**Bacon, Francis Thomas**



(Courtesy of Michigan State University, Chemistry Department)

(Dec. 21, 1904, Billericay, Essex, UK – May 24, 1992, Little Shelford, near Cambridge, UK) Bacon was educated at Eton College specializing in science and at the Trinity College in Cambridge obtaining a degree in mechanical sciences. He started to work on the hydrogen–oxygen fuel cell in 1932. He constructed the first practical and efficient → *fuel cells*. He used potassium hydroxide instead of acids which was less corrosive to the electrodes; therefore, platinum could be replaced by inexpensive nickel electrodes. The development of the porous → *gas–diffusion electrodes* of high surface area was the other important step. Beside everyday applications such as transport, the most notable success was that Bacon cells provided electrical power for the functioning of systems and the production of drinking water in the manned moon flights of the Apollo space program.

Francis Thomas Bacon was a direct descendant of Sir Francis Bacon (1561–1626). Among others he was elected a fellow of the Royal Society (1973), and awarded the first Grove Medal (1991) [ii].

*Refs.: [i] Williams KR (1994) Biog Memoirs of Fellows Roy Soc 39:2–9; [ii] Bacon FT (1979) J Electrochem Soc 126:7C*

GI

**Bacon cell**   Hydrogen–oxygen fuel cell initially developed by → *Bacon*. → *gas–diffusion electrodes* were prepared from carbonyl nickel by pressing and subsequent sintering. The three-phase boundary was fixed inside the porous electrode body by preparing the electrode as a bilayer structure. The "working layer" with pores of about 10–30 μm diameter is covered on the electrolyte solution side by a thin layer with an average pore diameter of 1.5 μm. Pressure of the feed gas needed for operation is adjusted to a value at which the large pores are kept filled with gas whereas the small pores are left filled with electrolyte solution by capillary action, bubbling of reactant gas is thus avoided. Because of the poor electrocatalytic activity of nickel and the limited actual (true) surface area the operation temperature had to be elevated to about 200 °C. Vapor pressure of the alkaline electrolyte solution (37–50% KOH) required operation pressures of 20–40 atm. Corrosion of the oxygen-consuming nickel electrode enhanced at these temperatures was limited by preoxidation of the porous cathode body. By oxidizing treatment of the electrode in lithium-containing caustic solution a doped semi-conducting nickel oxide is formed showing

improved corrosion resistance. Cell voltages of 0.9 V at current densities of $300\,\mathrm{mA\,cm^{-2}}$ were achieved.

*Ref.: [i] Kordesch G, Simader G (1996) Fuel cells and their applications. VCH, Weinheim*

RH

**Background current**  (i) Generally, in electrochemical systems, any current other than the wanted one (e.g., see → *dark current* in photovoltaics).

(ii) In → *voltammetry* any current that is not due to the analyte. At high → *potentials* the working window of the → *indicator electrode* is limited by the → *oxidation* of → *electrode material*, or → *anions* of the → *supporting electrolyte*, or the → *solvent*, and at low potentials it is limited by the → *reduction* of → *hydrogen* ions, or → *cations* of the supporting electrolyte, or the solvent, or the electrode material (e.g., → *mercury* in the presence of ammonium salts in → *non-aqueous* media). Within the window, a → *residual current* consists of → *capacitive* and → *faradaic* components. A → *double layer* charging current can not be avoided, but its influence can be diminished by the current sampling procedure in → *pulse voltammetric* techniques. Generally, the capacitive current is proportional to the rate of changing the → *electrode potential* (E), → *capacitance* (C) and → *surface* area (S): $I = \left[ CS + S\,(E - E_{\sigma=0}) \frac{\mathrm{d}C}{\mathrm{d}E} \right] \frac{\mathrm{d}E}{\mathrm{d}t} + C\,(E - E_{\sigma=0}) \frac{\mathrm{d}S}{\mathrm{d}t}$. The first term limits the range of scan rates that can be applied in → *cyclic voltammetry* on stationary electrodes ($\mathrm{d}S/\mathrm{d}t = 0$), while the second term is important only in DC → *polarography* with → *dropping mercury electrode*. However, care must be taken to avoid a leakage of solution into any gap between the active electrode disk and the insulating sheath, a porosity of electrode surface, and the formation of a thin film of the solution surrounding the lower end of the mercury thread within the tip of the capillary. In all these cases a fluctuating surface area may cause the fluctuation of capacitive current. In pulse voltammetry, the decay of charging current associated with these imperfections is slower than the decay of capacitive current of the electrode surface [i, ii].

Faradaic components of the background current are caused by the reduction of → *oxygen* or other impurities in the supporting electrolyte, and by the formation of oxide layers on metal electrodes. The concentration of oxygen in well-aerated electrolyte is about 0.1 mM. Oxygen is reduced at noncatalytic electrodes in two separate two-electron steps at potentials that vary between 0.05 V and −0.9 V vs. SCE, depending on pH and on electrode material. For the majority of measurements, oxygen must be removed from the solution. In the laboratory, solutions are saturated with nitrogen or argon to reduce the partial pressure of oxygen to a very low value. Ultrapure gases should always be preferred. However, there is a chance to contaminate solutions with oxygen due to the permeability of most plastic tubes used to propel nitrogen or argon. In extreme cases full glass apparatus has to be used. Oxygen adsorbed on particles of → *graphite* powder must be removed by heating the powder in nitrogen prior to the preparation the → *carbon paste electrode*. Otherwise the response may appear noisy. In → *anodic stripping voltammetry* the purity of mercury is very important. It must be ensured that no traces of investigated element are present in mercury prior to the accumulation. The supporting electrolyte should be prepared by using extrapure chemicals. Finally, the → *cell* response may appear noisy due to poor electrical contacts and faults in the interconnecting cables. The noise can be reduced by placing the cell in a → *Faraday cage*.

(iii) In → *electrolysis*, → *coulometry*, → *electrogravimetry*, → *electrosynthesis* and → *batteries*, the term background current is also used for currents that are not caused by the main process.

*Refs.: [i] Brett CMA, Oliveira Brett AM (1998) Electrochemistry. Oxford University Press, Oxford; [ii] Pelzer J, Scholz F, Henrion G, Nitschke L (1989) Electroanalysis 1:437*

ŠKL

**Back-titration**  A process for quantitative analysis in which an excess of → *titrant* is added to the → *titrand* and then a second titrant is used to determine the excess amount. This process is often required when the rate of reaction between

the → *analyte* and titrant is slow or when the → *standard solution* lacks stability [i].

*Ref.: [i] Mendham J, Denney R, Barnes J, Thomas M, Denney R (2000) Vogel's quantitative chemical analysis. Prentice Hall, New Jersey*

FG

**Bacterial corrosion** → *biocorrosion*

**Baghdad battery** A number of artifacts consisting of ca. 130 mm long clay jars containing a copper cylinder made of a rolled-up copper sheet, capped at the bottom, in turn covering and protecting an iron rod were discovered by Leroy Waterman in the village of Khuyut Rabua (Tel Omar) near Baghdad, Iraq in 1936. Wilhelm König, the German director of the National Museum of Iraq published a paper speculating that they may have been → *galvanic cells*, perhaps used for → *electroplating* gold onto silver objects. König thought the objects might be Parthian (between 250 BC and 224 AD). However, the style of the pottery is Sassanian (224–640 AD) which means that they are more recent than König thought. Although there is still a controversy regarding the real purpose of these artifacts, they could be or could have been used to generate electricity since the iron rods are isolated from the copper by asphalt plugs, and if the jars were filled with a liquid, e.g., with vinegar which was known also in ancient time, this surrounds the iron rod as well, therefore it is, in fact, a copper-iron battery. When filled with vinegar, the jar produces about 1.1 volts.

*Refs.: [i] Dunsch L (1985) Geschichte der Elektrochemie. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, pp 9–10; [ii] MacKechnie JC (1960) J Inst Electrical Eng 6:356; [iii] Dubpernell G (1978) Evidence of the use of primitive batteries in antiquity. In: Selected topics in the history of electrochemistry. The Electrochemical Soc, Princeton, I-22; [iv] Keyser PT (1993) J Near Eastern Studies 52:81–98*

GI

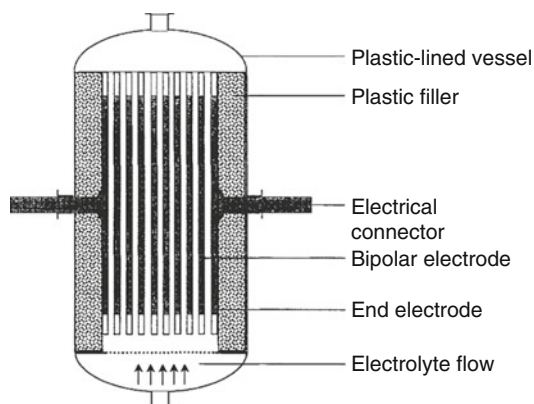**Baizer–Monsanto process** (also called *Monsanto* process) is the reductive electrohydrodimerization of acrylonitrile, ACN, to adipodinitrile, ADN, an intermediate in the manufacture of Nylon 66™:
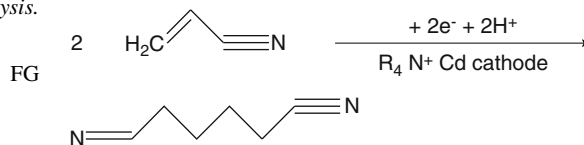


The principle has been known since the 1940s, but it was M.M. Baizer who initiated in 1959 the use of quaternary ammonium salts such as tetraethylammonium *p*-toluenesulfonate in this reaction, leading to mass yields of 90% ADN. Together with Monsanto he commercialized and improved the process ever since. First used process setups consisted of divided cell reactors with → *catholyte*s of an aqueous solution of ACN and ADN in 40% tetraethylammonium ethyl sulfate, an → *anolyte* of diluted sulfuric acid, separated by an ion exchange membrane, and lead electrodes (anode with 1% silver).

Soon after, the presently used undivided cell (see Fig.) was developed to overcome the shortcomings of the former, especially the high energy costs. The cadmium cathodes and steel anodes are kept at a 2 to 3 mm distance by plastic spacers in a pressure vessel. The aqueous sodium phosphate electrolyte containing hexamethylene bis(ethyltributyl)ammonium phosphate (0.4%) and emulsified acrylonitrile is pumped continuously through the cells with ca. 1 m s$^{-1}$ and at ca. 55 °C. The electrochemical process parameters are: cell voltage: 3.83 V, current density: 2.0 kA m$^{-2}$, power consumption: 2.43 kWh kg$^{-1}$. The crude ADN is passed through a multi-column distillation system, where the pure product is separated from by-products and ACN, which is returned to the process. The adipodinitrile purity must be over 90% to serve as initial product for the hydrogenation into hexamethylenediamine. Crucial points of the described process setup are a limited life span of the electrodes of only 2 to 3 months, and the thereby caused discontinuity of the process, as well as special safety considerations resulting from oxygen

**Baizer–Monsanto process — Figure**

and (by-product) hydrogen together with other volatile organics in one single gas phase. Nowadays [iii] production capacities of the B.–M. process are (in tons per year): Solutia (Dakatur, AL, USA): 181,000; BASF (Seal Sands, UK): 91,000; Asahi Chemical (Nobeoka, Japan): 37,000.

*Refs.: [i] Baizer MM (1964) J Electrochem Soc 111:215; [ii] Baizer MM, Danly DE (1979) Chem Ind (London) 435:439; [iii] Pütter H (2001) Industrial electroorganic chemistry. In: Lund H, Hammerich O (eds) Organic elec- trochemistry. Marcel Dekker, New York, pp 1259–1307; [iv] Pletcher D, Walsh FC (1990) Industrial electrochem- istry. Chapman & Hall, London, a 298*

MHer

**Balbach–Thum cell**  Electrolytic cell for silver refining ($\rightarrow$ *electrorefining*). On the bottom of the cell (about 250–300 dm$^3$ volume) a silver plate is placed as cathode. The anode made of raw silver is placed in a basket in a cloth bag. A solution of silver nitrate is employed. Dissolved silver ions are deposited as a dendritic mass on the cathode, metal ions less noble than silver stay in solution, whereas more noble metals are kept as anode sludge in the cloth bag. This cell is frequently employed in the USA, the $\rightarrow$ *Möbius cell* is used in Europe. As compared to the Möbius cell the anodes are consumed completely, only a single- piece cloth is needed, and no moving mechanical

parts are involved. As drawbacks the large floor space of the cell, the low current density, the large cell voltage because of the large interelectrode distance, the need for manual scraping of the cathode on the bottom of the cell, and the large solution inventory may be considered.

*Refs.: [i] Zirngiebl E (1993) Einführung in die Ange- wandte Elektrochemie. Salle & Sauerländer, Frankfurt; [ii] Pletcher D, Walsh FC (1993) Industrial electrochem- istry. Blackie Academic & Professional, London*

RH

**Band bending**  "Band bending" is an example of laboratory jargon, and refers to the occurrence of internal electric fields inside $\rightarrow$ *semiconductor* materials, howsoever caused. The origin of the term is as follows. A common way to visualize energy states inside semiconductors is to draw the positions of both band edges (the valence band edge and the conduction band edge) on an "energy band diagram" (a plot of energy versus distance). When an internal electric field exists inside the semiconductor material, the band edges appear curved on this plot, thus leading to the name "band bending". Experimentally, band bending arises in two ways. At thermo- dynamic equilibrium, band bending manifests spontaneously at the interface between two semi- conductors, or at the interface between a semi- conductor and a metal, if the $\rightarrow$ *electron work function* of each phase is different. Away from thermodynamic $\rightarrow$ *equilibrium*, band bending can be increased or decreased by applying an electric potential difference of appropriate sign and magnitude between the two phases. See also $\rightarrow$ *flat-band potential*.

SF

**Band gap**  $\rightarrow$ *semiconductor*

**Band-pass filter**  $\rightarrow$ *signal filtering*

**Band-stop filter**  $\rightarrow$ *signal filtering*

**Bardeen–Cooper–Schrieffer theory**    $\rightarrow$ *BCS theory*

## Barker, Geoffrey Cecil



(Reprinted from J. Electroanal Chem. 75 (1977) 1, Copyright (1977), with permission from Elsevier)

(Oct. 2, 1915, Belper, Derbyshire, UK – Mar. 31, 2000, Oxford, UK) invented in 1952 → *square-wave polarography* [i], in 1958 → *pulse polarography* [ii, iii], and → *radio frequency polarography* [iv] applying for the first time → *faradaic rectification*. Beside these techniques, Barker developed several other variants of polarography and he is the father of modern photoemission studies at electrodes [v, vi]. During World War II Barker took part in the radar development in the UK. The thorough learning of electronics during that period was certainly the basis for his great achievements in developing electrochemical measuring techniques. Barker was the first who developed the protocol of → *stripping voltammetry* [vii].

*Refs.: [i] Barker GC, Jenkins IL (1952) Analyst 77:685; [ii] Barker GC, Gardner AW (1958) At Energy Res Establ, Harwell, C/R 2297; [iii] Barker GC, Gardner AW (1960) Fresenius Z Anal Chem 173:79; [iv] Barker GC (1958) Anal Chim Acta 18:118; [v] Barker GC (1977) J Electroanal Chem 75:1; [vi] Parsons R (2000) J Electroanal Chem 494:77; [vii] Scholz F (2011) J Solid State Electrochem 15:1509*

FS

## Barker square-wave voltammetry

The protocol of → *square-wave voltammetry* developed by → *Barker* is based on a square wave potential train with a frequency that is high compared to the scan rate of the DC potential, i.e., a multiple number of positive and negative potential pulses is applied during a period where the DC potential changes only by a negligible increment (for a linear DC ramp) or not at all (for a staircase ramp).

*Refs.: [i] Barker GC, Jenkins IL (1952) Analyst 77:685; [ii] Bond AM (1980) Modern polarographic methods in analytical chemistry. Marcel Dekker, pp 391–399; [iii] Lovrić M (2010) Square-wave voltammetry. In: Scholz F (ed) Electroanalytical methods, 2nd edn. Springer, Berlin, pp 121–145; [iv] Mirčeski V, Komorsky-Lovrić Š, Lovrić M (2007) Square-wave voltammetry. In: Scholz F (ed) Monographs in Electrochemistry. Springer, Berlin*

FS

## Barrier oxide film

When the surface of a metal is anodically oxidized, a dense oxide film may grow that protects the metal underneath. Such barrier films are important for → *corrosion* protection and also for fabricating → *capacitors*.

*Ref.: [i] Marcus P, Maurice V (2000) Passivity of metals and alloys. In: Schütze M (ed) Corrosion and environmental degradation, vol 1. Wiley-VCH, Weinheim, pp 131*

FS

## Barrierless process

is a → *charge transfer reaction* occurring under small deviation from equilibrium (for example at low → *overpotential*) in the absence of an activation barrier, and with a → *transfer coefficient* equal to unity. In terms of the reaction energy profile, this situation corresponds to the term of products intersecting the term of reactants in its minimum. The → *activation energy* becomes equal to reaction → *free energy*. Simultaneously, the reverse reaction appears to be an → *activationless process*. The problem was addressed systematically by Krishtalik et al. starting from 1960 (see original refs. in [i, ii]). In the framework of the slow discharge theory of → *Frumkin* (see there → *Frumkin's slow discharge theory*), the kinetics of a b.p. is expected to be independent on solution composition, with a Tafel slope (→ *Tafel equation*) equal to $2.3RT/F$. The cathodic barrierless p. can be experimentally observed when one starts at potentials more negative than the → *equilibrium potential*, not being screened by a reverse anodic process. The features of the barrierless p. were observed experimentally for → *hydrogen evolution* on mercury in acidic aqueous and ethylene glycol solutions containing certain strongly adsorbing ions, as well as in concentrated solutions

of some acids. The observation of barrierless processes opens up possibilities to obtain the latent heat of the electrode process, the true activation energy, and the temperature derivative of the → *Galvani potential*. Similar behavior was found for → *hydrogen evolution* on Ag and chlorine evolution on graphite. Studies of b.p. stimulated an active development in understanding isotope effects [iii, iv] and high temperature electrochemical techniques for aqueous solutions [iv], as well as the analysis of the preexponential factor in terms of → *proton transfer* theory.

