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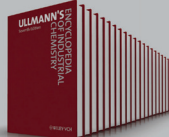
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Editor in Chief:

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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.

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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	$J\text{kg}^{-1}\text{K}^{-1}$	specific heat capacity
d	cm, m	diameter
d		relative density (ρ/ρ_{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	$\text{W}\cdot\text{s}^2$	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 ($6.023 \times 10^{23} \text{mol}^{-1}$)
P	Pa, bar*	pressure
Q	J	quantity of heat
r	m	radius
R	$\text{JK}^{-1}\text{mol}^{-1}$	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	$\text{Wm}^{-2}\text{K}^{-1}$	heat-transfer coefficient (heat-transfer number)
α		degree of dissociation of electrolyte
$[\alpha]$	$10^{-2}\text{deg cm}^2\text{g}^{-1}$	specific rotation
η	Pa·s	dynamic viscosity
θ	$^{\circ}\text{C}$	temperature
κ		c_p/c_v
λ	$\text{Wm}^{-1}\text{K}^{-1}$	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
<i>Mass</i>		
kg	pound (avoirdupois)	2.205
kg	ton (long)	9.842×10^{-4}
kg	ton (short)	1.102×10^{-3}
<i>Volume</i>		
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
<i>Temperature</i>		
$^{\circ}\text{C}$	$^{\circ}\text{F}$	$^{\circ}\text{C} \times 1.8 + 32$
<i>Force</i>		
N	dyne	1.0×10^5
<i>Energy, Work</i>		
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}
<i>Pressure</i>		
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	BGB1.	Bundesgesetzblatt (Federal Republic of Germany)
ACGIH	American Conference of Governmental Industrial Hygienists	BIOS	British Intelligence Objectives Subcommittee Report (see also FIAT)
ACS	American Chemical Society	BOD	biological oxygen demand
ADI	acceptable daily intake	<i>bp</i>	boiling point
ADN	accord européen relatif au transport international des marchandises dangereuses par voie de navigation intérieure (European agreement concerning the international transportation of dangerous goods by inland waterways)	B.P.	British Pharmacopeia
ADNR	ADN par le Rhin (regulation concerning the transportation of dangerous goods on the Rhine and all national waterways of the countries concerned)	BS	British Standard
ADP	adenosine 5'-diphosphate	ca.	circa
ADR	accord européen relatif au transport international des marchandises dangereuses par route (European agreement concerning the international transportation of dangerous goods by road)	calcd.	calculated
AEC	Atomic Energy Commission (United States)	CAS	Chemical Abstracts Service
a.i.	active ingredient	cat.	catalyst, catalyzed
AICHE	American Institute of Chemical Engineers	CEN	Comité Européen de Normalisation
AIME	American Institute of Mining, Metallurgical, and Petroleum Engineers	cf.	compare
ANSI	American National Standards Institute	CFR	Code of Federal Regulations (United States)
AMP	adenosine 5'-monophosphate	cfu	colony forming units
APhA	American Pharmaceutical Association	Chap.	chapter
API	American Petroleum Institute	ChemG	Chemikaliengesetz (Federal Republic of Germany)
ASTM	American Society for Testing and Materials	C.I.	Colour Index
ATP	adenosine 5'-triphosphate	CIOS	Combined Intelligence Objectives Subcommittee Report (see also FIAT)
BAM	Bundesanstalt für Materialprüfung (Federal Republic of Germany)	CLP	Classification, Labelling and Packaging
BAT	Biologischer Arbeitsstofftoleranzwert (biological tolerance value for a working material, established by MAK Commission, see MAK)	CNS	central nervous system
Beilstein	Beilstein's Handbook of Organic Chemistry, Springer, Berlin – Heidelberg – New York	Co.	Company
BET	Brunauer – Emmett – Teller	COD	chemical oxygen demand
		conc.	concentrated
		const.	constant
		Corp.	Corporation
		crit.	critical
		CSA	Chemical Safety Assessment according to REACH
		CSR	Chemical Safety Report according to REACH
		CTFA	The Cosmetic, Toiletry and Fragrance Association (United States)
		DAB	Deutsches Arzneibuch, Deutscher Apotheker-Verlag, Stuttgart
		d.c.	direct current
		decomp.	decompose, decomposition
		DFG	Deutsche Forschungsgemeinschaft (German Science Foundation)
		dil.	dilute, diluted

