$

where N_j is the flux of species j in $\mathrm{mol/cm^2}$; i_j/nF the current equivalent; c_j the concentration of species j in $\mathrm{mol/cm^3}$; $\delta c_j/\delta\zeta$ the concentration gradient in $\mathrm{mol/cm^4}$; D the diffusion coefficient in $\mathrm{cm^2/s}$; t the transference number; z_j the valence number (charges per ion i); and ζ the diffusion direction (cm). Addend 1 describes mass transport by diffusion, which is proportional to the (negative) gradient of the concentration $\mathrm{d}c_j/\mathrm{d}\zeta$ that often can be approximated as a linear slope $\Delta c = c_j - c_{j,\mathrm{o}}$ where c_j is the concentration of the concerned species at the electrode surface, while $c_{j,\mathrm{o}}$ denotes the corresponding concentration in the bulk of the electrolyte.

Diffusion can limit the reaction rate when the mass transport by diffusion precedes the electron transfer step. If the concentration c_j attains the value zero at the electrode surface, all the arriving ions or molecules are charged or discharged immediately, and further increase of the current by increased overvoltage is not possible. Thus the current cannot exceed a certain value, the *limiting current* (i_{lim}) that can be derived from the first term in Equation 8 with $c_j = 0$.

Addend 2 in Equation 8 describes ion transport by migration by the ionic current. The transference number t denotes the share of the total current that is carried by the corresponding ionic species. In a binary electrolyte, dissociated into A^+ and B^-, the transference numbers are related by

$$t_+ + t_- = 1 \qquad (9)$$

Transference numbers depend on the concentration of the ions and on temperature. In

Figure 2. Course of an electrochemical reaction. Charge transfer often can only occur with adsorbed species, then adsorption/desorption steps are included. Furthermore, chemical reactions may precede or follow the electron transfer step.