*Refs.: [i] Krishtalik LI (1968) Electrochim Acta 13:1045; [ii] Krishtalik LI (2002) Electrochim Acta 48:181; [iii] Krishtalik LI, Tsionsky VM (1971) J Electroanal Chem 31:363; [iv] Tsionskii VM, Kriksunov LB, Krishtalik LI (1991) Electrochim Acta 36:411*

GT, OP

**Batteries** Power sources that produce → *direct current* (DC) by converting chemical energy into electrical energy. These power sources employ spontaneous electrochemical reactions as the source of the electrical energy by forcing the electrons to flow from a reductant (anode) to the oxidant (cathode) externally, through the consumer. Each single battery cell contains a negative electrode (→ *anode*) that contains a reducing material in which an oxidation process takes place upon discharge, a positive electrode (→ *cathode*) containing an oxidizing material in which an oxidation process takes place upon discharge, and an electrolyte system (liquid, gel, or solid). Batteries can include several electrochemical cells interconnected in series or in parallel to provide the required potential and current levels. The main parameters that define battery performance are (i) → *voltage*, (ii) electrical → *energy*, (iii) electrical → *power*. The battery voltage depends on the electrode chemistry and on the number of cells in the stack. The overall electrical energy is usually expressed in watt-hours (Wh) and is calculated as the product of capacity and voltage: $E = UIt$ ($U$ in volt, $I$ in ampere, and $t$ in hours). The electrical power is the rate at which a battery can deliver electrical energy. The rate is expressed in watts (W) and calculated as the product of current and voltage:

$P = UI$ ($U$ in volt and $I$ in ampere). There are two significant types of batteries, primary and secondary. **Primary batteries** are not designed to be recharged. **Secondary batteries** are designed for repetitive use, and thus can be charged and discharged periodically. Batteries can be classified in different ways: primary vs. rechargeable, aqueous vs. nonaqueous, solid electrolyte vs. liquid electrolyte solution, stationary vs. flow, and ambient temperature vs. high temperature. The most important batteries are $Zn - MnO_2$ (primary) (→ *alkaline batteries*), $Li - MnO_2$ and $Li - SOCl_2$ (primary), $Pb/H_2SO_4/PbO_2$ (→ *lead–acid battery*), $Cd - NiOOH$ ($Ni - Cd$, secondary), Metal-hydride-based batteries like Ni-Metal-Hydride (NiMH, secondary) and secondary → *lithium batteries* (most common Li-graphite ($Li_xC_6$) vs. $Li_{1-x}CoO_2$, $0 < x < 1$). The field of batteries is very dynamic, and extensive efforts are devoted throughout the world to R&D of new battery systems and the improvement of existing systems.

*Refs.: [i] Linden D (1994) Handbook of batteries, 2$^{nd}$ edn. McGraw-Hill, New York; [ii] Crompton TR (2000) Battery reference book, 3$^{rd}$ edn. Newness, Oxford; [iii] Dell RM, Rand DAJ (2001) Understanding batteries. Royal Society of Chemistry*

OC, DA

**Baudet cell** This was a → *chromic acid battery* with zinc anodes, and a construction that the chromic acid solutions could be delivered from vessels containing solid potassium dichromate and sulfuric acid.

See also → *Daniell cell*, → *zinc*, → *$Zn^{2+}$/Zn electrodes*, → *$Zn^{2+}$/Zn(Hg) electrodes*, → *zinc–air batteries (cell)*, and → *Leclanché cell*.

*Ref.: [i] Hauck WP (1883) Die Galvanischen Batterien, Accumulatoren und Thermosäulen, 2$^{nd}$ edn. Hartleben's Verlag, Wien*

FS

**BCS theory** (Bardeen–Cooper–Schrieffer theory) describes the nature of superconductivity and other properties of the so-called Type I superconductors, a group of 30 pure metals such as Al, In, Sn, Hg, V, Pb, etc. These exhibit zero electrical resistivity below a certain "critical"

temperature, zero internal magnetic field, and a critical magnetic field leading to the disappearance of superconductivity. The critical magnetic fields in the Type I superconductors are very low, limiting possible applications. A better stability with respect to temperature and magnetic field is characteristic of the so-called Type II superconductors, usually alloys such as $Nb_3(AlGe)$.

One conceptual element of the BCS theory is the formation of → *Cooper pairs*, namely pairing of → *electrons* close to the → *Fermi level* due to a slight attraction resulting from phonon interaction with the crystal lattice. These pairs of electrons act like bosons which can condense into the same energy level. An energy band gap is to be left above these electrons on the order of $10^{-3}$ eV, thus inhibiting collision interactions responsible for the ordinary → *resistance*. As a result, zero electrical resistivity is observed at low temperatures when the thermal energy is lower than the band gap. The founders of the BCS theory, J. Bardeen, L. Cooper, and R. Schrieffer, were awarded the Nobel Prize in 1972.

See also: → *semiconductor*, → *conductor*, → *Ohm's law*, → *conductance*, → *conduction band*.
*Refs.: [i] Rohlf JW (1994) Modern physics from α to Ω. Wiley, New York; [ii] Cyrot M, Pavuna D (1992) Introduction to superconductivity and high-$T_c$ materials. World Scientific, London*

VK

**Beam deflection**   A deviation of the light beam wavefront when it passes from one medium to another with a different → *refractive index*, or through a medium with an inhomogeneous refractive index. The wavefront velocity is ($v = c/n$) and the wavelength ($\lambda$) is related to $n$ by $\lambda = vf$, where $c$ is the velocity of light in a vacuum, $n$ is the refractive index of the medium and $f$ is the beam frequency. Thus, the wavelength of a laser beam wavefront will increase when the refractive index of the electrolyte decreases [i]. See also → *refraction* or → *mirage effect*.
*Refs.: [i] Rosolen JM, Decker F, Fracastoro-Decker M, Gorenstein A, Torresi RM, Cordoba Torresi SI (1993) J Electroanal Chem 354:273; [ii] Garay F, Barbero CA (2006) Anal Chem 78:6740*

FG

**Beating mercury heart**   Under certain conditions a drop of mercury pulsates in a rhythmic fashion, resembling a beating heart [i–iv]. It is a demonstration of periodic behavior in electrochemical systems (see → *electrochemical oscillations*).
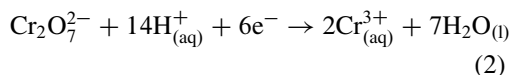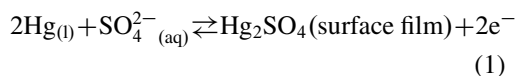
The following procedure has to be applied:
- Place a drop of pure mercury in a watch glass.
- Cover it with 6 mol dm$^{-3}$ H$_2$SO$_4$ solution.
- Add 1–2 cm$^3$ 0.1 mol dm$^{-3}$ K$_2$Cr$_2$O$_7$ solution.
- Put a steel needle which just touches the Hg drop.
- Add 0.5–2 cm$^3$ 18 mol dm$^{-3}$ H$_2$SO$_4$ solution until the Hg drop starts to pulsate.

During the pulsation the mercury drop will change its shape. A periodic variation between round and triangle shapes can be seen.
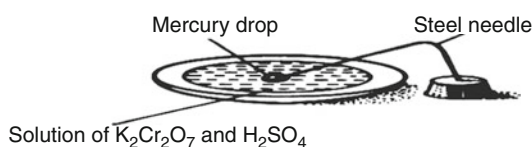
The phenomenon can be explained as follows.

The → *surface tension* ($\gamma$) of the mercury (see → *electrocapillary curves*) is a function of the potential (i.e., the → *surface charge*, $\sigma$). When $\sigma = 0$ $\gamma$ has a maximum value, consequently the mercury drop will take a spherical or round shape. When $|\sigma| > 0$ $\gamma$ decreases, and the drop tends to flatten.

At the two different metals the following reactions take place [ii]:

$$2Hg_{(l)} + SO_4^{2-}{}_{(aq)} \rightleftarrows Hg_2SO_4 \text{(surface film)} + 2e^-$$
(1)

$$Cr_2O_7^{2-} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$$
(2)

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

$$Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + e^-.$$
(4)

At the iron surface an oxide–hydrate layer may develop.



Mercury drop        Steel needle

Solution of K$_2$Cr$_2$O$_7$ and H$_2$SO$_4$

**Beating mercury heart — Figure.** The experimental arrangement

$Hg|Hg_2SO_4$ is the positive electrode (with excess positive charge on its surface), iron is the negative electrode in the → *galvanic cell* formed. When the iron nail contacts the mercury, as a consequence of the variation of the shape of the Hg drop, the cell will be short-circuited. Therefore, the electrons transferred from the iron to the $Hg|Hg_2SO_4$ electrode reduce the surface $Hg_2SO_4$ film back to metallic mercury. The surface tension increases again and the drop becomes rounder and it will lose the direct contact with the iron nail, i.e., the short-circuiting will be interrupted. Then, the whole process starts again.

*Refs.: [i] Summerlin LR, Ealy JL Jr (1985) Chemical demonstrations. American Chem Soc, Washington, pp 93–94; [ii] Marques MI, Zhao Y, Garcia N (1997) J Phys Chem B 101:2333; [iii] Smolin S, Imbihl R (1996) J Phys Chem 100:19055; [iv] Keizer J, Rock PA, Lin SW (1979) J Am Chem Soc 101:5637*

GI

### Beckman, Arnold Orville



(Courtesy of Arnold and Mabel Beckman Foundation)

(April 10, 1900, Cullom, Illinois, USA – May 18, 2004, La Jolla, California, USA) Earned his B.Sc. and M.Sc. degrees from the University of Illinois. Received a Ph.D. from the California Institute of Technology in 1928. He founded what eventually became Beckman Instruments in 1935 with the invention of the acidimeter which was later called a → *pH* meter. Beckman developed also the UV-VIS (1940) and IR spectrophotometers (1942) and the Helipot (helical potentiometer) (1940) as well as a dosimeter (1942).

*Refs.: [i] http://www.chemheritage.org/explore/Beckman/chptr1-9.htm; [ii] http://www.beckman.com/hr/memorial/mem_news.asp; [iii] Inzelt G (2005) J Solid State Electrochem 9:181*

GI

### Becquerel, Antoine César
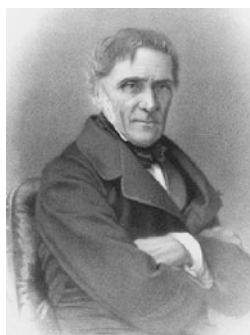


(© Collections Ecole Polytechnique)

(Mar. 8, 1788, Châtillon-sur-Loing, France – Jan. 18, 1878, Paris, France) French scientist, professor of physics at the Museum of Natural History (Paris), developed the "Constant Current Cell", but received recognition for this cell only in France whereas elsewhere the almost identical cell is called → *Daniell cell* (→ *Daniell*). Becquerel helped in validating → *Faraday's law*, extensively studied metal deposition in particular in metallurgy and surface finishing. He published more than 500 papers including studies on the electrocapillary effect and a textbook on electrochemistry in 1843.

*Refs.: [i] Magnusson M (ed) (1990) Chambers biographical dictionary. W&R Chambers, Edinburgh; [ii] Crystal D (ed) (1998) The Cambridge biographical encyclopedia. Cambridge University Press, Cambridge; [iii] Becquerel AC (1843) Éléments d'électro-chimie. Paris (German translation: Becquerel AC (1848) Elemente der Electro-Chemie, 2$^{nd}$ edn. Otto, Erfurt)*

RH

### Beetz, Wilhelm von



(Reproduced from [i])

(March 27, 1822, Berlin, Germany – January 22, 1886, Munich, Germany). Following his

University studies he became *Privatdozent*, later Professor at the cadet corps and the artillery and engineering school in Berlin. In 1855, he became Professor in Bern, in 1858 in Erlangen, and in 1868 in Munich (Technical Highschool). From 1874 to 1877 he was Director of the Polytechnic in Munich and in 1876 he was ennobled (personal nobility). Together with the physicists Gustav Karsten, Carl Hermann Knoblauch, Wilhelm Heintz, and the physiologists → *Bois-Reymond*, and, Ernst von Brücke, he has founded the "Physikalische Gesellschaft zu Berlin" ("Physical Society at Berlin"), the forerunner of the "Deutsche Physikalische Gesellschaft" ("German Physical Society") on January 14, 1845. In 1854 Beetz has shown that glass is a conductor of electricity below its melting point [ii].

Refs.: [i] Scholz F (2011) J Solid State Electrochem 15:5; [ii] Beetz W (1854) Ann Phys 168:452

<div align="right">FS</div>

**Behrend, Anton Friedrich Robert**



(Dec. 17, 1856, Harburg, Germany – Sep. 15, 1926, Hannover, Germany) Ph.D. in organic chemistry, Leipzig 1881. In 1893, Behrend performed the first → *potentiometric titration* (precipitation) in the laboratory of → *Ostwald, F.W.* in Leipzig, Germany. He titrated a mercury(I) nitrate solution with chloride, bromide, and iodide ions [i] using a mercury electrode as → *indicator electrode*. From 1894 to 1924 he was Professor of organic and physical chemistry in Hannover. Behrend is also well-known for the so-called Behrend rearrangement in organic chemistry [ii].

Refs.: [i] Behrend R (1893) Z phys Chem 11:466; [ii] Stock JT (1992) J Chem Educ 69:197

<div align="right">FS</div>

**Bending beam method**   The principles of the "bending beam" ("bending cantilever", "laser beam deflection", "wafer curvature") method were first stated by Stoney [i], who derived an equation relating the stress in the film to the radius of curvature of the beam. The bending beam method can be effectively used in electrochemical experiments, since the changes of the → *surface stress* ($\Delta g$) for a thin metal film on one side of an insulator (e.g. glass) strip (or a metal plate, one side of which is coated with an insulator layer) in contact with an electrolyte solution (→ *electrode*) can be estimated from the changes of the radius of curvature of the strip. If the → *electrode potential* changes, electrochemical processes resulting in the change of $g$ can take place exclusively on the metal side of the sample. The change in $g$ induces a bending moment and the strip bends. In case of a thin metal film on a substrate if the thickness of the film $t_f$ is sufficiently smaller than the thickness at of the plate, $t_s \gg t_f$, the change of $g$ can be obtained by an expression based on a generalized form of Stoney's equation

$$\Delta g = k_i \Delta(1/R), \qquad (1)$$

where $k_i$ depends on the design of the electrode [ii]. In most cases
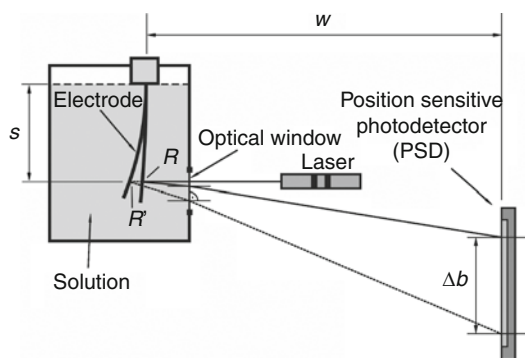


**Bending beam method — Figure.** Scheme of the electrochemical (optical) bending beam setup

**B**

$$k_{\mathrm{i}} = E_{\mathrm{s}} t_{\mathrm{s}}^2 / 6(1 - \nu_{\mathrm{s}}), \tag{2}$$

where $E_{\mathrm{s}}$, $\nu_{\mathrm{s}}$, and $R$ are Young's modulus, Poisson's ratio and radius of curvature of the plate, respectively.

The derivation of Eq. (1) implies the assumption that $\Delta g = t_{\mathrm{f}} \Delta \sigma_{\mathrm{f}}$, where $\Delta \sigma_{\mathrm{f}}$ is the change of the film stress. (In principle, if there are both plastic and elastic contributions to the total strain, the "generalized surface parameter" $(\gamma^{\mathrm{s}})$ [iii] can be determined ($\rightarrow$ *interfacial tension*).)

According to Eq. (1), for the calculation of $\Delta g$ the changes of the reciprocal radius $\Delta(1/R)$ of curvature of the plate must be known. The values of $\Delta(1/R) = \Delta g / k_{\mathrm{i}}$ can be calculated, if the changes $\Delta \theta$ of the deflection angle $\theta$ of a laser beam mirrored by the metal layer on the plate are measured using an appropriate experimental setup as shown in the Figure [iv]. The deflection can be determined also with other methods, e.g., with a $\rightarrow$ *scanning tunneling microscope* [v–vi]. For the geometry shown the following approximate equation can be derived for large $R$ and $s$, and small $\theta$:

$$\Delta\left(\frac{1}{R}\right) \approx \frac{\Delta\theta}{2n_{\mathrm{s,i}}s} \approx \frac{\Delta b}{2n_{\mathrm{s,i}}sw}, \tag{3}$$

where $s$ is the distance between the level of the solution in the cell (practically the lower end of the electrode holder) and the reflection point of the laser beam on the glass plate covered by a thin metal layer; $w$ is the distance between the electrode and the position sensitive photo detector (PSD) and $\Delta b$ is the change of the position of the light spot on the PSD. (Equation (3) is a good approximation only if the distance of the electrode from the optical window can be neglected compared to that of the PSD.) Since the laser beam is reflected inside the solution as shown in the Figure, and the deflection is measured outside the cell (in the air), the refractive index $n_{\mathrm{s,i}}$ of the solution also must be taken into account [vii–viii]. Consequently, from Eqs. (1) and (3) at small deflections one obtains with good approximation the relation

$$\Delta g \approx \frac{k_{\mathrm{i}} \Delta b}{2n_{\mathrm{s,i}}sw}. \tag{4}$$

If the actual values of $k_{\mathrm{i}}$ (or $t_{\mathrm{s}}$, $E_{\mathrm{s}}$, $\nu_{\mathrm{s}}$), $w$, $s$, and $n_{\mathrm{s,i}}$ are known, for the calculation of $\Delta g$ only the experimental determination of $\Delta b$ is necessary. See also the monograph [ix].