DIN	Deutsche Industrienorm (Federal Republic of Germany)		(regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by rail)
DMF	dimethylformamide		
DNA	deoxyribonucleic acid	GGVS	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter auf der Straße
DOE	Department of Energy (United States)		(regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by road)
DOT	Department of Transportation – Materials Transportation Bureau (United States)		
DTA	differential thermal analysis		
EC	effective concentration	GGVSee	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit Seeschiffen
EC	European Community		(regulation in the Federal Republic of Germany concerning the transportation of dangerous goods by sea-going vessels)
ed.	editor, edition, edited		
e.g.	for example		
emf	electromotive force		
EmS	Emergency Schedule		
EN	European Standard (European Community)	GHS	Globally Harmonised System of Chemicals (internationally agreed-upon system, created by the UN, 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)
EPA	Environmental Protection Agency (United States)		
EPR	electron paramagnetic resonance		
Eq.	equation		
ESCA	electron spectroscopy for chemical analysis	GLC	gas-liquid chromatography
esp.	especially	Gmelin	Gmelin's Handbook of Inorganic Chemistry, 8th ed., Springer, Berlin – Heidelberg – New York
ESR	electron spin resonance		
Et	ethyl substituent ($-C_2H_5$)		
et al.	and others		
etc.	et cetera	GRAS	generally recognized as safe
EVO	Eisenbahnverkehrsordnung (Federal Republic of Germany)	Hal	halogen substituent ($-F$, $-Cl$, $-Br$, $-I$)
exp (. . .)	$e^{(\dots)}$, mathematical exponent	Houben-Weyl	Methoden der organischen Chemie, 4th ed., Georg Thieme Verlag, Stuttgart
FAO	Food and Agriculture Organization (United Nations)		
FDA	Food and Drug Administration (United States)	HPLC	high performance liquid chromatography
FD&C	Food, Drug and Cosmetic Act (United States)	H statement	hazard statement in GHS
FHSA	Federal Hazardous Substances Act (United States)	IAEA	International Atomic Energy Agency
FIAT	Field Information Agency, Technical (United States reports on the chemical industry in Germany, 1945)	IARC	International Agency for Research on Cancer, Lyon, France
Fig.	figure	IATA-DGR	International Air Transport Association, Dangerous Goods Regulations
<i>fp</i>	freezing point	ICAO	International Civil Aviation Organization
Friedländer	P. Friedländer, Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige Vol. 1–25, Springer, Berlin 1888–1942	i.e.	that is
FT	Fourier transform	i.m.	intramuscular
(g)	gas, gaseous	IMDG	International Maritime Dangerous Goods Code
GC	gas chromatography	IMO	Inter-Governmental Maritime Consultative Organization (in the past: IMCO)
GefStoffV	Gefahrstoffverordnung (regulations in the Federal Republic of Germany concerning hazardous substances)	Inst.	Institute
GGVE	Verordnung in der Bundesrepublik Deutschland über die Beförderung gefährlicher Güter mit der Eisenbahn	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
(1)	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)
LC ₅₀	lethal concentration for 50 % of the test animals	NRDC	National Research Development Corporation (United States)
LCLo	lowest published lethal concentration	NSC	National Service Center (United States)
LD ₅₀	lethal dose for 50 % of the test animals	NSF	National Science Foundation (United States)
LDLo	lowest published lethal dose	NTSB	National Transportation Safety Board (United States)
ln	logarithm (base e)	OECD	Organization for Economic Cooperation and Development
LNG	liquefied natural gas	OSHA	Occupational Safety and Health Administration (United States)
log	logarithm (base 10)	p., pp.	page, pages
LPG	liquefied petroleum gas	Patty	G.D. Clayton, F.E. Clayton (eds.): Patty's Industrial Hygiene and Toxicology, 3rd ed., Wiley Interscience, New York
M	mol/L	PB	Publication Board Report (U.S. Department of Commerce, Scientific and Industrial Reports)
M	metal (in chemical formulas)	report	report
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
max.	maximum	Ph	phenyl substituent (—C ₆ H ₅)
MCA	Manufacturing Chemists Association (United States)	Ph. Eur.	European Pharmacopoeia, Council of Europe, Strasbourg
Me	methyl substituent (—CH ₃)	phr	part per hundred rubber (resin)
Methodicum	Methodicum Chemicum, Georg Thieme Chemicum Verlag, Stuttgart	PNS	peripheral nervous system
MFAG	Medical First Aid Guide for Use in Accidents Involving Dangerous Goods	ppm	parts per million
MIK	maximale Immissionskonzentration (maximum immission concentration)	P statement	precautionary statement in GHS
min.	minimum	q.v.	which see (quod vide)
mp	melting point	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)
MS	mass spectrum, mass spectrometry	ref.	refer, reference
NAS	National Academy of Sciences (United States)	resp.	respectively
NASA	National Aeronautics and Space Administration (United States)	R _f	retention factor (TLC)
NBS	National Bureau of Standards (United States)	R.H.	relative humidity
NCTC	National Collection of Type Cultures (United States)	RID	réglement international concernant le transport des marchandises dangereuses par chemin de fer (international convention concerning the transportation of dangerous goods by rail)
NIH	National Institutes of Health (United States)	RNA	ribonucleic acid
NIOSH	National Institute for Occupational Safety and Health (United States)	R phrase (R-Satz)	risk phrase according to ChemG and GefStoffV (Federal Republic of Germany)
NMR	nuclear magnetic resonance	rpm	revolutions per minute
		RTECS	Registry of Toxic Effects of Chemical Substances, edited by the National Institute of Occupational Safety and Health (United States)
		(s)	solid

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

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	Società 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 (and Germany before 1949)*	PT	Portugal
DK	Denmark	SE	Sweden
ES	Spain	SU	Soviet Union
FI	Finland	US	United States of America
FR	France	YU	Yugoslavia
GB	United Kingdom	ZA	South Africa
GR	Greece	EP	European Patent Office*
HU	Hungary	WO	World Intellectual Property 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 VIII A

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

^a provisional IUPAC symbol

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

* radioactive element; mass of most important isotope given.

Part 1

Energy Resources, Generation and Storage

Batteries, 1. General

DIETRICH BERNDT, (formerly VARTA Batterie AG), Kronberg, Germany

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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 (→ 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).

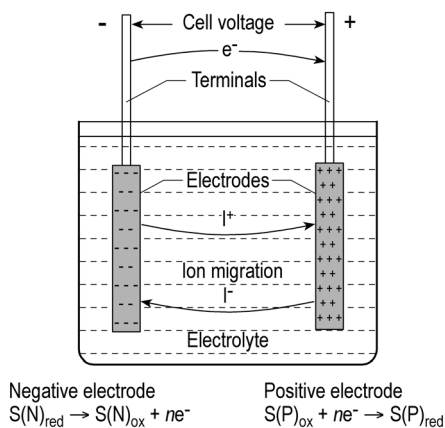


Figure 1. Electrochemical cell and the split-up of the cell reaction

$S(N)_{red}$ 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. ALESSANDRO 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].

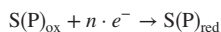
3. Fundamental Laws

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 $S(N)_{\text{red}}$ occurs at the negative electrode according to



while $S(P)_{\text{ox}}$ is reduced at the positive electrode:



Both together form the cell reaction



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 life 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:

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

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° is given by

$$U^{\circ} = -\frac{\Delta G}{n \cdot F} \quad (2)$$

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 $n \cdot F \cdot U^o$ 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:

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

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 ($R = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1}$); $\Delta G^{o,s}$ is the standard free enthalpy value when all activities are unity. The terms “*react*” 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:

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

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

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

under consideration that

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

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 8.3145 \text{ W s K}^{-1} \text{ mol}^{-1}$$

and

$$F = 96485 \text{ As/equiv.}$$

thus

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

or

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

The thermodynamic data also determine the temperature coefficient of the equilibrium cell

voltage according to:

$$\frac{dU^o}{dT} = -\frac{\Delta S}{n \cdot F} \quad (6)$$

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 *absolute potential*, 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 hydrogen electrode* (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* ($\text{Hg}/\text{Hg}_2\text{SO}_4$) 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” $T \cdot \Delta S_{\text{irr}}$).