*Refs.: [i] Stoney GG (1909) Proc R Soc London A32:172; [ii] Morcos I (1978) Specialist periodical reports electrochemistry, vol 6. In: Thirsk HR (ed) The Chemical Society. Burlington House, London, pp 65–97; [iii] Trasatti S, Parsons R (1986) Interphases in systems of conducting phases, Pure & Appl Chem 58:437; [iv] Láng GG, Ueno K, Ujvári M, Seo M (2000) J Phys Chem B104:2785; [v] Ibach H, Bach CE, Giesen M, Grossmann A (1997) Surf Sci 375:107; [vi] Haiss W (2001) Rep Prog Phys 64:591; [vii] Láng GG, Seo M (2000) J Electroanal Chem 490:98; [viii] Rokob TA, Láng GG (2005) Electrochim Acta 51:93; [ix] Láng GG, Barbero CA (2012) Laser techniques for the study of electrode processes. In: Monographs in electrochemistry. Scholz F (ed) Springer, Berlin*

GGL

**Berl reaction** $\rightarrow$ *electroreduction* reaction of dioxygen $(O_2)$ resulting in the formation of hydrogen peroxide $(H_2O_2)$ (in acidic solution) or hydrogen peroxide anions $(HO_2^-)$ (in alkaline solutions).

*Refs.: [i] Hoare JP (1974) In: Bard AJ (ed) The Encyclopedia of the electrochemistry of the elements, vol 2. Marcel Dekker, New York; [ii] Berl WG (1943) Trans Electrochem Soc 83:253*

RH

**Berthelot, (Pierre Eugène) Marcellin**



(Oct. 27, 1827, Paris, - March, 18, 1907, Paris, France) [i, ii] French chemist and statesman, first professor of organic chemistry at the Collège de France (1865), foreign minister

(1895–1896), one of the initiators of thermo-chemistry, introduced the terms exothermic and endothermic, synthesized numerous basic organic compounds and helped to overcome the division between inorganic and organic chemistry, observed peroxide formation during electrolysis of concentrated sulfuric acid [iii], the basis of the → *peroxodisulfate* production.

*Refs.: [i] Magnusson M (ed) (1990) Chambers Biograph-ical Dictionary. W&R Chambers, Ltd. Edinburgh; [ii] Crystal D (ed) (1998) The Cambridge Biographical En-cyclopedia, Cambridge University Press, Cambridge, [iii] Berthelot M Ann. chim. et de phys. Ser. V, 21, 190 (1880;. Ser. V, 14, 354 (1878)*

RH

### Berzelius, Jöns Jacob

(Courtesy of History of Technology Division, Technical University of Denmark)

(Aug. 20, 1779, near Linköping, Sweden – Aug. 7, 1848, Stockholm, Sweden). Berzelius was one of the founders of modern chem-istry [i, ii]. He studied about 2000 compounds; discovered Ce, Se, Si, and Th; first used the term "organic chemistry"; invented series of → *electronegativities*; suggested symbols for elements based on Latin letters (which have been modernized later) and invented modern chemical formulas; proposed the terms: isomerism, allotropy, catalysis, protein, polymer, halogen, and electronegative; proved law of definite proportions; generated first accurate list of atomic weights. Berzelius proposed ionic nature of chemical bonds that are caused, according to his theory, by electrostatic attraction between two atoms if one of the atoms was positively, and the other negatively charged. His particular contributions to electrochemistry include the first electrolysis of salts and the invention of a mercury cathode.

*Refs: [i] Jorpes JE (1970) Jacob Berzelius, his life and work. University of California Press, Berkeley; [ii] Ihde AJ (1961) In: Farber E (ed) Great chemists. Interscience Publishers, New York, pp 385–402*

EK

### Besenhard, Jügen Otto

(May 15, 1944, Regensburg, Germany – Nov. 4, 2006 in Graz, Austria) Besenhard studied chem-istry at the University of Munich where he also received his Ph.D. Since that time he has dedi-cated his research to → *lithium batteries*, and he became one of the pioneers in that field. In 1977 he was post-doc with Roger Parsons, and in 1986 he became Full Professor at the University of Münster, where he expanded his research activi-ties to a very large number of research topics from applied electrochemistry, and still maintained his activities in lithium electrochemistry. In 1993 he became head of the Institute of Chemistry and Technology at Graz University of Technol-ogy in Austria. Besenhard is the author or co-author of more than 800 publications, 50 patents, and was editor of the 'Handbook of Battery Materials' [i].

*Refs.: [i] Besenhard JO (ed) (1999) Handbook of Battery Materials. Wiley-VCH, Weinheim; [ii] Obituary: Winter M (2007) J Solid State Electrochem*

FS

**Beta cell** (also called beta battery or sodium sulfur battery) is a high temperature secondary Na/$\beta$-Al$_2$O$_3$/S battery cell. The anode metal Na is especially attractive on account of its high electrode potential and low atomic mass, which gives a high specific energy. → *$\beta$-alumina*

**B**

($Na_2O - 11Al_2O_3$) is an ideal solid electrolyte with fast $Na^+$ conduction. The cell operates at 300 to 350 °C and exhibits improved performance compared to ambient-temperature batteries, i.e., the ionic resistivity of $\beta$-alumina at 300 °C is 2 to 5 $\Omega$ cm, comparable to that of an aqueous NaCl solution. The cell must be sealed to prevent reaction with water and air. The preferred phase for battery operation with the highest ionic conductivity is $\beta''$-alumina (typical composition $Na_{1.67}Mg_{0.67}Al_{10.33}O_{17}$). The beta cell uses a molten Na cathode, the solid $\beta''$-alumina electrolyte, and a molten sulfur–sodium polysulfide mixture as the anode, respectively. Discharge involves $Na \rightleftarrows Na^+ + e^-$, followed by diffusion of $Na^+$ through $\beta''$-alumina ceramic to the cathode, where reduction of sulfur occurs in two steps, i.e.: $2Na^+ + 5S + 2e^- \rightleftarrows Na_2S_5$, and $\frac{2x}{5}Na^+ + \left(1 - \frac{x}{5}\right)Na_2S_5 + \frac{2x}{5}e^- \rightleftarrows Na_2S_{5-x}$, respectively. The first reaction gives an open-circuit voltage of 2.08 V, whereas the second reaction gives 2.08 to 1.76 V. A mixture of $Na_2S_5$ and unreacted sulfur in the first stage is converted to $Na_2S_5$, and further reaction proceeds in a single phase from $Na_2S_5$ to $Na_2S_{5-x}$ by addition of $Na^+$. The cell voltage decreases linearly with the Na composition and the discharge is stopped at 1.76 V, corresponding to the composition of $Na_2S_3$.

Currently, the full size cell (energy density: $200\,W\,h\,kg^{-1}$, capacity: 15 A h) is designed for a cycle of 5 h discharge and 7 h charging with a round-tip efficiency of 76%. Individual cells have regularly shown lives of 1000 to 2000 cycles. Better-quality, fine-grained materials are now routinely produced, and it has been found that the addition of $ZrO_2$ can refine the grain size of the ceramic. Also, special sulfur electrode designs, including the use of graded resistivity shaped graphite felt current collectors ($\rightarrow$ *carbon electrodes*, subentry $\rightarrow$ *carbon felt electrode*), have improved the rechargeability of the sulfur electrode. 10 to 50 A h batteries are now common. Newer beta cell designs comprise a flat solid electrolyte disc concept instead of a tubular design. This flat separator, typically 0.3 mm thick, offers uniform discharge and excellent thermal conduction and allows high specific power of $600\,W\,kg^{-1}$ and $1.65\,kW\,cm^{-3}$ for a bipolar cell, i.e., a higher performance by a factor 5 to 6 compared to the cylindrical cell design.

*Refs.: [i] Julien C (1997) Solid state batteries. In: Gellings PJ, Bouwmeester HJM (eds) The CRC handbook of solid state electrochemistry. CRC Press, Boca Raton, pp 374–410; [ii] Braithwaite JW, Auxer WL (2002) Sodium-beta batteries. In: Linden D, Reddy TB (eds) Handbook of batteries, 3rd edn. McGraw-Hill, New York, pp 40.00–40.31*

MHer

## Beutner, Reinhard Heinrich



(Reproduced with permission of: 'Archiv zur Geschichte der Max-Planck-Gesellschaft, Berlin-Dahlem')

(April 10, 1885, Berlin, Germany – April 15, 1964, Scranton, PA, USA) Ph.D. 1908 at "Technische Hochschule Karlsruhe" in the group of $\rightarrow$ *Haber* with studies on $\rightarrow$ *solid electrolyte* galvanic cells [i–ii]. Beutner studied the $\rightarrow$ *electromotive forces* at interfaces of solid metals with solid electrolytes, at that time a newly emerging field of electrochemistry. Later he performed pioneering studies on electromotive forces at the interface of aqueous and non-aqueous solutions [iii]. These studies were performed at the Rockefeller Institute, New York, in the group of $\rightarrow$ *Loeb*. Beutner reported for the first time series of electromotive forces at these interfaces for different electrolytes and different organic solvents ($\rightarrow$ *interface between two immiscible electrolyte solutions*). He published three important books [iii–v] and held leading position in US Medical Research laboratories [vi].

*Refs.: [i] Beutner R (1908) Neue Galvanische Elemente (PhD thesis). Druck von W Pilz, Berlin; [ii] Haber F (1908) Ann Phys 331:927, esp pp 947 (together with R Beutner); [iii] Beutner R (1920) Die Entstehung elektrischer Ströme in lebenden Geweben und ihre künstliche Nachahmung durch synthetische organische Substanzen (The origin of electric currents in living tissues and their artificial simulation with the help of synthetic*

*organic compounds). Ferdinand Enke Verlag, Stuttgart; [iv] Beutner R (1933) Physical chemistry of living tissues and life processes. The Williams & Wilkins Company, Baltimore; [v] Beutner R (1938) Life's beginning on earth. The Williams & Wilkins Company, Baltimore; [vi] Wußing H (ed) (1999) JC Poggendorff Biographisch-Literarisches Wörterbuch der exakten Naturwissenschaften, vol 8, Part 1. Wiley-VCH, Weinheim, p 384*

FS

**Biamperometry** Whereas in → *amperometry* the → *current* is limited by the electrode process proceeding at one → *indicator electrode* (and the → *counter electrode* has no effect), in biamperometry the current flowing between two indicator electrodes is measured, i.e., both electrodes can limit the overall current. This approach is useful in following some → *titrations*, and it may lead to zero current (dead-stop) at the equivalence point (dead-stop titration). Example: iodine in an iodide solution is titrated with As(III). Two platinum electrodes with a potential difference of around $100\,\text{mV}$ prompt iodine to be reduced on one electrode and iodide being oxidized at the other. The two processes maintain an almost constant current until the endpoint when iodine is exhausted.

*Refs.: [i] Foulk CW, Bawden AT (1926) J Am Chem Soc 48:2045; Bard AJ, Faulkner LR (2000) Electrochemical methods. Wiley, New York, p 439*

FS

**Bias** (*of error*) A measure of the → *systematic error* associated with an analysis. It is the difference between the → *population mean* and the accepted or → *true value* [i].

*Ref.: [i] Harris D (2002) Quantitative chemical analysis. WH Freeman, New York*

FG

**Bifunctional mediator** is a → *catalyst* containing two functional groups, both of which are involved in the rate-controlling step. The corresponding catalytic effect is larger that expected for catalysis by species containing only one of these functional groups. See also → *mediator*.

VM

**Biilmann, Einar Christian Saxtorp**



(May 10, 1873, Frederiksberg, Copenhagen, Denmark – Aug. 10, 1946, Copenhagen, Denmark) Biilmann started to study medicine, but obtained a Master degree in Chemistry in 1897. Later he became assistant of S. M. Jørgensen, a well-known coordination chemist. In 1904 he obtained his doctorate for studies in organic chemistry. Biilmann spent one year in the laboratory of Emil Fischer in Berlin, and in 1907 he was appointed professor of chemistry at the University of Copenhagen. Biilmann is best known for the introduction of the → *quinhydrone electrode* for → *pH* determinations.

*Refs.: [i] Biilmann E (1921) Ann Chim 15:109; [ii] Stock JT (1989) J Chem Educ 66:910*

FS

**Bimetallic electrodes** → *electrode, materials*, subentry → *bimetallic electrodes*

**BIMEVOX** (**bi**smuth **me**tal **v**anadium **ox**ide) is a family of → *solid electrolytes* with a high oxygen-ionic conductivity, based on high-temperature polymorph of bismuth vanadate, $\gamma\text{-Bi}_4\text{V}_2\text{O}_{11}$, stabilized by partial substitution. The crystal structure of the BIMEVOX family belongs to the Aurvillius series and consists of alternating $\text{Bi}_2\text{O}_2^{2+}$ and perovskite-like $\text{VO}_{3.5}^{2-}$ layers, with oxygen vacancies in the perovskite layers providing ion migration. Moderate → *doping* into the vanadium sites is necessary to stabilize the highly conductive $\gamma$-$\text{Bi}_4\text{V}_2\text{O}_{11}$ lattice down to low temperatures [i, ii]. The → *solid solutions* stabilized by partial

**B**

**BIMEVOX — Figure.**
Oxygen ionic conductivity
of solid oxide electrolytes
at atmospheric oxygen
pressure. See Ref. [ii] for
details
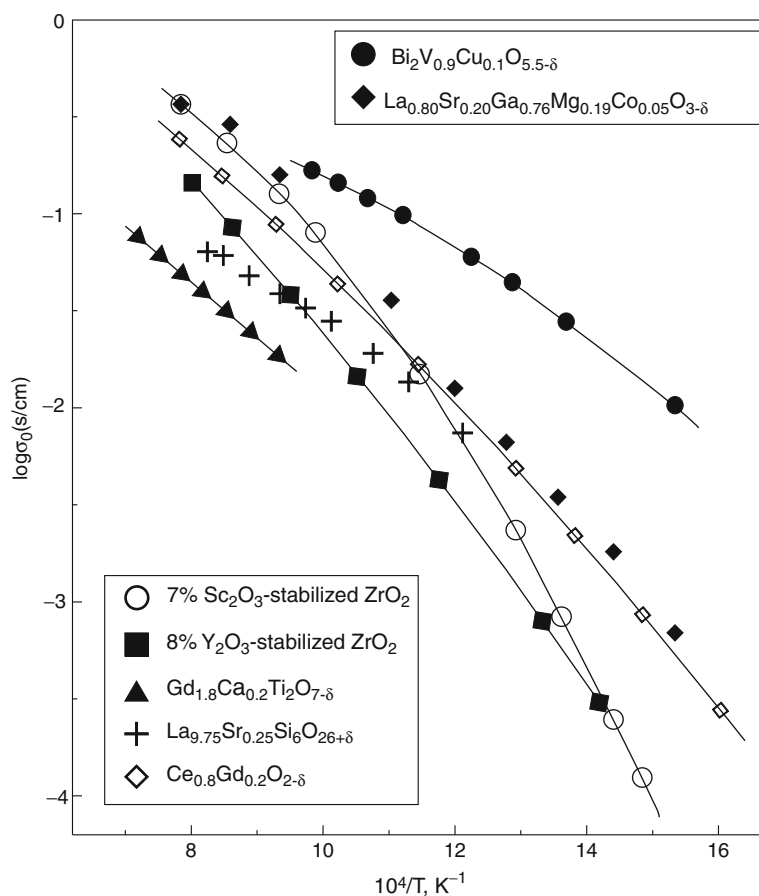


substitution with transition metal cations, such as $Bi_2V_{1-x}Me_xO_{5.5-\delta}$ (Me = Cu, Ni, and $0.07 \leq x \leq 0.12$), exhibit very high ionic conduction and oxygen ion → *transport numbers* close to unity at temperatures below 900 K under oxidizing conditions (see Fig. 1). Major disadvantages of bismuth vanadate-based ceramics, limiting their application, include a low mechanical strength, easy reducibility, and extremely high chemical reactivity.

*Refs.: [i] Vanier RN, Mairesse G, Abraham F, Nowogrocki G (1994) Solid State Ionics 70/71:248; [ii] Kharton VV, Marques FMB, Atkinson A (2004) Solid State Ionics 174:135*

VK

**Binary electrolyte**    An electrolyte consisting of anions and cations with equal absolute charge numbers, e.g., KCl (1:1), $MgSO_4$ (2:2).

*Ref.: [i] Newman J, Thomas-Alyea KE (2004) Electrochemical systems, 3$^{rd}$ edn. Wiley Interscience, Hoboken, pp 110, 277, 299*

FG

**Biochemical standard potential**  → *potential*

**Biocorrosion**    The deterioration of solid materials, organic as well as inorganic by living organisms. These can be higher organisms, like barnacles and mussels, and also microorganisms [i–iii]. Microbial corrosion, or microbiologically influenced corrosion can be the result of a direct attack of solid phases, e.g., the reduction of iron oxides by *Shewanella* or *Geobacter* [iii] species, or it may be the result of corrosive action of metabolites produced by the microbes. Such metabolites may be inorganic or organic acids (acidification) or also the production of corrosive compounds

like $H_2S$ under anaerobic conditions. Biofilms on metals do not produce a new kind of corrosion, but they affect the well-known corrosion mechanisms and may change considerably the rate of corrosion.

*Refs.: [i] Heitz E, Flemming HC, Sand W (eds) (1996) Microbially influenced corrosion of materials. Springer, Berlin; [ii] Dexter SC (2005) Microbiological effects. In: Baboian R (ed) Corrosion tests and standards, ASTM manual 20, 2nd edn. American Society for Testing and Materials, Philadelphia, pp 509–522; [iii] Dexter SC (2003) Microbiologically influenced corrosion. In: Corrosion fundamentals and protection, ASM Handbook, vol 13A. ASM International, Metals Park, pp 398–416; [iv] Lovley DR, Giovannoni SJ, White DC, Champine JE, Phillips EJP, Gorby YA, Goodwin S (1993) Arch Microbiol 159:336*

*FS*

**Bioelectrocatalysis** is that form of → *electrocatalysis* in which biocatalysts (enzymes, cell organelles or whole cells) are interposed between an electrode and a redox system, which is irreversible on the plane electrode. Thus the biocatalysts allow the oxidation or reduction to proceed at electrode potentials which are (more or less) approaching the reversible → *electrode potential* (see also → *Nernst equilibrium*). In many cases of bioelectrocatalysis → *redox mediators* shuttle the electrons between the electrode and the biocatalysts. These mediators can be natural constituents of the cells and enzyme systems, or they may be compounds deliberately added to the solution or immobilized on the electrode surface.
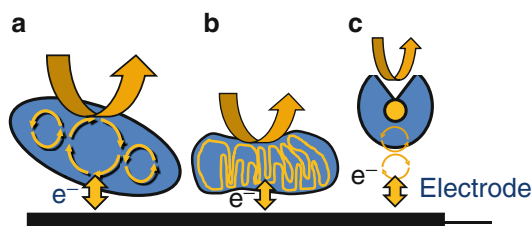


**Bioelectrocatalysis — Figure.** Simplified sketch of bioelectrocalytic systems based on A) microbial cells, B) cell organelles and C) redox enzymes (relative size not true to scale; and possible mediators not displayed)

Depending on the nature of the biological component one can distinguish between (a) systems based on redox enzymes (→ *enzyme electrodes*), (b) cell organelle (e.g., mitochondria) based systems and (c) whole cell based bioelectrocatalysis. In many cases of cell based processes (e.g., microbial fuel cells) it may be more appropriate to use the term biotransformation instead of biocatalysis since the living cell is directly involved and often takes advantage of in the overall electrochemical conversion. Bioelectrocatalysis has great importance in the field of → *biosensors* and → *biofuel cells*.