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^0 . The difference $U - U^0$, 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.,

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

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

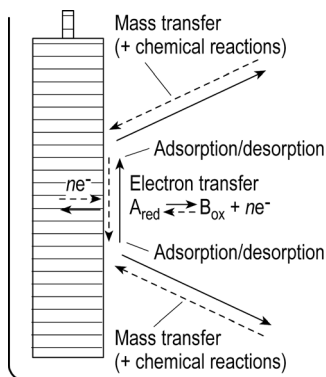


Figure 2. Course of an electrochemical reaction. Charge transfer often can only occur with adsorbed species, then adsorption/desorption steps are included. Furthermore, chemical reactions may precede or follow the electron transfer step.

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:

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

where N_j is the flux of species j in mol/cm^2 ; i_j/nF the current equivalent; c_j the concentration of species j in mol/cm^3 ; $\delta c_j/\delta \zeta$ the concentration gradient in mol/cm^4 ; D the diffusion coefficient in 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 $dc_j/d\zeta$ that often can be approximated as a linear slope $\Delta c = c_j - c_{j,o}$ where c_j is the concentration of the concerned species at the electrode surface, while $c_{j,o}$ 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

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

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

binary-salt solutions they are fairly close to 0.5, which means that both ion species more or less equally share in ion conductivity. Larger deviations are observed in acids and bases on account of the much higher ion mobility of H^+ and OH^- ions. The values for the battery electrolytes sulfuric acid (dissociated into H^+ and HSO_4^-) and potassium hydroxide are:

Sulfuric acid	$t_+ = t_{H^+} = 0.9$	$t_- = t_{HSO_4^-} = 0.1$
Potassium hydroxide	$t_+ = t_{K^+} = 0.22$	$t_- = t_{OH^-} = 0.78$

These transference numbers for sulfuric acid, given in [19, p. 255] for diluted solutions, are also true for concentrations used in batteries. The numbers for potassium hydroxide are valid for a wide concentration range [22].

The transference number indicates how much the concentration of the concerned ion is changed by migration due to the current flow. The small value for the HSO_4^- ion means that its concentration is only slightly influenced by migration. In lithium ion batteries, where lithium ions swing between the negative and the positive electrode, a transference number $t_{Li} = 1$ would be desirable, since then a constant concentration profile would be maintained during discharging and charging. This is one reason to aim at utilization of conducting salts with large anions in such systems as mentioned in \rightarrow Batteries, 3. Secondary Batteries, Section 3.1.4.4. Electrolytes.

3.2.1. Electron Transfer

The electron transfer reaction denotes the central reaction step where electric charge is exchanged (cf. Fig. 2). Current flow affords additional forces because of an energy barrier that has to be surmounted by electrons. The required additional energy is the activation energy and the dependence of reaction rates on the activation energy is expressed by the Arrhenius equation

$$k = k_0 \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \quad (10)$$

where k is the reaction constant and E_A the activation energy (J/mol). In electrode reactions,

$n \cdot U \cdot F$ is the driving force, and the corresponding relation is:

$$i = k' \cdot c_j \cdot \exp\left(\frac{n \cdot F}{R \cdot T} U\right) \quad (11)$$

k' includes the "equivalence factor" $n \cdot F$ between mass transport and current i , U is the electrode potential, and c_j the concentration of the reacting substance that releases or absorbs electrons. Electron transfer, however, does not occur only in one direction: the reverse reaction is possible as well, and the balance between both depends on the electrode potential. Thus, Equation 11 has to be completed.

$$i = k_+ \cdot c_{\text{red}} \cdot \exp\left(\frac{\alpha \cdot n \cdot f}{R \cdot T} U\right) - k_- \cdot c_{\text{ox}} \cdot \exp\left(-\frac{(1-\alpha) \cdot n \cdot F}{R \cdot T} U\right) \quad (12)$$

where addend 1 describes the anodic reaction (e.g., $Pb \rightarrow Pb^{2+}$), addend 2 its reversal; α denotes the transference factor (usually ≈ 0.5) that indicates how symmetrically the reaction and its reversal depend on electrode potential (difference in activation energies); n is the number of charges, and c_{red} , c_{ox} are the concentrations of the reduced and oxidized states of the reactants. Such an electron transfer occurs also during equilibrium at equal rates in both directions as a dynamic equilibrium, although no current flow is observed through the electrodes. The equilibrium voltage (U^0) is determined by the point at which the forward and reverse reaction rates equal each other.

At the equilibrium potential $U = U^0$, the current flow in both directions is balanced, which means

$$i_+(0) = -i_-(0) = i_0$$

This balancing current is called *exchange-current density* (it is necessarily related to the surface area, therefore it is a current density given, e.g., in mA/cm²). In battery practice, such current densities often are referred to the nominal capacity (Ah or 100 Ah, because the true surface area of the porous material is not known, but there is a certain relation between surface area and nominal capacity). Often the current-voltage curves are related to the

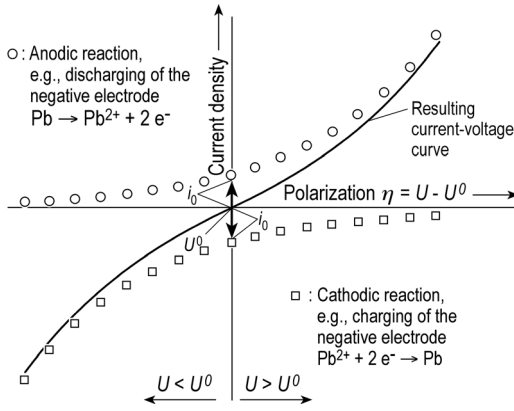


Figure 3. The current voltage curve. The horizontal axis (abscissa) represents the overvoltage $\eta = U - U^0$; The vertical axis (ordinate) the current density i , which is synonymous to the reaction rate; i_0 is the exchange current density that characterizes the dynamic equilibrium. The reaction of the lead electrode is inserted as an example.

deviation from the equilibrium potential, the overvoltage $\eta = U - U^0$. This leads to the usual form of Equation 12:

$$i = i_0 \left[\exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} \eta\right) - \exp\left(-\frac{(1-\alpha) \cdot n \cdot F}{R \cdot T} \eta\right) \right] \quad (13)$$

where i_0 is the exchange current density that characterizes the dynamic equilibrium as shown in Figure 3. The resulting current is represented in Figure 3 by the solid curve as the combination of anodic and cathodic current-voltage curves.