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**Bioelectrochemistry** is a discipline that includes all aspects of the overlap of biology and → *electrochemistry* [i], including all electrochemical phenomena of living cells and organisms, as, for instance, → *nerve conduction*, muscle contraction, membrane phenomena and electrical organs. Whereas the modern, interdisciplinary bioelectrochemistry was established by Giulio Milazzo (1912–1993), the origin of bioelectrochemistry goes back to → *Galvani* and → *Volta*.

In electrochemistry, the term bioelectrochemistry is generally used to indicate electrochemistry *of* or *in* biological systems [ii]. Examples are: → *enzyme electrodes*, → *biofuel cells*, → *biosensors*, → *immunoassays, electrochemical* → *protein electrochemistry*. See also → *bioelectricity*, → *bioelectrocatalysis*, → *bioelectrogenesis*, → *bioimpedance*, → *cell polarization (of biological cell)*.

*Refs.: [i] Caplan SR, Miller IR, Milazzo G (eds) (1995) Biochemistry: General introduction. Birkhäuser Verlag, Basel; [ii] Bard AJ, Stratmann M, Wilson GS (eds) (2002) Bioelectrochemistry. Encyclopedia of electrochemistry, vol 9. Wiley-VCH, Wertheim*

*US*

**Bioelectrogenesis** is the generation of → *electricity* by living organisms. It can be (i) static charge due to ion activity differences across membranes, or (ii) dynamic charge due to ionic currents. In case of electric fishes the purpose

of generation is defense and/or orientation, recognition and communication, where it needs → *electroreception* for detection. The electricity generating cells are called electrocytes. A typical single electrocyte produces a voltage of the order of 100 mV. They are arranged in series and parallel. The number of electrocytes in series determines the produced voltage, while the number in parallel determines the current output. Electrocytes produce a voltage and generate a current by a metabolic pumping of sodium and potassium ions through their membrane. See also → *action potential*, → *biofuel cells*, → *electrical organ*, → *electrophysiology*, → *graded potential*, → *ion transport through membranes and channels*, → *plantphysiology*.

*Refs.: [i] Schoffeniels E, Margineanu D (1990) Molecular basis and thermodynamics of bioelectrogenesis. Kluwer Acad Publ, Dordrecht; [ii] Bullock ThH, Hopkins CD, Popper AN, Fay RR (2005) Electroreception. Springer, New York*

FS

**Biofuel cells** also referred to as biochemical, or bioelectrochemical → *fuel cells*, exploit biocatalysts for the direct conversion of chemical energy to electrical energy. Based on the nature of the biocatalyst, biofuel cells are generally classified as enzymatic fuel cells and microbial fuel cells [i]. Enzymatic fuel cells use purified enzymes to catalyze the oxidation of substrates at the → *anode* and the reduction of an oxidant at the → *cathode*. Depending on the targeted substrate (fuel) the oxidative reactions are usually catalyzed using dehydrogenases (e.g., lactate dehydrogenase, alcohol dehydrogenase, glucose dehydrogenase) or oxidases (glucose oxidase GOx) [ii]. For the cathodic reaction various oxidases (cytochrome oxidase, bilirubin oxidase), laccases (horseradish peroxidase), or peroxidases have been used to catalyse the reduction of oxygen or hydrogen peroxide. Different strategies have been followed to immobilize the biocatalysts to the fuel cell electrodes, including adsorptive immobilization, cross-linking, and the embedding in → *conducting polymer* matrices → *polyaniline*, → *polypyrrole*). Electron transfer from the enzyme to the electrode is achieved either via direct electron transfer (DET) or mediated electron transfer (MET) [iii].

Based on the high specificity of enzymatic reactions enzymatic fuel cells can be constructed compartment-less, i.e., without a physical separation of the anodic and the cathodic
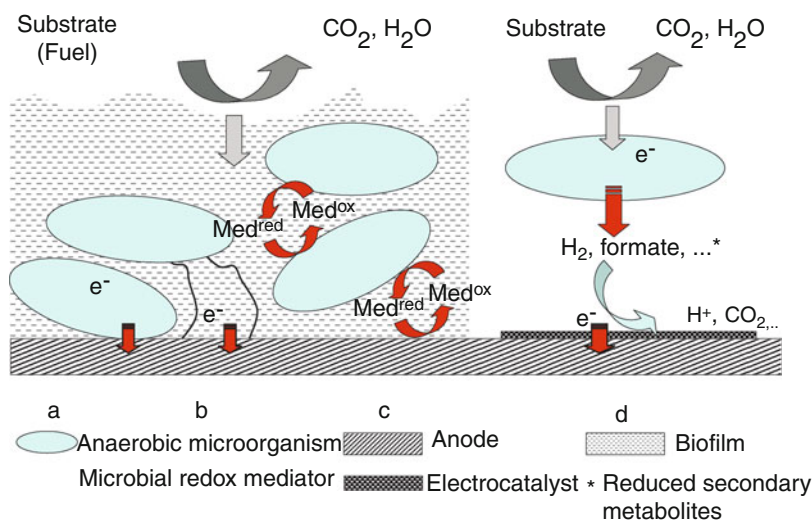


**Biofuel cells — Figure.** Schematic illustration of identified electron transfer mechanisms in microbial fuel cells. Electron transfer via (*a*) cell membrane-bound cytochromes, (*b*) electrically conductive pili (nanowires), (*c*) microbial redox mediators, and (*d*) via oxidation of reduced secondary metabolites [v]

compartments. This allows miniaturization of the devices, e.g., for biomedical (implantable) devices and → *biosensors* [iii].

In microbial fuel cells living microorganisms serve as biocatalysts for the conversion of chemical energy to electricity. Since the majority of microorganisms are electrochemically inactive some early microbial fuel cells required the use of artificial electron-shuttling compounds (mediators) such as thionine or neutral red to be added to the bacterial solution in order to establish an → *electron transfer* to the fuel cell anode. As the use of such redox mediators is technologically impractical and environmentally questionable, the development of mediator-based microbial fuel cell concepts appears abandoned. Recent MFC types are typically "mediator-less", i.e., they do not require artificial redox mediators for their operation. The classification as mediator-less, however, not exclude electron mediation via microbial electron shuttling compounds [iv]. Different electron transfer mechanisms have been identified and used (Fig.), however, many mechanisms are still under investigation.

Thus, electrons can be directly transferred (DET) to the anode via the cell membrane (a) or via so-called nanowires (b) [vi, vii]. Alternatively, mediated electron transfer (MET) can take place via bacterial electron-shuttling compounds [viii] or reduced secondary metabolites like, e.g., hydrogen, formate, or ethanol [v, ix].

*Refs.: [i] Bullen RA, Arnot TC, Lakeman JB, Walsh FC (2006) Biosens Bioelectron 21:2015; [ii] Katz E, Shipway AN, Willner I (2003) Biochemical fuel cells. In: Vielstich W, Gasteiger HA, Lamm A (eds) Handbook of fuel cells – Fundamentals, technology and applications. Fundamentals and survey of systems, vol 1. Wiley, New York; [iii] Barton SC, Gallaway J, Atanassov P (2004) Chem Rev 104:4867; [iv] Logan BE, Hamelers B, Rozendal R, Schröder U, Keller J, Freguia S, Aelterman P, Verstraete W, Rabaey K (2006) Environ Sci Technol 40:5193; [v] Rosenbaum M, Zhao F, Schröder U, Scholz F (2006) Angewandte Chemie int Ed 45:6658; [vi] Bond DR, Lovley DR (2003) Appl Microbiol Biotechnol 69:1548; [vii] Gorby YA, Yanina S, McLean JS, Rosso KM, Moyles D, Dohnalkova A, Beveridge TJ, Chang IS, Kim BH, Kim KS, Culley DE, Reed SB, Romine MF, Saffarini DA, Hill EA, Shi L, Elias DA, Kennedy DW, Pinchuk G, Watanabe K, Ishii SI, Logan B, Nealson KH, Fredrickson JK (2006) PNAS 103:11358; [viii] Rabaey K, Boon N, Verstraete W, Höfte M (2005) Environ Sci Technol 39:3401; [ix] Niessen J, Schröder U, Rosenbaum M, Scholz F (2004) Electrochem Commun 6:571*

US

**Bioimpedance** Bioimpedance deals with → *impedance* properties of tissue, i.e., the ability to oppose (impede) electric current flow. Bioimpedance methods use electrodes with galvanic coupling to tissue. The charge carriers in living tissue are (with some exceptions) ions. An electrode proper is the site of charge carrier conversion from ions to electrons and vice versa. The tissues behave as → *conductor*s due to mostly the ionic → *diffusion*, → *counterion* effects at the frequencies lower ca. 10 kHz, however, their dielectric properties can also be investigated even in this frequency range. At the medium frequency interval between ca. 10 kHz and 100 MHz the Maxwell-Wagner effect, the cell membrane capacitance and the response of the protein molecules can be measured. At higher frequencies the dielectric properties of tissue usually dominate. It is mainly associated with the → *dielectric relaxation* of water (in the GHz region) including water molecules in the hydration sphere in the MHz-GHz range. Electrochemistry plays a very important role in the study of tissues and living cells since when electric current flows, chemical changes also occur. In practice both in vivo and in vitro measurements are carried out by using → *two-*, → *three-* or → *four-electrode system*s. In the case of 4-electrode system one pair of electrodes are the current carriers, the two other electrodes serve for the potential measurements at different places of the tissue. Single cells are measured with the help of → *microelectrode*s by using → *clamp* and patch techniques (→ *patch clamp*). Mathematical equations and equivalent circuit diagrams having the same electrical behavior as the tissue are used for the construction of the models, which are mostly based on the → *Cole equation* and the → *Cole-Cole*

**B**

*equation*. Medical and commercial applications of bioimpedance measurements include e.g., skin cancer screening, body composition analysis, and impedance cardiography for non-invasive hemodynamic monitoring [ii, iii]. Tomographic techniques based on bioimpedance measurement are currently under developement [iv].

See also → *dielectric relaxation*, → *Cole-Cole diagram*, → *Cole element*, → *voltage clamp*, → *current clamp*, → *bioelectricity*, → *cell polarization (of biological cell)*.

*Refs.: [i] Grimnes S, Martinsen ØG (2008) Bioimpedance and Bioelectricity. Basics. Elsevier, Amsterdam; [ii] Kyle UG, Bosaeus I, De Lorenzo AD, Deurenberg P, Elia M, Gómez JM, Heitmann BL, Kent-Smith L, Melchior JC, Pirlich M, Scharfetter H, Schols AMWJ, Pichard C (2004) Clin Nutr 23:1226–1243; [iii] Bernstein DP (2010) J Electr Bioimp 1:2–17; [iv] Bayford RH (2006) Annu Rev Biomed Eng 8:63–91*

                                                                                            GI

**Biological membrane**  → *membrane*, subentry → *biological membrane*

**Biomimetic sensors**  → *biosensors*, subentry → *biomimetic sensors*

**Biosensors** Sense organs have developed during evolution by adapting the organism towards the properties of their environment. They recognize chemical signals by the binding to structurally complementary receptor areas followed by the transduction of this event into electrical nerve impulses. The biosensors represent the technical counter part [i] by coupling the recognition by a biological recognition element, e.g., enzymes, antibodies, nucleic acids, receptors, and recognition systems, e.g., organelles, cells, tissues, with a chemical or physical sensor [ii] (Table). Different transducer types, e.g., electrochemical, optical, piezoelectric, thermal, or magnetic, transfer the signal from the recognition part to the electrical domain. Biosensors have been classified according to the biological recognition mechanism or the mode of signal transduction or, alternatively, a combination of the two. The characteristic feature of the biosensor is (according to the definition of IUPAC) the **direct** (spatial) contact of the recognition element and the **transducer** [ii]. This integration leads to a compact functional unit which allows re-usage of the biological component and **miniaturization** of the sensor body. These properties allow for online measurement and are the basis of the combination of different recognition elements on one transducer array resulting in the biochip. Integration of the biochemical and electronic signal processing have been realized in "intelligent biosensors" and BioFETs, resp. The combination of the biosensor with microfluidics and actuators on a chip has led to total microanalysis systems (μTAS).

**Biosensors — Table.** Types of biosensors

| Biochemical receptors | Transducers | Configuration |
|---|---|---|
| *Biological:* | *Electrochemical:* | |
| Enzymes | Amperometric, potentiometric, | |
| Antibodies | Conductometric, capacitive | |
| Receptors | ISFET | Biosensor |
| Nucleic acids | | |
| Cells | *Optical:* | Microanalysis System (μTAS) |
| | Photometers, interferometers, | |
| *Biomimetic:* | refractometers, fluorimeters, | Biochip |
| Aptamers | luminometers | |
| Ribozymes | | |
| | *Mechanical & Thermodynamic:* | |
| | Thermistors, viscosimeters | |
| Molecularly imprinted | oscillating quartz crystals | |
| polymers (MIPs) | | |
| | *Magnetic:* | |
| | Toroids | |

The IUPAC definition may also be extended in respect to biomimetic recognition elements, e.g., aptamers and molecularly imprinted polymers, which are derived from biology (Table).

On the other hand, biochemical tools used for analytical purposes which do not include sensor components should not be assigned as a biosensor. This holds for molecular or cellular recognition systems with biochemical signal generation, e.g., allosteric enzymes, cells carrying a reporter gene and for bioassays or bio tests which do not include a chemical or physical transducer [iii]. Furthermore, plain chemical sensors which do not contain a biological recognition element, e.g., pH or oxygen electrodes, do not fulfill the criteria of the IUPAC definition in spite of the frequently used term "biological sensor". See also → *enzyme electrode*, → *glucose sensor*.

*Refs.: [i] Thevenot DR, Toth K, Durst RA, Wilson GS (2001) Biosens Bioelectron 16:121; [ii] Cammann K (1977) Fresenius Z Anal Chem 287:1; [iii] Scheller F, Schubert F (1992) Biosensors. Elsevier, Amsterdam*

FSche

— **Biomimetic sensors** Biomimetic sensors exploit **M**olecularly **I**mprinted **P**olymers (MIPs) and artificial nucleotide-based binders (Aptamers) as recognition elements mimicking the function of enzymes, antibodies and even nucleic acids. See Table → *Biosensors.*

Recognition sites in MIP particles are created by bulk polymerisation of a functional and a cross-linking monomer in the presence of the analyte (**Fig.**). On the other hand, formation of → *self-assembled monolayers* or → *electropolymerisation* in the presence of the target molecule (surface imprinting) are used for the preparation of MIP-electrodes. Removal of the template forms binding sites which are ideally complementary in size and shape. Electrochemical MIP sensors have been developed for the measurement of low molecular weight substances, biopolymers, viruses and living cells.

Aptamers are single stranded DNA or RNA molecules which are prepared by in vitro selection from libraries of synthetic oligonucleotides. Once the sequence of an aptamer is identified, it can be reproducibly synthesized with high purity and easily modified by various tags or markers including electrochemical indicators and anchors for the electrode surface. Aptamers for almost 250 different analytes including metal ions, organic dyes, drugs, amino acids, cofactors,
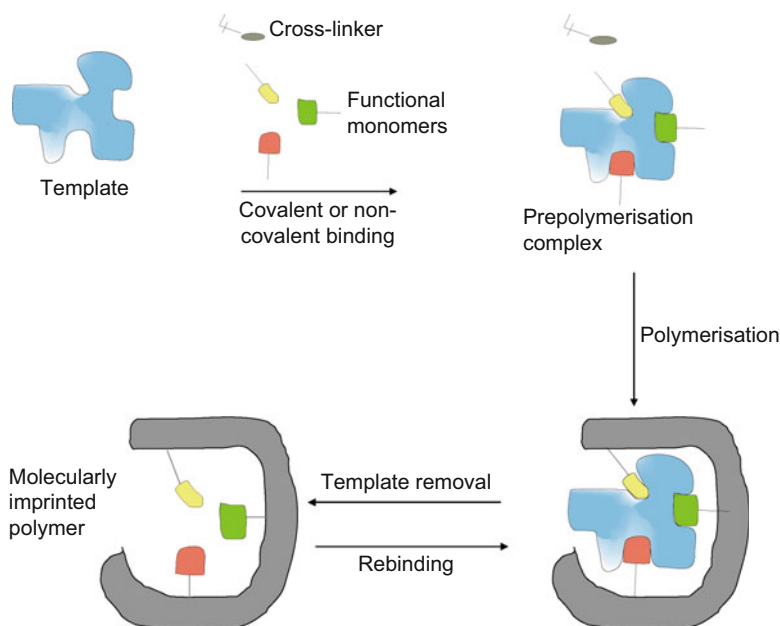


**Biosensors - Biomimetic sensors — Figure.**
Preparation of molecularly imprinted polymers

**B**

antibiotics and nucleic acids were synthesized. Aptamers may even distinguish the chirality of molecules or the secondary structure of proteins.

By analogy with electrochemical immunosensors (→ *Immunoassay, electrochemical*), the signal of biomimetic sensors is generated by evaluating changes of the recognition layer upon binding of the analyte by → *potentiometry*, → *conductometry* and → *impedance spectroscopy* or by amperometric indication (→ *amperometry*, and → *amperometric sensors*) of redox markers and enzyme labels. The exchange rate of the analyte-binder complex can be considerably higher than for antibodies thus allowing for online measurement and sensor regeneration.

*Refs.: [i] (1997) IUPAC Compendium of Chemical Technology 69:1269; [ii] Hianik T, Wang J (2010) Electroanalysis 21:1223; [iii] Suryanarayanan V, Wu CT, Ho KC (2010) Electroanalysis 22:1795; [iv] Mirsky V, Yatsimirsky A (eds) (2011) Artificial Receptors for Chemical Sensors WILEY-VCH, Weinheim*

FSche, AY

— **Biosensors, conducting polymer based** → *Conducting polymer* based biosensors [i–xii] make use of the electrochemically induced polymerization of suitable monomers such as pyrrole, *N*- and 3-substituted pyrrole derivatives, thiophene, thiophene derivatives, aniline, phenol and phenol derivatives, and azulene for the formation of polymer films at electrode surfaces under simultaneous immobilization of suitable biological recognition elements such as enzymes, antibodies, whole cells, etc. Initially, main focus was directed on using the formed conducting polymer films not only as immobilization matrix but additionally as molecular cable for fast electron transfer between redox sites within the biological recognition compound and the electrode. However, electron transfer between, e.g., polymer-entrapped enzymes and the electrode via the ramified conducting polymer network was prevented due to the far distance between the prosthetic group isolated by the protein shell and the polymer network. In the case of multi-cofactor enzymes exhibiting an internal fast electron transfer pathway (e.g., quinohemoprotein alcohol dehydrogenase) a direct electron transfer via polypyrrole chains was observed [xiii].

*Refs.: [i] Zotti G (1992) Synthetic Metals 51:373; [ii] Bartlett PN, Cooper JM (1993) J Electroanal Chem 362:1; [iii] Trojanowicz M, Krawczynski T, Krawczynski vel T, Krawczyk (1995) Mikrochim Acta 121:167; [iv] Schuhmann W (1995) Mikrochim Acta 121:1; [v] Adeloju SB, Wallace GG (1996) Analyst 121:699; [vi] Wallace GG, Smyth M, Zhao H (1999) Trends Anal Chem 18:245; [vii] Cosnier S (1999) Biosensors & Bioelectronics 14:443; [viii] Cosnier S (2000) Appl Biochem Biotechnol 89:127; [ix] Palmisano F, Zambonin PG, Centonze D (2000) Fresenius' J Anal Chem 366:586; [x] Gerard M, Chaubey A, Malhotra BD (2002) Biosensors & Bioelectronics 17:345; [xi] Vidal JC, Garcia-Ruiz E, Castillo JR (2003) Microchim Acta 143:93; [xii] Trojanowicz M (2003) Microchim Acta 143:75; [xiii] Ramanavicius A, Habermüller K, Csöregi E, Laurinavicius V, Schuhmann W (1999) Anal Chem 71:3581*

WSchu

— **Biosensors, reagentless** Reagentless biosensors are biosensors in which all components necessary for the overall sensing process are securely immobilized on the transducer surface. Thus, reagentless biosensors do not use any free-diffusing compound with exception of the analyte to be detected. Reagentless biosensors are mainly addressed in amperometric enzyme electrodes and imply an electrode architecture in which a suitable electron-transfer pathway between an immobilized redox enzyme and the electrode surface is tailored using either direct → *electron transfer* in monolayer arrangements based on self-assembled monolayers or in redox-polymer based biosensors in which charge transport is achieved by means of electron hopping between polymer bound redox relays.

*Refs.: [i] Heller A (1990) Acc Chem Res 23:128; [ii] Kulys J, Bilitewski U, Schmid RD (1991) Anal Lett 24:181; [iii] Heller A (1992) J Phys Chem 96:3579; [iv] Schuhmann W, Kranz C, Huber J, Wohlschlager H (1993) Synth Met 61:31; [v] Schmidt HL, Schuhmann W (1996) Biosens Bioelectron 11:127; [vi] Schuhmann W (2002) Rev Mol Biotechnol 82:425*

WSchu

**Bipolaron** Bipolarons are double-charged, spinless quasiparticles introduced in solid state physics [i]. A bipolaron is formed from two → *polarons* (charged defects in the solid).

For chemists the double-charged states mean dications or dianions, however, bipolarons are not localized sites, they alter and move together with their environment. By the help of the polaron–bipolaron model the high conductivity of → *conducting polymers* can be explained.

The interaction of polarons produce bipolarons which are uncorrelated charged → *soliton*s, e.g., in → *polyacetylene*, and correlated dications, e.g., in → *poly(p-phenylene)* [i]. The bipolarons can take part in both the intrachain and interchain → *charge transport* in conducting polymers, which is called spinless conductivity [ii, iii]. Bipolarons are formed at higher charging (doping) levels creating bipolaron bands within the gap of the valence and conducting bands. At high doping levels the electronic structure of the polymer entirely differs from that of the original polymer, and the charged defects overlap spatially along the polymer chain. It causes an elimination of the energy gap between occupied and unoccupied states.

*Refs.: [i] Chance RR, Boundreaux DS, Brédas J-L, Silbey R (1986) Solitons, polarons and bipolarons in conjugated polymers. In: Skotheim TA (Ed) Handbook of conducting polymers, vol 2, Marcel Dekker, p 825; [ii] Inzelt G (1994) Mechanism of charge transport in polymer-modified electrodes. In: Bard AJ (Ed) Electroanalytical chemistry, vol 18, Marcel Dekker; [iii] Lyons MEG (1994) Charge percolation in electroactive polymers. In: Lyons MEG (ed) Electroactive polymer electrochemistry, Part 1, Plenum, New York, p 1*

GI

**Bipolar electrode**   An electrode shared between two neighboring electrolysis cells, this way acting as anode in one and as cathode in the second cell. Useful if cells are series-coupled, since the electrode material itself forms the interconnection between cells. Applied preferably in → *secondary batteries*, in → *fuel cells*, and in → *alkali chloride electrolysis*.

PG

**Bipotentiometry**   Whereas in → *potentiometry* the → *potential* of one → *indicator electrode* is measured versus the constant potential of a → *reference electrode*, in bipotentiometry the potential difference between two indicator electrodes is measured. This approach is especially useful in following → *titrations* provided that the response of the two indicator electrodes differs and that difference should be largest at the equivalence point. The two indicator electrodes may be made from different materials (metals), or in some cases it is sufficient to have two electrodes of the same metal; however, with different surface layers.

*Refs.: [i] Kékedy L (1975) Rev Anal Chem (Tel Aviv) 3:27; [ii] Schumacher E, Umland F (1977) Mikrochim Acta 449:60; [iii] Schumacher E, Umland F (1981) Neue Titrationen mit elektrochemischer Endpunktanzeige. In: Bock R, Fresenius W, Günzler H, Huber W, Tölg G (eds) Analytiker Taschenbuch, vol 2, Springer Verlag, Berlin, pp 197*

FS

**Bipotentiostat**   An instrument that can control the potential of two independent → *working electrodes*. A → *reference electrode* and an → *auxiliary electrode* are also needed; therefore the cell is of the four-electrode type. Bipotentiostats are most often employed in electrochemical work with → *rotating ring-disk electrodes* and → *scanning electrochemical microscopes*. They are also needed for monitoring the electrode-reaction products with probe electrodes that are independently polarized. All major producers of electrochemical equipment offer this type of → *potentiostat*. The instruments that can control the potential of more than two working electrodes are called multipotentiostats.

*Refs.: [i] Bard AJ, Faulkner LR (2000) Electrochemical methods. Wiley, New York; [ii]* http://www.ijcambria.com/CHI700C_series_%20bipotentiostats.htm

ZS

**Biradical (or diradical)**   An even-electron → *molecular entity* with two (possibly delocalized) → *radical* centers which act nearly independently of each other, e.g.,
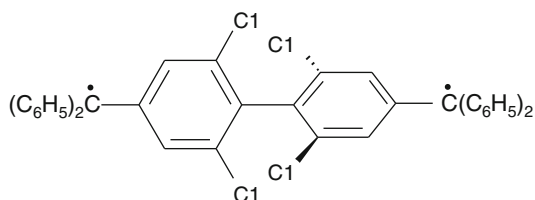
Species in which the two radical centers interact significantly are often referred to as "biradicaloids". If the two radical centers are located on the same atom, the species are more properly referred to by their generic names: carbenes, nitrenes, etc. The lowest-energy triplet state of a biradical lies below or at most only a little above its lowest singlet state (usually judged relative to $k_B T$, the product of the → *Boltzmann constant*, $k_B$, and the absolute temperature, $T$). The states of those biradicals whose → *radical* centers interact particularly weakly are most easily understood in terms of a pair of local doublets. Theoretical descriptions of low-energy states of biradicals display the presence of two unsaturated valences (biradicals contain one fewer bond than permitted by the rules of valence): the dominant valence bond structures have two dots, the low-energy molecular orbital configurations have only two electrons in two approximately nonbonding molecular orbitals, two of the natural orbitals have occupancies close to one, etc.

*Ref.: [i] Muller P (1994) Pure Appl Chem 66:1077*

WK

**Bismuth electrode (or bismuth–bismuth oxide electrode)** → *pH-sensitive electrodes*

**Bismuth film electrodes** The development of reliable non-mercury electrodes is considered a major challenge for electroanalysis. Bismuth-film electrodes offer an attractive alternative to the use of mercury-coated electrodes in → *stripping voltammetry* of trace metals, with an attractive analytical performance. Bismuth-film electrodes offer a well-defined, undistorted and highly reproducible response, excellent resolution of neighboring peaks, high hydrogen evolution, with signal-to-background characteristics comparable to those of common mercury electrodes. Among the alternative ('non-mercury') electrodes, the bismuth one thus offers the closest stripping-voltammetric performance to mercury. Such favorable stripping behavior of bismuth electrodes reflects the ability of bismuth to form 'fused' alloys with heavy metals.

The design of the bismuth electrode plays a major role in the resulting stripping performance. In most cases, a carbon substrate is used to support the bismuth film. A variety of → *carbon electrodes*, of different sizes and geometries, can be used (with the majority of studies employing a glassy carbon disk). Such films can be prepared ex-situ (preplated) or in-situ (by adding 0.25–1.0 ppm bismuth(III) directly to the sample solution, and simultaneously depositing the target heavy metals and bismuth).

Different versions of stripping analysis have been successfully employed in connection to bismuth-film electrodes. While most early studies have been devoted to conventional stripping-voltammetric measurements, recent activity expanded the scope of bismuth electrodes to adsorptive- and potentiometric stripping experiments.

*Refs.: [i] Wang J, Lu J, Hocevar S, Farias P, Ogorevc B (2000) Anal Chem 72:3218; [ii] Economou A (2005) Trends Anal Chem 24:334; [iii] Wang J (2005) Electroanalysis 17:1341*

JW

**Bismuth oxide** Bismuth (Bi) forms a variety of oxide compounds with the Bi cations oxidation state from $+2$ to $+5$ [i, ii]. Bismuth oxides, particularly $Bi_2O_3$, have numerous applications as components of ceramic materials, glasses, and films having specific electrical and electrochemical properties (→ *solid electrolytes*, → *mixed ionic–electronic conductors*, → *electrochromic devices*, high-temperature superconductors, various coatings, glass-ceramic sealants etc.). One attractive phenomenon relates to the very high oxygen-ionic conductivity of the high-temperature polymorph of bismuth (III) oxide, $\delta$-$Bi_2O_3$, which has a disordered cubic fluorite-like lattice and forms at temperatures above 978–1013 K [i, iii]. The level of oxygen-ionic transport in undoped $\delta$-$Bi_2O_3$ is highest among known oxygen → *ion conductors*. The stabilization of the $\delta$-$Bi_2O_3$ phase down to moderate temperatures can be achieved by substitution of bismuth with rare-earth dopants, such as Y, Dy, or Er, and their combinations with

**Bismuth oxide — Figure.**
Comparison of the → *electrolytic domain* boundaries for solid oxide electrolyte materials. The electrolytic domains, where ionic conduction is predominant, correspond to the wedges in the right part of the diagram. The lines show their approximate boundaries where the ion transference numbers are equal to 0.99. See ref. [iv] for details
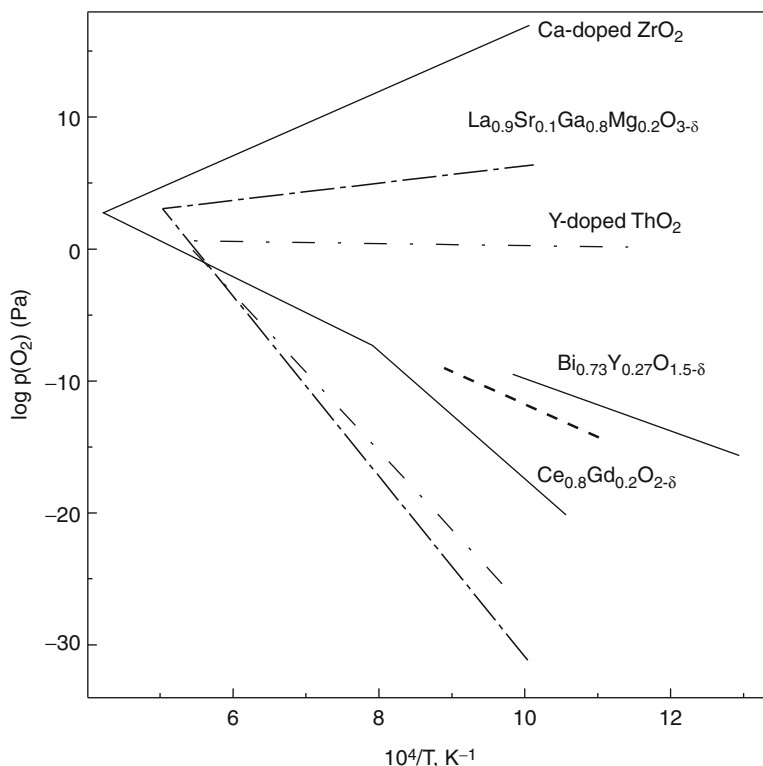


higher-valence cations, such as W or Nb. The maximum conductivity in the binary systems is observed for Er- and Y-containing phases, namely $Bi_{1-x}Er_xO_{1.5}$ ($x \approx 0.20$) and $Bi_{1-x}Y_xO_{1.5}$ ($x = 0.23$–$0.25$). However, either binary or ternary → *solid solutions* with disordered fluorite structure are metastable at temperatures below 770–870 K, exhibiting a slow phase decomposition and a decrease in the conductivity with time. Other disadvantages of $Bi_2O_3$-based solid electrolytes include a low stability towards reduction (see Figure), high thermal expansion and chemical reactivity, and a significant electronic transport. Bismuth oxide is also a component of other ion-conducting phases, such as → *BIMEVOX*.

*Refs.: [i] Kharton VV, Naumovich EN, Yaremchenko AA, Marques FMB (2001) J Solid State Electrochem 5:160; [ii] http://www.marketresearch.com/map/prod/1190139. html; [iii] Sammes NM, Tompsett GA, Nafe H, Aldinger F (1999) J Europ Ceram Soc 19:1801; [iv] Kharton VV, Marques FMB, Atkinson A (2004) Solid State Ionics 174:135*

VK

**Bjerrum, Niels Janniksen**



(© Morten J. Bjerrum)

(Mar. 11, 1879, Copenhagen, Denmark – Sep. 30, 1958, Copenhagen, Denmark) Bjerrum studied chemistry in 1905 in Leipzig (Germany), 1907 in Zurich (Switzerland), 1910 in Paris (France), and 1911 in Berlin (Germany). Full doctorate in 1908, University of Copenhagen (Denmark). 1914–1949 Professor at the Royal Veterinary and Agricultural College in Copenhagen. Bjerrum worked on protolysis equilibria [i], amphoteric electrolytes, indicators, activity coefficients of concentrated electrolytes [ii], heat capacity of

B

gases, infrared spectroscopy, colloid chemistry, kinetic theory, salt effects in kinetics, and complex formation equilibria. Bjerrum introduced the → *log c-pH diagrams* [iii]. In 1909 he was the first to suggest that strong electrolytes are completely dissociated, which was strongly debated by → *Arrhenius*. On the basis of spectroscopic evidence he attributed the conductivity changes to interionic forces. He also corroborated the theory of ion-pair formation (association of ions) [iii]. For more biographical details see [iv, v].

*Refs.: [i] Bjerrum N (1914) Die Theorie der alkalimetrischen und azidimetrischen Titrierungen. Verlag von Ferninand Enke, Stuttgart; [ii] Bjerrum N (1918) Z Elektrochem 24:321; [iii] Bjerrum N (1915) Sammlung chemisch und chemisch-technischer Vorträge 21:1; [iv] Bjerrum N (1926) K dansk vidensk Selsk 7 No 9; [v] Nielsen AK (2001) Dansk Kemi 82:38; [v] Brosset C, Sillén LG (1958) Svensk Kem Tidskr 70:432; [vi] Nielsen AK (ed) (2004) Niels Bjerrum (1879–1958). Liv og værk. The Danish Society for History of Chemistry, Copenhagen*

FS

**Bjerrum length** The distance $\lambda_B$ between two charges at which the Coulomb interaction (→ *Coulomb force*) is equal to the thermal energy $k_B T$ ($k_B$:→ *Boltzmann constant*, $T$: absolute temperature). For monovalent ions in a solvent with the → *dielectric constant* $\varepsilon_r$ the Bjerrum length is: $\lambda_B = \frac{e^2}{4\pi\varepsilon_r\varepsilon_0 k_B T}$ , where $e$ is the → *elementary electric charge*, and $\varepsilon_0$ the permittivity of vacuum (see → *permittivity*). $\lambda_B$ is for univalent charged ions in water 0.71 nm, for apolar solvents up to several tens nanometer, and in vacuum it is around 57 nm. The relation between the Bjerrum length and the → *Debye length* $r_D$ is for electrolyte solutions: $r_D = \frac{1}{\sqrt{8\pi\lambda_B N_A I}}$, where $N_A$ is the → *Avogadro constant* and $I$ is the → *ionic strength*.

*Ref.: Zwanikken J, van Roij R (2009) J Phys, Condens Matter 21:424102*

FS

**Bjerrum pair** Sometimes ion pairs are called Bjerrum pairs because → *Bjerrum* has suggested their formation for the first time [i]. See → *ion association*.