Polarization. Polarization is an important parameter given by the relations

$$\eta_+ = U_+ - U_+^0 \text{ or } \eta_- = U_- - U_-^0 \quad (14)$$

where η_+ and η_- are the polarization of the positive and negative electrodes, respectively; U_+ and U_- are the actual potentials; and U_+^0 and U_-^0 the equilibrium potentials of the positive and negative electrodes. The cell voltage $U_+ - U_-$ results in

$$U = U^0 + \eta_+ - \eta_- \quad (15)$$

According to the definition in Equation 14, the polarization of the negative electrode has a

negative sign when the electrode potential is below its equilibrium value. If the cell voltage is considered, η_+ and η_- are summed up to η .

Polarization is a very important parameter. The negative electrode is only kept fully charged when its polarization is negative or zero ($\eta_- \leq 0$) while for a charged positive electrode a positive polarization is required ($\eta_+ \geq 0$).

3.2.2. Tafel Lines

If the potential is shifted far enough from the equilibrium value, the reverse reaction can be neglected in Equation 13. Then the resulting current-voltage curve in Figure 3 becomes a simple exponential function

$$i = i_0 \cdot \exp\left[\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta\right] \quad (16)$$

This equation can be rearranged into

$$\eta = \frac{R \cdot T}{\alpha \cdot n \cdot F} \cdot \ln(|i|) - \frac{R \cdot T}{\alpha \cdot n \cdot F} \cdot \ln(|i_0|) \quad (17)$$

that can be written in a form known as the Tafel equation (J. TAFEL was the first to describe this relation in connection with hydrogen-overvoltage measurements on noble metals [23])

$$\eta = a + b \cdot \log(|i|) \quad (18)$$

The curves represented by Equation 18 are linearized when plotted semi-logarithmically and are called *Tafel lines*. The constant b represents the slope of the Tafel line and denotes the potential difference that causes a current increase of one decade. Tafel lines are important tools when reactions are considered that occur at high overvoltages, since such a linearization allows quantitative considerations (cf. → Batteries, 3. Secondary Batteries, Figure 8).

3.2.3. Influence of Temperature

Temperature is an important parameter for all electrochemical reaction rates. In general, the approximation can be used that the rates of electrochemical reactions like hydrogen evolution, oxygen evolution, and corrosion are

doubled per temperature increase of 10°C. Then the corresponding Tafel lines are shifted upwards in parallel.

3.3. Heat Effects

Like chemical reactions electrochemical reactions are always connected with heat effects, determined by the reversible heat effect, mentioned in Equation 1. When current flows through the cell, additional heat is generated by overvoltages due to kinetic parameters and by ohmic resistances in the electrodes. The sum of both is the polarization that causes the Joule effect (Section 3.3.2).

3.3.1. Reversible Heat Effect

The reversible heat effect

$$Q_{\text{rev}} = T \cdot \Delta S \quad (19)$$

represents an unavoidable heat absorption or heat emission that is connected with electrochemical reactions. It is related to the thermodynamic (equilibrium) parameters of the concerned reaction, and is strictly connected with the amount of material (in electrochemical equivalents) that reacts. Thus, the reversible heat effect does not depend on discharge or recharge rates. When the cell reaction is reversed, the reversible heat effect is reversed too, i.e., it acquires the opposite sign. Thus, energy loss in one direction means energy gain when the reaction is reversed.

The reversible heat effect per unit time can be related to current flow, because each multiple of the cell reaction requires the current amount $n \cdot F$:

$$\frac{dQ_{\text{rev}}}{dt} = \frac{Q_{\text{rev}}}{n \cdot F} \cdot i \quad (20)$$

Q_{rev}/nF has the unit volts. So it is equivalent to a voltage, although it is not a voltage that can be measured, but for caloric evaluations it is convenient to combine U^0 with Q_{rev}/nF . The difference

$$U_{\text{cal}} = U^0 - \frac{Q_{\text{rev}}}{n \cdot F} \quad (21)$$

is called calorific voltage (or *thermoneutral potential* E_{tp} [24]). U_{cal} is a hypothetical voltage that includes the reversible heat effect, and is used instead of the equilibrium voltage for caloric calculations. The combination with Equations 1 and 2 shows that U_{cal} also can be written as

$$U_{\text{cal}} = -\frac{\Delta H}{n \cdot F}$$

3.3.2. Current Related Heat Effects (Joule Effect)

Current flow through any conducting object generates heat proportional to the voltage drop caused by the current itself according to

$$dQ_{\text{Joule}}/dt = \Delta U \cdot i \quad (22)$$

This heat is called the Joule effect; it always means loss of energy.

Strictly speaking, the negative absolute value should be used in Equation 22 for consistency with the arithmetical sign of the thermodynamic parameters (lost energy always has a negative sign).

In an electrochemical cell, the voltage drop caused by the current is represented by the difference between the cell voltage under current flow U and the open-circuit cell voltage U^0 . Then the Joule effect reads according to Equation 22:

$$dQ_{\text{Joule}}/dt = (U - U^0) \cdot i \quad (23)$$

or its integrated form for a period t (in hours)

$$Q_{\text{Joule}} = \int_0^t \{(U - U^0) \cdot i\} dt \quad (24)$$

Strictly speaking Equation 23 describes a composite parameter of

1. The “genuine” Joule effect $dQ/dt = i^2 \cdot R$, which describes the heat generation by current flow (i) through the ohmic resistance (R) of the conducting elements and the electrolyte, and
2. The irreversible heat effect $T \cdot \Delta S_{\text{irr}}$, which causes voltage drops between the electrode surface and the electrolyte on account of

reaction hindrance (overvoltage according to Eq. 7). This additional heat is caused by an additional entropy of reaction (ΔS_{irr}) which cannot be recouped when the reaction is reversed.