*Ref.: [i] Bjerrum N (1926) K Dan Vidensk Selsk Mat-Fys Medd 7:1*

FS

**Blank determination** A process in which all steps of an analysis are performed in the absence of the → *analyte* [i].

*Ref.: [i] Skoog D, West D, Holler F, Crouch SR (2003) Fundamentals of analytical chemistry, 8th edn. Brooks/Cole, Belmont*

FG

**Blocking boundary/interface (also called "reflective boundary")** A conducting media contains mobile charge carriers which are not bound to a certain spatial region and may be transported to distances well beyond the molecular scale, contrary to bound charges (induced or permanently existing) which can only be displaced at the molecular scale under the influence of an external electric field. The mobile charges can be of ionic or electronic type (the latter includes "free" electrons in metals, hopping electrons, or → *holes* in semiconductors, delocalized charged segments of a conducting polymer matrix called → *polarons* and → *bipolarons*, or cation-radicals and dications, etc.). This conducting phase forms boundaries with other media (which may also be conducting or insulating). Frequently, such a boundary is "blocking", i.e., it does not allow an exchange by charged species across the → *interface* and consequently the passage of a → *faradaic current*. It is usually the case of an interface between a conducting and an insulating phase (or two insulating ones). This situation may also occur at the contact of two conducting media which possess mobile charge carriers of different types. Important examples are: electronic conductor (metal, semiconductor. . .)|electrolyte solution (without solute electroactive species), two ionic conductors with different types of mobile ions in these phases, interface of two immiscible liquids (each liquid must contain "specific" ions which cannot penetrate in significant amounts into another phase). The concept of a blocking interface may also be applicable for a contact of two media having one or several corresponding mobile charge carriers so that one could theoretically expect an → *electron* or/and → *ion transfer*

across the boundary but in practice this exchange is so slow due to an interfacial barrier that it can be disregarded (a thin insulating layer between two electronic conductors, an adsorbed layer of nonpolar molecules for the ion exchange...).

An important example of a system with a blocking boundary is an electrode coated with a conducting layer (whose thickness is sufficiently great compared to the internal Debye screening length) in contact with a solution if the film|solution boundary does not allow the interfacial exchange of the electroactive species diffusing inside the layer. The nonstationary distribution of this species inside the layer corresponds to → *finite diffusion* problem. Its solution for the film with a blocking external boundary and with the concentration modulation at the electrode|film contact in the course of the passage of an alternating current results in one of two expressions for "finite-Warburg impedance" for the contribution of the layer: $Z_{layer} = \tau_d(C(0))^{-1}\coth(i\omega\tau_d)^{1/2}/(i\omega\tau_d)^{1/2}$ containing the characteristic → *diffusion time*, $\tau_d = L^2/D$ ($L$, layer thickness, $D$, → *diffusion coefficient*), and the low-frequency capacitance, $C(0) = dQ/dE$, this derivative being equal to the ratio of the charge, $dQ$, to pass through the circuit to change the equilibrium concentration of electroactive species inside the film, to the small-amplitude change of the external potential, $dE$.

*Ref.: [i] Retter U, Lohse H (2010) Electrochemical impedance spectroscopy. In: Scholz F (ed) Electroanalytical methods, 2nd edn. Springer, Berlin, pp 159–177*

MAV

**Blocking electrode** → *ideally polarizable electrode*

### Blodgett, Katharine Burr



(Emilio Segrè Visual Archives)

(Jan. 10, 1898 Schenectady, N.Y., USA – Oct. 12, 1979, Schenectady, N.Y., USA) Katharine Blod-

gett attended the Bryn Mawr College, a women's college in Pennsylvania, where she received a degree in physics. → *Langmuir*, whom she met at a visit of the General Electric Company, encouraged her to continue her education and aim at a position at GE. In 1917 she entered the University of Chicago and in 1918 she received a MS. Langmuir hired her as his assistant at GE, and in 1924 she was accepted at Sir Ernest Rutherford's Cavendish Laboratory. In 1926 she was the first woman to receive a Ph.D. in physics from the University of Cambridge. In 1926 she returned to GE to continue her work with Langmuir. Langmuir had previously developed a technique to transfer monolayers from a water surface to a metal plate. Blodgett developed the technique for multilayer films which are now known as → *Langmuir–Blodgett films* [i, ii].

*Refs.: [i] Blodgett KB (1932) J Am Chem Soc 57:1007; [ii] Blodgett KB, Langmuir I (1937) Phys Rev 51:964*

FS

**Bockris–Devanathan–Müller model** → *double-layer models*

### Bode, Hendrik Wade



(Courtesy of the American Institute of Physics)

(Dec. 24, 1905, Madison, Wisconsin, USA. – June 21, 1982, USA.) Bode contributed to electrical engineering and systems design [i]. He received patents for transmission networks, transformer systems, electrical wave amplification, broadband amplifiers, and electronic artillery control. Bode's work in electric filters and equalizers led to broader aspects of communication transmission [ii]. His name is mainly remembered because of the → *Bode plot* used in → *impedance* analysis named after him.

*Refs.: [i] Van Valkenburg ME (1984) IEEE Transactions on Automatic Control AC-29:193; [ii] Bode HW (1975)*

*Network analysis and feedback amplifier design, 14th ed, RE Krieger Pub Co, Huntington, NY (1st ed 1945)*

EK

**Bode plot** Experimental data for complex → *impedance*, $Z$, measured for a set of → *frequency* values, $\omega = 2\pi f$ ($f$, in hertz), may be analyzed with the use of various coordinates. One of the most popular treatments is based on Bode plots: the absolute value of $Z$ ("magnitude of impedance") and its argument ("phase angle"), $|Z|$ and arg $Z$ (or their logarithms), respectively, are presented as a function of the decimal logarithm of frequency, $\log f$ (called "Bode magnitude and Bode phase plots"). Sometimes, the same terminology is used for similar graphs for other complex characteristics, → *admittance*: $Y = Z^{-1}$, complex capacitance: $C(\omega) = Y(\omega)/i\omega$ or $C(\omega) = (i\omega \, (Z(\omega) - R(\infty)))^{-1}$, $R(\infty)$ being the high-frequency limit of impedance, e.g., $|C|$ and arg $C$ as functions of $\log f$.

*Refs.: [i] Bard AJ, Faulkner LR (2001) Electrochemical methods. Wiley, New York; [ii] Retter U, Lohse H (2010) Electrochemical impedance spectroscopy. In: Scholz F (ed) Electroanalytical methods, 2nd edn, Springer, Berlin, pp 159–177; [iii] Barsoukov E, Macdonald JR (ed) (2005) Impedance spectroscopy. Theory, experiment, and applications. Wiley, Hoboken*

MAV

### Bois-Reymond, Emil Heinrich du



(Nov. 7, 1818, Berlin, Germany – Dec. 26, 1896, Berlin, Germany) The son of a family of French refugees in Germany; studied theology, philosophy, mathematics, geology, and finally medicine in Berlin and Bonn. In 1843 he wrote his doctoral thesis about the understanding the old Greeks and Romans had of electric fishes. In 1845 he founded together with E.W. von Brücke → *Wilhelm von Beetz*, Gustav Karsten, Carl Hermann Knoblauch, and Wilhelm Heintz the Physical Society in Berlin. In 1846 he finished his habilitation as physiologist, became in 1855 extraordinary Professor, and in 1858 full Professor of Physiology at the University of Berlin. Throughout his life du Bois-Reymond studied electric phenomena in the living world and he is regarded as one of the founders of → *electrophysiology*.

*Ref.: Beneke K (1999) Mitteilungen der Kolloid-Gesellschaft 8:92*

FS

### Boltzmann, Ludwig Eduard



(Feb. 20, 1844, Vienna, Austria – Sep. 5, 1906 in Duino, Austro-Hungarian Empire, now Italy) is justly famous for his invention of statistical mechanics. At different times in his life he held chairs in theoretical physics at Graz, and in mathematics at Vienna. He also lectured in philosophy. His principal achievement, and the trigger for innumerable vitriolic attacks from the scientific establishment, was his introduction of probability theory into the fundamental laws of physics. This radical program demolished two centuries of confidence that the fundamental laws of Nature were deterministic. Astonishingly, he also introduced the concept of discrete energy levels more than thirty years before the development of quantum mechanics.

Among Boltzmann's discoveries were the logarithmic law connecting entropy and probability, the Stefan–Boltzmann law giving the energy flux emitted by a black body at temperature $T$, the Maxwell–Boltzmann formula for the distribution

of molecular speeds in a gas, and the Boltzmann distribution formula for the fractional number of particles occupying discrete energy levels in a closed system at equilibrium. In 1906, while on holiday with his wife and daughter at the Bay of Duino, near Trieste, he hanged himself. A version of the entropy formula that he inspired, *viz.*

$$S = k_B \ln W$$

is engraved on his tombstone. Here, $S$ is the → *entropy*, $k_B$ is the → *Boltzmann constant*, and $W$ is the number of possible microstates corresponding to the macrostate of the system.

"When a true genius appears in the world, you may know him by this sign, that the dunces are all in confederacy against him." Jonathan Swift, *Thoughts on Various Subjects* (1706).

SF

**Boltzmann constant** ($k$ or $k_B$) is the physical constant relating the thermal energy of an equilibrium system (per accessible degree of freedom) to the practical thermometric temperature scale (based on absolute zero and the triple point of water). Its units are joules per kelvin. Although widely attributed to Boltzmann, it was actually Max → *Planck* who first introduced the symbol $k$, and gave an accurate value for it, in his famous derivation of the law of black body radiation [i]. The 2006 CODATA recommended value [ii] of $k$ is $1.380\,650\,4(24) \times 10^{-23}\,\mathrm{J\,K^{-1}}$.

*Refs.: [i] Planck M (1901) Ann Phys 309:553; [ii] Mohr PJ, Taylor BN, Newell DB (2007) The 2006 CODATA Recommended Values of the Fundamental Physical Constants (Web Version 5.0)*

SF

**Boltzmann distribution** The Boltzmann distribution describes the number $N_i$ of indistinguishable particles that have energy $E_i$, after $N$ of them have been independently and identically distributed among a set of states $i$. The probability density function is

$$\frac{N_i}{N} = \frac{g_i \exp\left(-E_i/k_B T\right)}{Z(T)}, \tag{1}$$

where $k_B$ is the Boltzmann constant, $T$ is the thermometric temperature (assumed uniform), $g_i$

is the number of states having energy $E_i$ (i.e., the degeneracy of the states), and $Z(T)$ is the partition function (*Zustandsumme*). An important insight from the Boltzmann distribution is that the energy in a collection of molecules at equilibrium is not distributed uniformly, it is distributed exponentially. This means that a small fraction of the molecules have energies that are very much higher than the average.

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**BOR** → *Direct borohydride fuel cell*

**Born, Max**



(Dec. 11, 1882, Breslau, Germany, now Wrocław, Poland, – Jan. 5, 1970, Göttingen, Germany) He studied in Breslau, Heidelberg, Zurich, Cambridge, and Göttingen, first law and philosophy, later mathematics (among his teachers were Felix Klein, David Hilbert and Hermann Minkowski), and finally physics and astronomy (under Karl Schwarzschild). He received his Ph.D. in 1907 and habilitation in 1909 at the University of Göttingen. In 1919, after a period in the German army, he became a professor at the University of Frankfurt am Main, and then professor at Göttingen in 1921. In 1920 he showed that the free energy of solvation of an ion had a very simple dependence on the ionic charge, the ionic radius, and the dielectric constant of the solvent [i]. In 1926, in collaboration with Robert Oppenheimer, he propounded the now-famous "Born–Oppenheimer approximation" which provides the foundation for nearly all modern computational studies of chemical binding and reactivity [ii]. Finally, throughout the same period, he maintained a famous correspondence with → *Einstein*, in which he argued in favor

**B**

of his (Born's) statistical interpretation of the wavefunction in quantum mechanics. Born belatedly received the Nobel Prize for this work in 1954 [iv]. Tragically, Born was forced to leave Göttingen in 1933 because of his Jewish descent. In 1935–1936 he worked for six months in Bangalore at the Indian Institute of Science with C. V. Raman. From 1936 to 1953 he stayed in Edinburgh, Scotland, as Tait Professor of Natural Philosophy. Following his retirement he returned to Germany, where he died in 1970 [vi]. See also $\rightarrow$ *Born equation*, $\rightarrow$ *Born–Haber cycle*, $\rightarrow$ *Born–Mayer equation*, and $\rightarrow$ *Born solvation energy*.

*Refs.: [i] Born M (1920) Z Phys 1:45; [ii] Born M, Oppenheimer JR (1927) Ann Phys 389:457; [iii] Born M (1954) The statistical interpretation of quantum mechanics. Nobel Lecture; [iv] http://nobelprize.org/index.html; [vi] Thorndike Greenspan N (2005) The end of the certain world. The life and science of Max Born. The Nobel physicist who ignited the quantum revolution. Basic Books (German translation: Thorndike Greenspan N (2006) Max Born – Baumeister der Quantenwelt. Elsevier, München)*

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**Born equation** This equation gives the free energy of a sphere of charge *ze* and radius *r*, immersed in a medium of permittivity, $\varepsilon$, relative to the gaseous ion as the reference state. The solvent is assumed to be a continuum, and no specific solvent–solvent or solvent–ion interactions are considered. This assumption is inadequate in aqueous solution, however, on the basis of the $\rightarrow$ *Gibbs energy* that can be calculated by the Born equation [i], a useful approximation of the relative hydration of ions can be made:

$$\Delta G_S = -\frac{N_A z^2 e^2}{8\pi\varepsilon_0 r}\left(1 - \frac{1}{\varepsilon_r}\right).$$

$\varepsilon_o$ is the $\rightarrow$ *permittivity* of the vacuum; $\varepsilon_r$ is the $\rightarrow$ *dielectric constant* of the medium; $z$ is the charge of the ions; $e$ is the $\rightarrow$ *elementary electric charge*; $N_A$ is the $\rightarrow$ *Avogadro constant*.

$\Delta G_S$ is also referred to as the free energy of $\rightarrow$ *solvation* of the ions in the respective medium. The Born energy ($\Delta G_S$) required to transfer one mole of ions from one phase with dielectric con-

stant $\varepsilon_1$ into another phase of dielectric constant $\varepsilon_2$, is given by [ii]:

$$\Delta G_S = -\frac{N_A z^2 e^2}{8\pi\varepsilon_0 r}\left(\frac{1}{\varepsilon_1} - \frac{1}{\varepsilon_2}\right).$$

The last equation, with several correction factors, has been used to accurately calculate the solvation energies of spherically distributed charges [iii], and to nonspherical charged and polar groups [iv, v]. Those equations are known as Modified Born Equations [iv–vi]. It is worth noting that the Born equation has been also used by Marcus for the description of the kinetics of the outer-shell electron transfer [vii, viii].

*Refs.: [i] Born M (1920) Z Phys 1:45; [ii] Marcus Y (1997) Ion properties. Marcel Dekker, New York; [iii] Rashin AA, Honig B (1985) J Phys Chem 89:5588; [iv] Stilly WC, Tempczyk A, Hawley RC, Hendrickson TA (1990) J Am Chem Soc 112:6127; [v] Rashin AA (1990) J Phys Chem 94:1725; [vi] Shoichet BK, Leach AR, Kuntz ID (1999) Proteins 34:4; [vii] Marcus RA (1977) Theory and application of electron transfer at electrodes and in solutions. In: Rock PA (ed) Special topics in electrochemistry. Elsevier, Amsterdam, pp 61; [viii] Millery CJ (1995) Heterogeneous electron transfer kinetics at metallic electrodes. In: Rubinstein I (ed) Physical electrochemistry. Marcel Dekker, New York, pp 46–47*

                                                                RG

**Born–Haber's cycle** Hess's law establishes that the enthalpy of a reaction is the same independently whether the reaction proceeds in one or several steps. It is a consequence of the first law of thermodynamics, which states the conservation of energy. $\rightarrow$ *Born* and $\rightarrow$ *Haber* applied Hess's law to determine the $\rightarrow$ *enthalpy* of formation of an ionic solid. The formation of an ionic crystal from its elements according to Born–Haber's cycle can be represented by the following diagram.

It is necessary that

$$\Delta H_f = \Delta H_{AM} + \Delta H_{AX} + \Delta H_{EI} + \Delta H_{AE} + U_0.$$

The terms $\Delta H_{AM}$ and $\Delta H_{AX}$ constitute the enthalpies of atomization of the element and the nonmetal respectively, $\Delta H_{EI}$ is the ionization
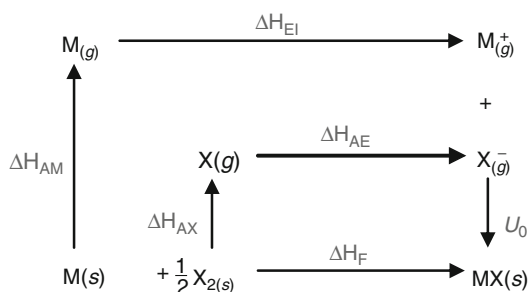
**Born–Haber's cycle — Figure**

enthalpy of the metal, $\Delta H_{AE}$ is the ionization enthalpy of the nonmetal, and $U_o$ is the lattice energy. For gaseous diatomic nonmetals, $\Delta H_{AX}$ is the enthalpy for dissociation (i.e., bond energy plus $RT$) of the diatomic molecule. In the cases of metals evaporated to form monatomic gases, $\Delta H_{AM}$ is identical to the sublimation energy. If the sublimation takes place for a diatomic molecule, $M_2$, then it is necessary to include the enthalpy of reaction.

*Ref.: [i] Huheey JE (1972) Inorganic chemistry, principles of structure and reactivity. Harper & Row, New York*

MBS

**Born–Mayer equation** This equation predicts the lattice energy of crystalline solids [i]. It is based on a simple model, in which the attraction and repulsion for a given arrangement of ions is calculated. The Born–Mayer energy ($E_{B-M}$) is given by [i]:

$$E_{B-M} = \frac{N_A e^2 A z_A z_B}{4\pi\varepsilon_o d_o}\left(1 - \frac{d^*}{d_o}\right), \qquad (1)$$

where $\varepsilon_o$ is the $\rightarrow$ *permittivity* of the vacuum; $z_A$ is the charge of the ions "A", while $z_B$ is the charge of the ions "B"; $e$ is the $\rightarrow$ *elementary electric charge*; $N_A$ is the $\rightarrow$ *Avogadro constant*; $A$ is the Madelung constant (which results from large positive and negative Coulomb interactions); $d_o$ is the distance between the cations and anions (in Angstroms); $d^*$ is the exponential scaling factor for repulsive term ($0.345 \times 10^{-10}$ m).