For heat effects this is not relevant, since heat generation is proportional to polarization.

$U - U^0$ does not remain constant during charging or discharging, because it is related to the internal resistance, that usually increases with proceeding discharge, because of the lower conductivity of the discharged products. In lead–acid batteries the conductivity of the electrolyte also decreases with discharge, and acid dilution also influences U^0 . In quite a number of battery systems the U^0 -value is also influenced by the state of charge. An example is the manganese dioxide–zinc system [25].

3.3.3. Heat Generation in Total

Summation of the Joule effect and the reversible heat effect gives the total heat generated in the cell or the battery, i.e.,

$$Q_{\text{total}} = Q_{\text{Joule}} + Q_{\text{rev}} \quad (25)$$

as energy, e.g., Wh, or as energy per time unit, i.e., power, e.g., W,

$$\frac{dQ_{\text{total}}}{dt} = \frac{dQ_{\text{Joule}}}{dt} + \frac{dQ_{\text{rev}}}{dt} \quad (26)$$

Depending on the sign of dQ_{rev}/dt , the total energy generation may be larger or smaller than the Joule effect.

According to Equation 23, dQ_{Joule}/dt can be substituted by $(U - U^0) \cdot i$, which gives:

$$\frac{dQ_{\text{total}}}{dt} = (U - U^0) \cdot i + \frac{dQ_{\text{rev}}}{dt} \quad (27)$$

Substitution of dQ_{rev}/dt by Equation 20 and application of Equation 21 results in the simple relation that is convenient for heat calculations:

$$\frac{dQ_{\text{total}}}{dt} = (U - U_{\text{cal}}) \cdot i \quad (28)$$

Strictly speaking, Equation 28 should have a negative sign according to thermodynamic

parameters, since the Joule effect is always lost energy, as mentioned in connection with Equation 22. To overcome this difficulty, $Q_{\text{gen}} = -Q_{\text{total}}$ is introduced below.

3.4. Heating of the Battery

While a battery is being charged or discharged, the heat generation caused by the flowing current raises the temperature until balance is achieved between heat generation in the cell and heat dissipation to the environment. This balance depends on both: the rate of heat generation and the possibility of heat dissipation.

Heating Effects, Heat Capacity. The change of battery temperature during discharge (dT/dt) can be estimated by heat generation values:

$$\frac{dT}{dt} = \frac{1}{C_{\text{Batt}}} \cdot \left(\frac{dQ_{\text{gen}}}{dt} - \frac{dQ_{\text{diss}}}{dt} \right) \quad (29)$$

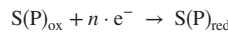
where dQ_{gen}/dt is the generated energy per unit time and dQ_{diss}/dt the dissipated energy per unit time; Q_{gen} corresponds to Q_{total} in Equation 28. C_{Batt} is the heat capacity of the battery (in kJ/K) defined by

$$\sum [m(i) \cdot C_p(i)] = C_{\text{Batt}} \quad (30)$$

where i denotes one of the various components of the battery; $m(i)$ is the mass of component i in kg; and $C_p(i)$ is the specific heat of component i in $\text{kJ kg}^{-1} \text{K}^{-1}$.

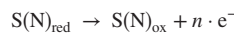
4. Battery Properties and Characteristics

Figure 1 shows the basic design of a single cell. When the battery is discharged, the active material in the positive electrode is reduced



Such a reducing current flow is called “cathodic”.

In the negative electrode, the active material is oxidized



by an “anodic” current. The terms cathodic and anodic are strictly connected to the direction of current flow. *Cathodic* means that a negative current (i.e., negatively charged ions) flows from the cathode to the anode via the electrolyte, *anodic* means a positive current (positively charged ions) flowing from the anode to the cathode via the electrolyte, i.e., in opposite direction. Thus, during charging, these currents are reversed. In accordance with these terms, in the field of *primary batteries* the positive electrode is usually called “cathode” since the positive electrode is discharged by a cathodic current, while the negative electrode is called “anode”, and this is unambiguous, since only discharge occurs.

In *secondary batteries*, it depends on charge or discharge which of the two electrodes is anode or cathode. Thus, in lead–acid batteries, the negative electrode is anode during discharging ($\text{Pb} \rightarrow \text{Pb}^{2+}$), but cathode during charging. The opposite applies to the positive electrode: $\text{Pb}^{4+} + 2 \cdot \text{e}^- \rightarrow \text{Pb}^{2+}$ is a cathodic reaction, and the PbO_2 electrode is cathode during discharging but anode during charging. Because of this ambiguity, the terms positive electrode and negative electrode are preferred for secondary batteries.

For secondary lithium-ion batteries, however, that partially have been developed commonly with primary lithium batteries, the terms cathode and anode have become customary. Then the terms anode and cathode correspond to the discharging situation.

4.1. Cell and Battery

The basic element of each battery is the cell, corresponding to Figure 1. The term *battery* refers usually to several cells (at least two) being connected in series or in parallel. The International Electrotechnical Commission IEC, however, has meanwhile extended the term “battery” to also include single cells, if they have terminal arrangements, such that they can be placed into a battery compartment while providing adequate contact. Furthermore the single cell must carry markings as required by the IEC Standard in order to be called a battery [26, 27].

According to IEC the term *cell* still applies when referring to the component cells inside a

multicell battery, like, e.g., a 9 V battery. Terms like smart batteries, battery packs, etc., are discussed in Sections 5.2.1 and → Batteries, 3. Secondary Batteries, Section 3.1.4.7. Practical Batteries.

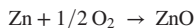
4.1.1. Active Material

The term active material refers to the components of the cell reaction being used up or regenerated in consequence of a discharge or charge. The term active material includes in the first place materials in the positive and negative electrode, but may also include certain components of the electrolyte.