*Ref.: [i] Born M, Huang K (1954) Dynamical theory of crystal lattices. Oxford University Press, Oxford*

RG

**Born solvation energy** $\rightarrow$ *Born equation*

**Borohydride oxidation reaction (BOR)** $\rightarrow$ *Direct borohydride fuel cell*

**Boron-doped diamond electrodes** Electrode material made from synthetic diamond ($\rightarrow$ *diamond electrode*) for example via vapor deposition techniques. In an atmosphere of methane (as a carbon source) and hydrogen (as etchant) at ca. 600 °C diamond seeds tend to grow whereas graphitic carbon deposits are etched away. As a result thin polycrystalline films of diamond are grown (with a growth rate of ca. 1 to 10 $\mu$m h$^{-1}$) directly onto suitable substrates (silicon, niobium, tungsten, etc.). By introducing traces of boron into the gas phase (e.g., $B_2H_6$ or trimethylborate), effective boron-doping of the diamond is achieved. At a boron-doping level of ca. $10^{20}$ cm$^{-3}$ a blue-black diamond material with good electrical conductivity and unique electrode characteristics is obtained [i–iii]. At lower doping levels $p$-type $\rightarrow$ *semiconductor* characteristics are observed. The diamond electrode surface is mechanically inert (towards polishing, or cavitation under exposure to ultrasound) and chemically inert (towards aggressive chemicals and under extreme polarization).

Applications of this electrode material include (i) the anodic formation of hydroxyl radicals, (ii) the anodic formation of ozone and peroxo species, (iii) waste degradation in aqueous solution (hazardous and a range of organic wastes have been broken down without toxic intermediates), (iv) as a mechanically robust electrode for solid state electrochemistry or in the presence of power ultrasound, (v) as a dimensionally stable electrode, (vi) as a IR and Vis transparent electrode material, and (vii) as an inert substrate for electro-catalysts.

*Refs.: [i] Pleskov YV (2002) Russ J Electrochem 38:1275; [ii] Swain GM, Anderson AB, Angus JC (1998) MRS Bull 23:56; [iii] Rao TN, Ivandini TA, Terashima C, Sarada BV, Fujishima A (2003) New Diamond Frontier Carbon Technol 13:79*

FM

B

## Böttger, Wilhelm Carl
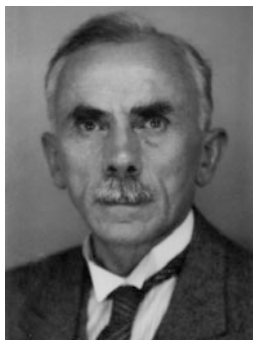


(Universitätsarchiv Leipzig)

(Oct. 2, 1871, Leising, Germany – Oct. 23, 1949, Hannover, Germany) From 1893 to 1895 Böttger studied pharmacy in Leipzig. He continued by studying chemistry in the institute of → *Ostwald, F.W.* and devoted his further work to electrochemistry. His Ph.D. (1897) concerned the "application of the → *electrometer* as indicator for acid and base titrations". Following a one-year assistantship in Göttingen (with Otto Wallach) he returned to the Ostwald institute and habilitated in 1903 for analytical and physical chemistry. In 1904/05 he was Research Associate at the Institute of Technology, Boston, USA (with A. A. Noyes). In 1910 he became extraordinary Professor at the University of Leipzig and from 1922 until his retirement he was 'ordentlicher Honorarprofessor' (full honorary Professor) and chief of the chemical department of the Institute of Physical Chemistry [i]. Three years following the first potentiometric precipitation titration by → *Behrend*, Böttger performed the first potentiometric acid–base titration [ii]. Böttger contributed to the establishment of potentiometric analysis and further development → *electrogravimetry* [iii].

*Refs.: [i] Brennecke E (1950) Angew Chem 62:279; [ii] Böttger W (1897) Z Physik Chem 24:253; [iii] Böttger W (1949) Elektroanalyse. In: Physikalische Methoden der Analytischen Chemie. Böttger W (ed) 2$^{nd}$ part, Geest & Portig, Leipzig, pp 315*

FS

**Böttcher's accumulator**  This was an → *accumulator* with a lead and a zinc electrode in a zinc sulfate electrolyte. Upon discharge zinc ions are reduced to the metal, and lead is oxidized to lead sulfate. These processes are reversed upon charging.

*Ref.: [i] Hauck WP (1883) Die Galvanischen Batterien, Accumulatoren und Thermosäulen, 2$^{nd}$ edn. Hartleben's Verlag, Wien*

FS

**Boundary layer**  → *hydrodynamic boundary layer*

**Boundary value**  A boundary value is the value of a parameter in a differential equation at a particular location and/or time. In electrochemistry a boundary value could refer to a concentration or concentration gradient at $x = 0$ and/or $x = \infty$ or to the concentration or to the time derivative of the concentration at $t = \infty$ (for example, the steady-state boundary condition requires that $(dc/dt)_{t=\infty} = 0$). Some examples: $(dc/dx)_{x=0} = 0$ for any species that is not consumed or produced at the electrode surface; $(dc/dx)_{x=0} = -f_{x=0}/D$ where $f_{x=0}$ is the flux of the species, perhaps defined by application of a constant current (→ *von Neumann boundary condition*) and $D$ is its diffusion coefficient; $c_{x=0}$ is defined by the electrode potential (→ *Dirichlet boundary condition*); $c_{x=\infty}$, the concentration at $x = \infty$ (commonly referred to as the bulk concentration) is a constant.

SWF

**Boxcar averaging**  → *digital filter*

## Branica, Marko
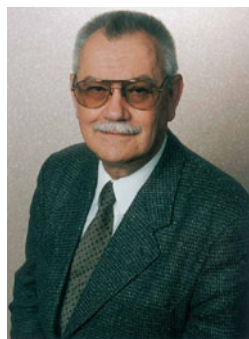


(Reproduced with permission of the Croatica Chemica Acta)

(Jan. 14, 1931, Zagreb, Croatia – Nov. 17, 2004, Zagreb, Croatia) [i]. From 1952 to 1956 Branica studied chemistry in Zagreb. He obtained his PhD from the Faculty of Science, University of Zagreb in 1963, during which time he

was already employed at the "Ruđer Bošković" Institute. In this Institute he advanced to the positions of research associate (1963), senior research associate (1966) and senior scientist (1970). In the beginning of his career Branica was interested in → *polarography* and developed several new methods of applying electrochemistry to environmental analysis and speciation. His most prominent achievement was the development of → *pseudopolarography* [ii], the method that enables the speciation of metal ions at trace concentrations [iii]. In several terms he presided the Chemical Oceanography Committee of the International Commission of the Scientific Exploration of the Mediterranean Sea. He was awarded the Heineken Prize for the Environment by the Royal Netherlands Academy of Arts and Sciences in 1992 and the National Life-achievement Award for chemistry in 1996.

*Refs.: [i] Kniewald G, Lovrić M (2006) Croat Chem Acta 79(1):XIII; [ii] Bubić S, Branica M (1973) Thalassia Jugoslav 9:47; [iii] Nicolau R, Louis Y, Omanović D, Garnier C, Mounier S, Pižeta I (2008) Anal Chim Acta 618:35*

ŠKL

## Braun, Ferdinand

(© The Nobel Foundation)

(June 6, 1850, Fulda, Germany – Apr. 20, 1918, Brooklyn, NY, USA) German physicist, Ph.D. 1872. In 1874 Braun discovered the non-ohmic behavior of metal-semiconductor contacts, and in 1878 he disproved the Thompson–Berthellot principle (assumption that the heat of a reaction is the driving force) in studies of the → *Daniell element* [i]. This work was an important impetus for → *Helmholtz* to develop independent of → *Gibbs* the idea of the → *free energy* of a reaction as the driving force. In 1897/98, B. developed

the wireless telegraphy for which he was awarded together with Guglielmo Marconi the Nobel Prize in physics in 1909. Braun also invented the cathode ray tube.

*Refs.: [i] Braun F (1878) Ann Phys 241:182; [ii] http://nobelprize.org/index.html*

FS

**Bravais lattice** used to describe atomic structure of crystalline → *solid materials* [i, ii], is an infinite array of points generated by a set of discrete translation operations, providing the same arrangement and orientation when viewed from any lattice point. A three-dimensional Bravais lattice consists of all points with position vectors $\boldsymbol{R}_L$:

$$\boldsymbol{R}_L = N_1 \cdot \boldsymbol{w}_1 + N_2 \cdot \boldsymbol{w}_2 + N_3 \cdot \boldsymbol{w}_3,$$

where the three primitive lattice vectors $\boldsymbol{w}_i$ are not all in the same plane, and the lattice can be generated varying the integers $N_j$. The smallest parallelepiped with a lattice point (site) at each corner corresponds to the so-called primitive unit cell. A crystal structure may also be described in terms of non-primitive unit cells, which are larger than the primitive cell. There are 14 possible three-dimensional Bravais lattices. These are named for French physicist Auguste Bravais (1811–1863), who made a great contribution in the crystal lattice theory.

*Refs.: [i] West AR (1984) Solid state chemistry and its applications. Wiley, Chichester; [ii] Kittel C (1996) Introduction to solid state physics, 7th edn. Wiley, Chichester*

VK

## Brdička, Rudolf

(Feb. 25, 1906, Prague, Austro-Hungarian Empire, now Czech Republic – June 25, 1970,

Mariánské Lázně, then Czechoslovakia) Student, assistant, and finally successor of → *Heyrovský* at Charles University in Prague, later director of the Institute of Physical Chemistry, Academy of Sciences, Prague. Introduced polarographic "Brdička reaction" – sensitive → *catalytic current* signal due to evolution of hydrogen at → *mercury electrodes* from cobalt-containing solutions of proteins, used in analysis of proteins and in medical diagnostics, esp. in treatment of cancer [i–ix]. Besides, he studied and expressed quantitatively adsorption of electroactive substances at the electrode [x], and contributed essentially to exact formulation of the effect of chemical reactions in electrode processes [xi–xiii]. Author of a comprehensive textbook of physical chemistry, which was translated into several languages.

*Refs.: [i] Brdička R (1933) Coll Czech Chem Commun 5:112; [ii] Brdička R (1937) Nature 139:1020; [iii] Brdička R (1947) Research 1:25; [iv] Brdička R, Březina M, Kalous V (1965) Talanta 12:1149; [v] Müller OH (1963) Polarographic analysis of proteins, amino acids and other compounds by means of Brdicka reaction. In: Glick D (ed) Methods of biochemical analysis, vol 11. Interscience, New York, pp 329–403; [vi] Homolka J (1971) Polarography of proteins, analytical principles and applications in biological and clinical chemistry. In: Glick D (ed) Methods in biochemical analysis, vol 19. Wiley, New York, pp 436–555; [vii] Hart JP (1990) Electroanalysis of biologically important compounds. Ellis Horwood, New York, p 92; [viii] Brabec V, Vetterl V, Vrana O (1996) Electroanalysis of biomacromolecules. In: Brabec V, Walz D, Milazzo G (eds) Techniques in bioelectrochemistry, vol 3. Birkhäuser Verlag, Basel, p 287; [ix] Luo D, Lan J, Zhou C, Luo C (2003) Anal Chem 75:6346; [x] Brdička R (1942) Z Elektrochem 48:278; [xi] Brdička R, Wiesner K (1947) Coll Czech Chem Commun 12:138; [xii] Brdička R (1955) Z Elektrochem 59:787; [xiii] Brdička R, Hanuš V, Koutecký J (1962) General theoretical treatment of the polarographic kinetic currents. In: Zuman P, Kolthoff IM (eds) Progress in Polarography, vol 1. Interscience, New York London, pp 145–199*

MHey

**Breyer, Bruno Zdenko**



(Courtesy of Petr Zuman, USA)

(Nov. 14, 1900, Zábřeh, then Austro-Hungarian Empire, now Czech Republic – Nov. 12, 1967, Milano, Italy) Ph.D. (Bonn), MD (Padua), from 1941 professor of agricultural chemistry, University of Sydney, author of "alternating (or AC) polarography" – i.e., → *polarography* with superimposed alternating voltage of small amplitude, and of "→ *tensammetry*" – i.e., AC polarography of surface-active substances.

*Ref.: [i] Breyer B, Bauer HH (1963) Alternating current polarography and tensammetry. Interscience, New York*

MHey

**Brick-layer model** describes electrical properties of ceramic materials, either → *solid electrolytes* or electronic → *conductors*, by treating their microstructure as an array of cubic grains separated by flat grain boundaries and assuming one-dimensional → *current* flow [i, ii]. The model has two limiting cases, with highly-resistive and highly-conductive boundaries. The former makes it possible to describe numerous practical systems where interfacial boundaries possess relatively high → *resistance* due to impurity segregation, space-charge effects, local compositional deviations, and the presence of secondary phases, pores, microcracks and other defects. Owing to its simplicity, this approach is widely used to analyze experimental results collected by the → *AC techniques*, including the → *electrochemical impedance spectroscopy*. When the grain-boundary → *conductivity* is much lower with respect to the grains, the impedance spectra are described by equivalent → *circuits* of several elements comprising a parallel → *resistor* and

→ *capacitor* or → *constant phase element*, connected in series. If these elements can be ascribed to definite physical processes, the brick-layer model enables to evaluate → *conductance* of grain-boundary phases, dielectric → *permittivity* of material components, pore and boundary → *capacitance*, and other properties of ceramics.

Refs.: [i] Barsoukov E, Macdonald JR (eds) (2005) *Impedance Spectroscopy: Theory, Experiment and Applications*, 2nd edn. Wiley-Interscience, Hoboken, NJ; [ii] *Beekmans NM, Heyne L (1976) Electrochim Acta 21:303*

VK

**Bridge, electrical** An electrical bridge is the connection between two points of an electrical network through which no current will pass when the bridge is "balanced". A number of electrical bridge circuits, i.e., circuits with such connecting bridge, have been developed for the purpose of measuring → *resistance*, → *capacity*, → *impedance*, inductance, etc. The most prominent is the → *Wheatstone bridge*.

FS

**Briggs–Haldane conditions** → *Michaelis–Menten kinetics*

**Brighteners** → *electroplating additives*

**Brönsted (Brønsted), Johannes Nicolaus**

(Feb. 22, 1879, Varde, Denmark – Dec. 17, 1947, Copenhagen, Denmark) Ph.D. Copenhagen 1908, since 1908 Professor of Chemistry (the 3rd chair, i.e., the chair of Physical Chemistry at the Univ. of Copenhagen). 1926/27 visiting Professor at Yale Univ., New Haven, Connecticut, USA. Famous for his work on chemical reaction kinetics, chemical affinity, indicators, and

thermodynamics of solutions. He could explain the effect of activity coefficients on reaction rates in solutions. In 1923 he developed independently of → *Lowry*, and → *Bjerrum* a new → *acid-base theory*, the so-called *Brönsted (Brønsted) acid-base theory*.

Ref.: [i] *Brönsted JN (1923) Rec Trav Chim Pays-Bas 42:718*

FS

**Brönsted (Brønsted) acid–base theory** → *acid-base theories*

**Brönsted (Brønsted)–Bjerrum equation** The rate constant $k$ of a chemical reaction involving ionic species A and B may be influenced by other ionic species in solution not directly participating in this reaction (i.e., a dissolved salt, thus the associated observation is called primary salt effect). The change of the rate as a function of the ionic charge of the involved species and the → *ionic strength* of the solution is given by the Brönsted (Brønsted)–Bjerrum equation

$$\ln k = \ln k_0 + 1.018 z_A z_B I^{1/2}$$

with the rate constant $k_0$ in the absence of other species; $k$ in the presence of other species, $z_A$ and $z_B$ are the ionic charge of the reacting species, and $I$ is the → *ionic strength*. In case of reactants having charges of equal sign the reaction is accelerated, in case of opposite signs the rate decreases. Reactions involving both neutral and charged reactants show no dependency.

Ref.: [i] *Weston RE, Schwarz HA (1972) Chemical kinetics. Prentice-Hall, Englewood Cliffs*

RH

**Brönsted's (Brønsted's), salt effect** → *Brönsted (Brønsted)–Bjerrum equation*, → *charge transfer reaction*

**Brown–Walker reaction** Important generalization and extension of the Kolbe reaction (1891) (→ *Kolbe synthesis*) leading to the synthesis of a variety of long-chain dicarboxylic acids and esters using monoesters of dicarboxylic precursors. Among the most used application belongs the production of sebacic acid diethylester from hydrogen ethyladipate
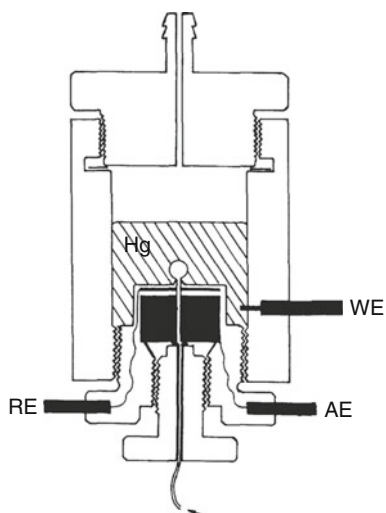
$$C_2H_5 - OOC - (CH_2)_4 - COO^- - e^- \rightarrow$$
$$1/2 C_2H_5 - OOC - (CH_2)_8 - COO - C_2H_5$$
$$+ CO_2$$
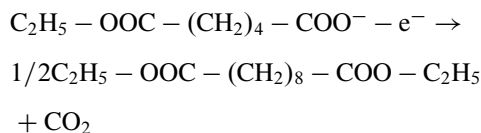
*Refs.: [i] Torii S, Tanaka H (1991) Carboxylic acids. In: Lund H, Baizer M (eds) Organic electrochemistry. Marcel Dekker, New York; [ii] Schaefer HJ (1991) Electrolytic oxidative coupling. In: Lund H, Baizer M (eds) Organic electrochemistry. Marcel Dekker, New York*
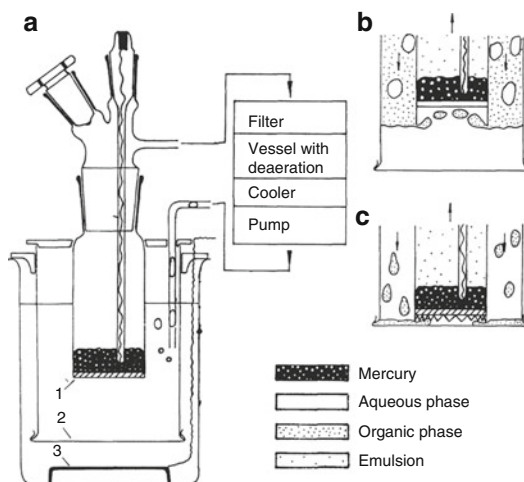
<div align="right">JL</div>

**Bubble electrodes**   Mercury electrodes constructed in such a way that an electrolyte solution is entering a mercury-filled vessel through one or many small orifices in the bottom (cf. Fig. 1). The solution bubbles grow and will finally ascend in the mercury. The counter and the reference electrode have to be situated in the tubing fed to the orifice. Bubble electrodes have been developed as flow-through detectors for HPLC and FIA [i–iii, vi], as electrodes to generate ESR-active species [iii–iv], for → *tensammetry* [vii], and for electrosynthesis (cf. Fig. 2) [v]. The fact that they are mercury based impeded further developments of this electrode type.