4.1.1.1. Change of Volume

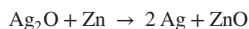
The active material changes its volume on charge and discharge. When the volume of the active material is increased, mechanical forces may be generated inside the battery that even may disrupt the battery casing, if no volume for expansion is provided. Reduction in volume, on the other hand, can cause contact problems between the electrodes and the separator that contains the immobilized electrolyte unless there is a mechanical component like a spring that provides pressing forces.

For example, during discharge of the alkaline air–zinc system, its zinc anode reacts with the oxygen of the air according to the overall reaction



The molar volume of ZnO is ca. 65% larger than that of metallic zinc, and the battery construction must provide adequate space to allow for this change in volume, which is actually caused by the intake of atmospheric oxygen. Otherwise the battery would swell during discharge.

Other electrochemical systems exhibit a reduction in partial molar volume in consequence of discharge, like the monovalent silver oxide–zinc system. According to the overall reaction



its partial molar volume decreases by ca. 15%. The CuO–Li system exhibits even a reduction in partial molar volume of ca. 42%.

4.1.1.2. Change of Electrode Structure

The solubility of reaction products is a very important parameter for electrode reactions that occur via dissolution of the reactants, as in the case of lead, cadmium, zinc, or lithium electrodes. If the product or the discharge is highly soluble the electrode will—to a large extent—be dissolved during discharge and will lose its former structure. This leads to problems during recharge because the redeposition of the metal is favored where the concentration of the solution has its highest value. As a consequence, the structure of the electrode will be changed as demonstrated in the upper line of Figure 4.

Connected to the shape change is a further drawback of the high solubility, namely the tendency that during recharging the precipitated material forms dendrites that may penetrate the separator and reach the opposite electrode, thus gradually establishing a short circuit.

A typical example of this situation is the zinc electrode, which allows only limited discharge-charge cycles before it starts to establish electron conducting bridges between the electrodes. Zinc electrodes are therefore not used for commercial secondary batteries with the exception of the rechargeable alkaline zinc manganese dioxide battery (RAM) [28, 29], which is a within certain limits rechargeable battery of low initial cost, but limited cycle life.

The metallic lithium electrode is another case where cycling causes problems, in this case, however, not only due to shape change but also due to unwanted reactions with the electrolyte (see → Batteries, 2. Primary Batteries,

Chap. 3. Batteries with Nonaqueous Electrolyte and → Batteries, 3. Secondary Batteries, Section 3.1. Rechargeable Lithium Batteries).

Extremely low solubility of the reaction products leads to immediate precipitation and thus to the formation of an impermeable covering layer (lower line in Fig. 4). As a consequence, the discharge reaction comes to a halt as soon as the passivating layer is completed. To counteract such a passivation, the active material in corresponding technical electrodes, e.g., lead and cadmium electrodes, is used as a spongy structure that has a large surface area of the order of square meters per gram. A further advantage of such a porous structure is that the reaction products are precipitated immediately after their formation within the pores of the active material, close to the place of their origin, and the structure of the electrode remains nearly stable.

4.1.2. Nonactive Components

The split-up of the cell reaction into two electrode reactions as indicated in Figure 1 requires a number of nonactive components. They can be classified into conducting and nonconducting components.

4.1.2.1. Conducting Components

The current has to be collected from the active material and conducted to the terminals. Often the current conductor simultaneously acts as a support for the active material. In some systems

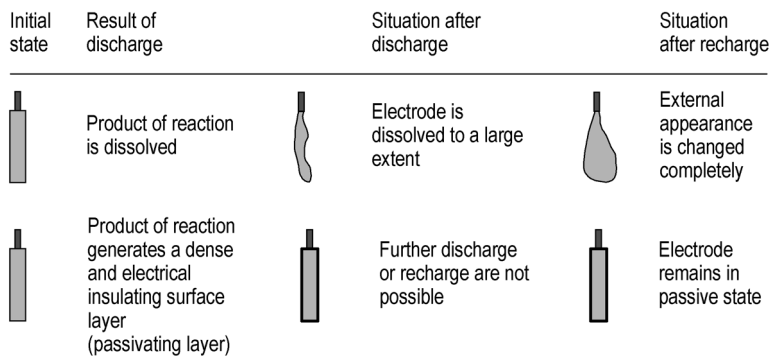


Figure 4. Effect of the solubility of the reaction products on electrode structure, when the discharging-charging mechanism occurs via the dissolved state

the container of the cell is made of metal and often simultaneously acts as terminal. In Leclanché cells the container represents simultaneously the active material of the negative electrode.

When a number of electrodes are connected in parallel within the cell, corresponding connecting parts like pole bridges are required.

Additives, like carbon or metal powder, sometimes are required to improve the conductivity of the active material, especially in thick electrodes, and in electrode materials with low conductivity.

4.1.2.2. Nonconducting Components

Separators. The electronic separation of the two electrodes is another important condition. Any electronic contact between positive and negative electrodes constitutes a short circuit that discharges the cell concerned. On the other hand, the ionic current through the separator should be impeded as little as possible. In the early days of battery development, the widely spaced electrodes were only separated by rods of glass or rubber. In modern batteries, thin sheets of plastic materials, e.g., polyethylene, are used with a fine pore system in the micrometer range that provides a void volume of more than 80%. Fiber felts of plastic or glass are also used as separators.

In batteries with an internal oxygen cycle, like valve-regulated lead–acid, sealed nickel–cadmium, or nickel–metal hydride batteries, the separator is important also for the functioning of the oxygen cycle: the fine pores of the separator hold the electrolyte while the large pores stay open for fast oxygen transport through the gaseous phase.

In some alkaline batteries ion-conducting films like cellophane are used to prevent gas flow between the cells.

Polymer electrolytes can also be regarded as ion-conducting separators.

A semipermeable membrane that only allows the permeation of sodium ions is the β -alumina in sulfur–sodium or nickel chloride–sodium batteries (\rightarrow Batteries, 3. Secondary Batteries, Chap. 3. Batteries with Nonaqueous Electrolyte and \rightarrow Batteries, 3. Secondary Batteries, Section 3.2.3 Nickel Chloride - Sodium (ZEBRA) Batteries).

Containers for rechargeable batteries are often made of nonconducting material. In lead–acid batteries it is a must to use glass, rubber, or plastics on account of the high cell voltage that would destroy all metals. Various types of plastic materials are used in the different systems. The advantage of a plastic container is that no insulation is required between adjacent cells. A general drawback of plastic materials is their permeability for gases, water vapor, and volatile substances. For this reason in sealed nickel–cadmium and nickel–metal hydride batteries metal has to be used instead of plastic material.

Seals. The seal of the terminals is a critical element. In *vented batteries* with liquid electrolyte it has to prevent creeping of the electrolyte which is especially observed for the negative terminal of batteries with alkaline electrolyte. With *sealed batteries*, the post seal has to prevent escape of electrolyte or its vapor, and the intake of oxygen from the surroundings. Special techniques have been developed for the different battery systems. Premium cells for space-craft applications but also lithium batteries for long service life often are equipped with metal–glass–metal seals that prevent any transport phenomena because of their glass body.

Vent plugs and valves are required, since a number of battery systems involve secondary reactions that generate gases which must escape. *Vents* as used for some rechargeable batteries are simple openings that allow gas flow in both directions, i.e., from outside into the battery and vice versa. The openings in such vent plugs are small to minimize water loss by evaporation. In modern batteries, such vents mostly are equipped with porous disks to prevent ignition sparks or flames from entering the cell and also the escape of acid or alkaline fumes from the cell.

Valves allow only the escape of gas and are used in most sealed batteries to prevent damage of the cell in the case of a too high internal pressure when the battery is abused, e.g., overcharged at a too high current rate (see Sections \rightarrow Batteries, 3. Secondary Batteries, 2.1.12 Vents, Valves and \rightarrow Batteries, 3. Secondary Batteries, 2.1.11 Container Material, Post Seals).

Rechargeable button cells in general have a *rupture vent* (breaking point) embossed in their metallic cell container that opens on a preset overpressure before the cell explodes. Safety features of this type are also employed in primary batteries but may be incorporated in their plastic seal instead.

4.2. Battery Parameters

The discharge/charge behavior of a battery depends on a number of parameters, like current, voltage, and temperature. These parameters have to be specified when such data are compared.

4.2.1. Voltage

In the case of reversible systems the *cell voltage* may be derived from the thermodynamic data of the cell reactions according to Equation 2. (But often, this equilibrium voltage cannot exactly be measured (even not at open circuit), since secondary reactions cause a slight deviation (see Fig. 9). Then the *open cell voltage* (OCV) is actually measured, which, depending on the system, is often a function of the state of charge (SOC). Other systems, like some primary lithium systems, offer a rather high initial open circuit voltage, obviously due to the presence of higher valence oxides. This voltage collapses by several hundred millivolts on the slightest load and never recovers to its initial value.

The cell voltage under load, the *closed circuit voltage* (CCV) depends on the current, the state of charge, and on the cell's history, like, e.g., its lifetime or storage period.

A further term is the *nominal voltage* of a cell or battery that approximates the voltage of the concerned battery system. It is generally an open circuit voltage, rounded off to achieve a simple voltage designation, e.g., 3 V instead of 3.14 V or 2.86 V.

The *coup de fouet* or *initial voltage minimum* is a voltage minimum as indicated in Figure 5 at the beginning discharge of fully charged lead-acid batteries and is in the range of 20 mV per cell. It is caused by the positive electrode and can be ascribed to crystallization overvoltage [30]. Initial voltage minima are also known for lithium batteries. They are referred to as *initial voltage*

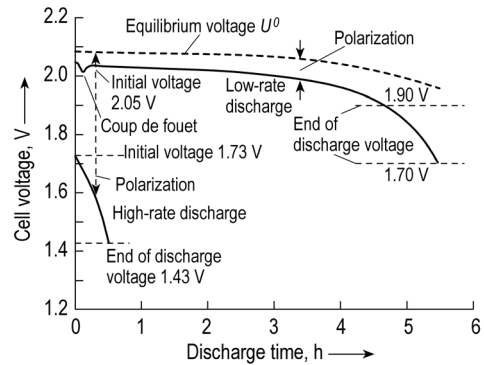


Figure 5. Typical low-rate discharge and high-rate discharge curves of a lead-acid battery and the main discharge parameters. The broken curve denotes the equilibrium or open circuit voltage.

delay and are caused by protecting layers being formed on the surface of the negative electrode during storage and being dissolved on discharge.

4.2.2. Capacity

The capacity of a battery is defined by international convention as the electrical charge in units of ampere hours that can be drawn from the battery. Thus, when the battery is discharged with a constant current, its capacity is given by the relation

$$C_{AH} = i \cdot \Delta t \quad (31)$$

A more general definition would be

$$C_{AH} = \int_0^t i(t) \cdot dt \quad (32)$$

The discharge parameters that, besides the design of a battery, mainly influence the capacity are:

- Discharge current,
- Voltage limit that has to be specified and is known under various names: the final, the end point, the cut-off, or end-of-discharge voltage (EOD) and
- Temperature.

Further parameters that also influence the capacity, are the state of charge and the history

of the battery, e.g., the preceding storage period. Any comparison of capacity data must always consider these parameters.

4.2.2.1. Secondary Batteries

Figure 5 shows as an example two typical discharge curves of a lead–acid battery. The upper curve represents a low-rate discharge, the lower curve a high-rate discharge.

The broken curve in Figure 5 represents the equilibrium voltage that for a lead–acid battery gradually decreases with progressing discharge on account of acid dilution. In other systems, where the electrolyte is not involved in the cell reaction, e.g., nickel–cadmium or nickel–metal hydride batteries, U^o remains approximately constant. The difference between the actual discharge curves and U^o is due to polarization according to Equation 7. This difference usually increases with progressing discharge because of a gradual increase of the internal resistance.

The *nominal* or *rated capacity* of a battery is specified by its manufacturer as the standard value that characterizes this battery. Usually it is specified for a constant-current discharge at 20°C or at room temperature. For the various applications, nominal or rated capacities are often referred to different discharge duration, termed as C_{20} , C_{10} , or C_5 , respectively, where the subscript denotes the discharge period in hours.

Capacity ratings expressed as multiples of the nominal capacity were initially introduced for nickel–cadmium batteries. But it became common practice to address the current that characterizes charging or discharging of small lead–acid batteries and other rechargeable battery systems also in terms of capacity ratings. In this case the discharge current is written

$$i = m \cdot C_r \quad (33)$$

where i is the current in amperes; m is a number that indicates the multiple or fraction of C_r ; C_r is the rated or nominal capacity in ampere hours, but expressed in amperes; and r is the discharge period in hours, the capacity is rated to. To indicate that the current is expressed as a multiple of the capacity, it is often written as “CA” or “C(A)”. In this case “C” does not mean a capacity in ampere hours but a corresponding

current in amperes. In regard to the dimensions, Equation 33 is not correct because it mixes quantities with units (i in A, C_r in Ah, m without unit). But in the battery field, this description of discharging and charging currents is well established and understood. It is even used in the standards of IEC/SC21A [31].

The factor m has no relation to discharge time: it is a pure number. For this reason, discharge rates in terms of multiples of the capacity cannot be converted into discharge durations. To evaluate the discharge duration, the discharge curves must be known.

The IEC Standard for lead–acid batteries [36], however, continues to use the corresponding currents, e.g., I_5 , I_{10} , I_{20} , that describe the actual discharge duration.

The *depth of discharge* (DOD) is an important parameter in regard to the number of cycles that can be reached with rechargeable batteries. For lead–acid batteries, deep discharges that are continued beyond the recommended maximum DOD, can reduce the service life dramatically [14].

4.2.2.2. Primary Batteries

For primary batteries the term “capacity” as defined by Equations 31 or 32 is of course also applicable. Two discharge methods are in use:

1. Constant current discharge
2. Constant resistance discharge

Some test houses prefer method (1). By far predominant is, however, method (2) as is evident from manufacturer’s technical handbooks. Method (2) prevails also in the IEC Standard for Primary Batteries [26, 33].

The discharge capacity of a battery decreases with increasing load as indicated in Figure 5 for a lead–acid battery. The same applies to primary batteries. The results of constant resistance discharges can be represented in a generalized form, shown in Figure 6: For a given cut-off voltage U_c , the discharge capacity $C(R)$ is plotted versus the discharge resistance R_d , measured in ohms.

Typical for this C – R curve is the sharp increase in capacity C on increase of R_d in the range of low resistance values (high rate range), whereas in the low rate range (i.e., large R_d

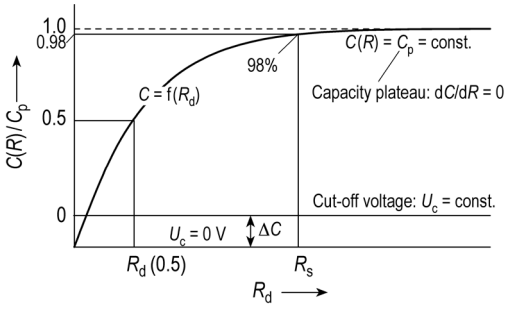


Figure 6. Schematic diagram of discharge capacity C versus discharge resistance R for a given end-point voltage and temperature. For the purpose of normalization $C(R)$ was divided by the plateau capacity C_p , that is reached at a sufficient high resistance. For the plateau $C(R)/C_p = 1$ is valid.

values) the discharge capacity C becomes finally independent of R_d . This is the battery's capacity plateau for which $dC/dR \approx 0$ is valid [32], i.e., $C \approx \text{const}$. The C - R plot is typical for all batteries. However, depending on the system's self-discharge which acts in parallel to the external discharge current, the plateau value of C_p may decrease again on further increasing R values. The plateau value $C_p \approx \text{const}$ is the battery's maximum capacity. $C_p \approx \text{const}$ implies that within the plateau region also the discharge voltage $U(\text{plateau})$ is approximately constant. $U(\text{plateau})$ is independent of size and construction of the battery, and typical for its electrochemical system, because with such a low load, transport reactions are fast enough, and the battery's polarization is only determined by the charge-transfer resistance of its electrodes.

Depending on manufacturer, the capacity of primary batteries may be given in terms of a service output duration, when simulating a certain application (e.g., transistor radio test, portable lighting test, toy test, etc.). The service output duration (in hours), as given for the individual application test, is proportional to the battery's capacity. The IEC Standard for Primary Batteries, which so far has proposed most of the existing application tests, quotes only "Minimum Average Duration Values" [26, 33] instead of capacities to describe battery performance. The "Minimum Average Duration Values" are exceeded significantly by at least 90% of battery products available on the market.

4.2.3. Energy Content

In general form, the energy E that can be drawn from the battery is represented by the product

$$E = \int_0^t U(t) \cdot i(t) \cdot dt \quad (34)$$

where E is the energy content in watt hours; U the voltage in volts; i the discharge current in amperes; and t the discharge period in hours. Direct measurements of the drawn energy are made with constant load (W), which means that the voltage decrease with proceeding discharge has to be compensated by an increase in current.

Usually, the battery is discharged with a constant current and the energy output is calculated by multiplying the measured Ah capacity by the discharge voltage. Characteristic voltages that are used for such an approximation are:

- *Initial discharge voltage*: voltage at the moment the load is applied.
- *Averagedischargevoltage* or *mean discharge voltage*: approximate average of the voltage during the whole discharge period (average discharge voltage \times current = discharged energy).
- *Mid-point discharge voltage*: voltage after 50% of the capacity has been discharged (\approx average voltage).

For constant resistance discharge as normally carried out for primary batteries, with $R = \text{const}$ as resistive load, Equation 35 applies

$$E = \frac{1}{R} \int_0^t U(t)^2 dt \quad (35)$$

Figure 7 is a schematic battery discharge curve with load resistance R for a given end-point voltage U_c at constant temperature ϑ . The average discharge voltage (and average discharge current) is given by the horizontal line that is defined by equal areas for $t(A1 = A2)$. For a symmetrical curvature this average voltage equals the mid point discharge voltage for $t_D = 50\%$.

Specific Energy and Energy Density. For system comparison it has become common