*Refs.: [i] Scholz F, Henrion G (1983) Z Chem 23:152; [ii] Trojánek A, Křestan L (1983) J Liq Chromatog 6:1759; [iii] Scholz F, Henrion G (1984) Z Chem 25:121; [iv] Stößer R, Scholz F, Pragst F, Henrion G (1985) Z Chem 25:157; [v] Pragst F, Scholz F, Woitke P, Kollek V,*



**Bubble electrodes — Figure 2.** Bubble electrode for electrosynthesis: *1* – bubble electrode, *2* – ion exchange membrane, *3* – PbO$_2$ anode. Arrangement A is for single-phase operation, and arrangement B and C are for two-phase electrolysis (electrolysis of emulsion) (reproduced from [v])

*Henrion G (1985) J prakt Chem 327:1028; [vi] Trojánek A (1985) J Chromatog 323:406; [vii] Scholz F, Kupfer M, Seelisch J, Glowacz G, Henrion G (1987) Fresenius Z Anal Chem 326:774*

<div align="right">FS</div>

### Buck, Richard (Dick) Pierson



(July 29, 1929, Los Angeles, USA – July 22, 2011, Palo Alto, USA) He received his B.S. (1950) and M.S. (1951) from the California Institute of Technology, and his PhD from the Massachusetts Institute of Technology in 1954. He served as a research chemist in industry in California until he joined the faculty at the University of North Carolina at Chapel Hill in 1967 as an associate professor, and in 1975 he became professor of chemistry until his retirement in 2001. He was an outstanding

**Bubble electrodes — Figure 1.** Bubble electrode for analytical measurements (reproduced from [vii])

scientist in the field of → *ion-selective electrodes* (ISE's) and made enormous contributions to fundamental understanding of ISE's. In the 1960's and 1970's he studied theoretical aspects of interfacial potential development and selectivity of solid-state and glass membrane electrodes, including calculations of the potential profiles at electrode/membrane interfaces (using numerical solutions of the Nernst-Planck-Poisson equation) [i] (See → *Nernst-Planck equation* and → *Poisson equation*). He applied and improved → *impedance* methods to describe the charge-transfer kinetics at the interfaces and within the bulk of membrane electrodes [ii-iv]. In 1970's he turned his interest to understanding the ion → *permselectivity* of new organic liquid and polymer-membrane ion-selective electrodes [v]. Later, he worked on the development of novel microfabricated ion and biosensor arrays based on flexible Kapton substrates, and further demonstrated that such devices can be implanted within living heart muscle [vi, ix]. He was an active fellow of the IUPAC and has coordinated several projects as the chair of the Commission of Electroanalytical Chemistry [x-xiv].

*Refs: [i] Buck RP, Boles JH, Porter RD, Margolis JA (1974) Anal Chem 46:255; [ii] Buck RP (1968) J Electroanal Chem 18:381; [iii] Buck RP (1990) Electrochim Acta 35:1609; [iv] Buck RP, Mundt C (1997) J Chem Soc Faraday Trans 93:3511; [v] Buck RP, Lindner E (1998) Acc Chem Res 31:257; [vi] Marzouk SAM, Buck RP, Dunlap LA, Johnson TA, Cascio WE (2002) Anal Biochem 308:52; [vii] Buck RP, Lindner E (2001) Anal Chem 73:88 A; [viii] Buck RP (1991) Electrochim Acta 36:243; [ix] Buck RP, Ciani S (1975) CRC Crit Rev Anal Chem 5:323 [x] Buck RP, Lindner E, Kutner W, Inzelt G (2004) Pure Appl Chem 76:1139; [xi] Buck RP, Rondinini S, Covington AK, Baucke FGK, Brett CMA, Camoes MF, Milton MJT, Mussini T, Naumann R, Pratt KW, Spitzer P, Wilson GS (2002) Pure Appl Chem 74:2169; [xii] Kutner W, Wang J, L'her M, Buck RP (1998) Pure Appl Chem 70:1301; [xiii] Buck RP, Lindner E (1994) Pure Appl Chem 66:2527; [xiv] Buck RP, Cosofret VV (1993) Pure Appl Chem 65:1849*

HK

**Buckingham's $\pi$-theorem and dimensional analysis** Buckingham's $\pi$-theorem [i] predicts the number of → *dimensionless parameters* that are required to characterize a given physical system. A relationship between $m$ different physical parameters (e.g., flux, → *diffusion coefficient*, time, concentration) can be expressed in terms of $m$–$n$ dimensionless parameters (which Buckingham dubbed "$\pi$ groups"), where $n$ is the total number of fundamental units (such as m, s, mol) required to express the variables. For an electrochemical system with semi-infinite linear geometry involving a diffusion coefficient ($D$, units: $cm^2\,s^{-1}$), flux at $x = 0$ ($f_{x=0}$, units: moles $cm^{-2}\,s^{-1}$), bulk concentration ($c_\infty$, units: moles $cm^{-3}$) and time ($t$, units: s), $m = 4$ ($D, f_{x=0}, c_\infty, t$) and $n = 3$ (cm, s, moles). Thus $m - n = 1$; therefore only one dimensionless parameter can be constructed and that is $f_{x=0}\,(t/D)^{1/2}/c_\infty$. Dimensional analysis is a powerful tool for characterizing the behavior of complex physical systems and in many cases can define relationships without any additional computation (see → *dimensional analysis*). For the most economical graphical or tabular representation, parameter correlations should be expressed in terms of the relevant $\pi$ groups. This will become particularly important when a system's behavior has been quantified using numerical analysis and no analytic mathematical expressions are available. A dimensionless group which can be produced by combination of two or more other dimensionless groups may be more convenient in form for a particular application but is not counted as a new group.

*Ref.: [i] Buckingham, E (1914) Phys. Rev. 4:345*

SWF

**Budevski, Evgeni Bogdanov**
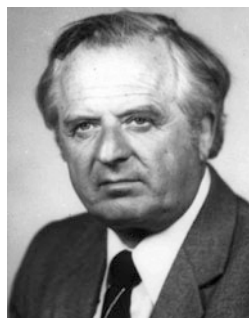


(July 29, 1922, Sofia, Bulgaria – October 13, 2008, Sofia, Bulgaria) Budevski was graduated in chemistry from the Sofia University and in 1949 joined the research group of → *Kaishev*

at the Department of Physical Chemistry, where he started his studies in the field of → *electrocrystallization*. In 1959 Budevski was elected head of the Electrochemistry Department of the Institute of Physical Chemistry, Bulgarian Academy of Sciences (BAS). In 1967 he founded the Central Laboratory of Electrochemical Power Sources, BAS (now Institute of Electrochemistry and Energy Systems, BAS) and was its Director till 1993. Budevski became professor in 1964, corresponding member of BAS in 1984 and full member of BAS in 1995. He was member of the Advisory Committee of the President of Republic Bulgaria within the period 1997–2001. Budevski is well-known in the field of → *electrochemistry* and → *electrocrystallization* science with his profound studies of two-dimensional → *nucleation* and crystal growth phenomena performed by means of the unique → *capillary method* [i-iii]. He contributed also to the field of electrochemical → *power sources* and hydrogen economy.

*Refs.: [i] Budevski E, Bostanov V (1964) Electrochim Acta 9:477; [ii] Budevski E, Bostanov V, Vitanov T, Stoynov Z, Kotzeva A, Kaischev R (1966) Electrochim Acta, 11:1697; [iii] Budevski E, Staikov G, Lorenz WJ (1996) Electrochemical phase formation and growth: an introduction to the initial stages of metal deposition. VCH, Weinhein*

<div align="right">AM</div>

## Buff, Johann Heinrich



(May 23, 1805, Rödelheim–December 24, 1878, Gießen) [i]. Buff studied chemistry in Göttingen and made his doctorate under the supervision of Justus von Liebig in Gießen. He worked with Joseph Louis Gay-Lussac in Paris, and later he was in Kassel at the same time when → *Bunsen* was there. With Friedrich Wöhler, he performed

a study on $SiH_4$ which paved the way for silane chemistry. Buff was professor of physics at the University of Gießen. In a textbook on physical and theoretical chemistry (1857) which was co-authored by H. Kopp and F. Zamminer, the field of Physical Chemistry was, for the first time, treated as a specific topic [ii]. Buff studied the conductivity of glasses and observed appreciable conductivities already at temperatures of 40–50 °C, thus changing the perception of glass as being an ideal insulator [iii]. See also → *Beetz, Wilhelm von*, → *solid electrolyte*.

*Refs: [i] Scholz F (2011) J Solid State Electrochem 15:5; [ii] Buff H, Kopp H, Zamminer F (1857) Lehrbuch der physikalischen und theoretischen Chemie (Volume 1 of „Graham-Otto's Ausführliches Lehrbuch der Chemie). Vieweg und Sohn, Braunschweig 2$^{nd}$ edn. 1863; [iii] Buff H (1854) Ann Chem 90:254*

<div align="right">FS</div>

**Buffer** A solution that, by virtue of containing sufficiently high concentrations of certain species, tends to resist changes in some solution property, such as → *pH*, → *equilibrium potential*, or → *ionic strength*.

<div align="right">DT</div>

— **pH buffer** A solution containing appreciable concentrations of a conjugate acid/base pair that resists changes in → *pH* upon further addition of small amounts of acid or base. Example conjugate acid/base pairs include $CH_3COOH/CH_3COO^-$, $H_2PO_4^-/HPO_4^{2-}$, and $NH_4^+/NH_3$, where the ionic species are typically introduced as salts. An accurate expression relating the pH of the buffer to the → *acidity constant* for the conjugate pair ($pK_a$) and the analytical concentrations of the acid ($c_{HB}$) and base ($c_B$) forms is given by:

$$pH = pK_a + \log \frac{\gamma_B}{\gamma_{HB}}$$
$$+ \log \frac{c_B + [H_3O^+] - [OH^-]}{c_{HB} - [H_3O^+] + [OH^-]},$$

where $\gamma_B$ and $\gamma_{HB}$ are the → *activity coefficients* for the base and acid forms and $[X]$ represents the molar concentration of species $X$. The above expression is often simplified to give the approximate → *Henderson–Hasselbalch equation* [i]:

$$pH \approx pK_a + \log \frac{c_B}{c_{HB}}.$$

The buffer capacity $\beta$, defined as the moles of acid or base necessary to change the pH of one liter of solution by one unit, is given by

$$\beta = \frac{2.3 c K_a 10^{-pH}}{(K_a + 10^{-pH})^2},$$

where $c$ is the sum of the molar concentrations of the acid and its conjugate base ($c_{HB} + c_B$) [ii]. The buffer capacity increases with $c$ and is at maximum when $pH = pK_a$. The above expressions are approximations for a conjugate pair formed from a polyprotic system (capable of multiple ionization steps).

DT

— **ionic strength buffer**   Sometimes referred to as an ionic strength adjustment buffer (ISAB), this is a solution that attempts to minimize differences (or changes) in → *ionic strength*. → *Ion selective electrode* (ISE) measurements often involve standards and samples that have differing ionic strengths. Therefore, the → *activity coefficient* ($\gamma$) of the target ion (and, hence, the response of the ISE to a given concentration of ion) also differs from standard to standard, from standard to sample, and from sample to sample. To overcome the effect of variable ionic strength, a solution of high ionic strength (which does not contain the ion to be measured or any likely interferent) is added to all standards and samples. This solution (the ISAB) effectively swamps out the ionic effects of the host solutions, resulting in a uniform ionic strength in all standards and samples [iii].

In → *voltammetry*, the electrode redox reaction necessarily involves a change in ionic strength near the electrode (i.e., an ion is consumed, produced, or undergoes a change in charge number). Therefore, the activity coefficients of the electroactive species vary as a function of time and distance from the electrode. In this case, the presence of an excess of a → *supporting electrolyte* serves as an ionic strength buffer [iv].

DT

— **redox buffer**   A solution containing appreciable concentrations of two species (a → *redox couple*) that are rapidly interconvertable by an electron exchange. The interconversion may involve chemical species (e.g., protons) as well as electrons. The equilibrium (redox) potential ($E$) of the solution is fixed by the ratio of the concentrations of the two species (as given by the → *Nernst equation*) and resists change upon further addition of small amounts of oxidant or reductant. By analogy with → *pH buffer* capacity, the redox buffer capacity $\beta$ for a single redox couple involving a one-electron transfer and having → *formal potential* $E_c^{\ominus\prime}$ is given by:

$$\beta = \frac{2.3 c 10^{-f\left(E + E_c^{\ominus\prime}\right)}}{\left(10^{-fE} + 10^{-fE_c^{\ominus\prime}}\right)^2},$$

where $f = F/2.3RT$ and $c$ is the sum of the molar concentrations of the two redox species. The buffer capacity increases with $c$ and is a maximum when $E = E_c^{\ominus\prime}$. Expressions are also available for redox systems involving several one-electron steps or one multielectron step [v].

*Refs.: [i] Segal IH (1976) Biochemical calculations, 2nd edn. Wiley, New York; [ii] van Slyke DD (1922) J Biol Chem 52:525; [iii] Frant MS, Ross JW Jr (1968) Anal Chem 40:1169; [iv] Oldham KB, Myland JC (1994) Fundamentals of electrochemical science, 1st edn. Academic Press, San Diego, p 265; [v] de Levie R (1999) J Chem Educ 76:574*

DT

## Bugarszky, István



(May 21, 1868, Zenta, Hungary – March 3, 1941, Budapest, Hungary) Bugarszky received

**B**

his doctoral diploma in chemistry at the Budapest University in 1891. He was appointed lecturer at the Veterinary College, Budapest and awarded the title of professor of chemistry in 1902. He worked at → *Nernst's* laboratory in Göttingen in 1896. He became a professor at the Budapest University in 1913 where he remained until his retirement in 1935.

His most famous achievement was the discovery of the → *endothermic galvanic cells* in 1897 [i, ii]. It was the first evidence that endothermic reactions can proceed spontaneously. Therefore, it supplied a verification of the concept of → *Gibbs* and → *Helmholtz* regarding the nature of affinity, i.e., the Gibbs free energy of reaction is of importance and not the heat of reaction (enthalpy) as claimed by Pierre Eugéne Marcellin → *Berthelot* (1827–1907) and Hans Peter Jørgen Julius Thomsen (1826–1909).

*Refs.: [i] Bugarszky I (1897) Magyar Chem Folyóirat 3:38, Z anorg Chem 14:145; [ii] Nernst W (1926) Theoretische Chemie. Stuttgart*

GI

### Bunsen, Robert Wilhelm



(March 30, 1811, Göttingen, Germany – Aug. 16, 1899, Heidelberg, Germany)[1] Bunsen started his chemistry studies in Göttingen 1828, obtained his Ph.D. in 1831, and habilitation in 1833. In 1836 he became successor of Friedrich Wöhler in Kassel (Germany), was appointed as Professor and Director of the Chemical Institute of Marburg University in 1839, in 1851 he was in Breslau, Germany (now Wrocław, Poland), and from 1852 until 1889 he was Professor at Heidelberg University [i]. At the start of his scientific career he performed some research in the field of organic chemistry (with cacodyls compounds). Later his activities were most diverse and he contributed to many fields of chemistry: He is one of the founders of gas analysis, and, together with Gustav Kirchhoff, he is the founder of spectral analysis. Together with Kirchhoff he discovered the chemical elements cesium and rubidium. He invented what is now known as the 'Bunsen burner', and also the water suction pump. In electrochemistry he is remembered for two kinds of batteries (→ *Bunsen cell* [ii], and → *Bunsen's chromic acid battery* [iii] developed to produce electric sparks for spectral analysis). He was the first to point out the possibility to use electricity for lighting. Bunsen also pioneered studies in photochemistry (together with H.E. Roscoe). His collected works have been published [iv] and a very detailed memorial lecture given by Henry Roscoe is also available [v].

[1] Most sources wrongly give March 31st as his birthday [i].

*Refs.: [i] Lockemann G (1949) Robert Wilhelm Bunsen – Lebensbild eines deutschen Naturforschers. In: Frickhinger HW (ed) Große Naturforscher, vol 6. Wissenschaftliche Verlagsgesellschaft, Stuttgart; [ii] Bunsen R (1841) Annal Chem Pharm 38:311 (DOI: 10.1002/jlac.18410380306); [iii] Bunsen R (1875) Ann Phys 231:230; [iv] Ostwald W, Bodenstein M (eds) (1904) Gesammelte Abhandlungen von Robert Bunsen, 3 vols. Engelmann, Leipzig; [iii] Roscoe H (1901) Bunsen Memorial Lecture. In: Memorial lectures delivered before the Chemical Society 1893–1900. Gurney and Jackson, London, pp 513*

FS

**Bunsen cell** → *Bunsen* replaced the platinum electrode in the → *Grove cell* by a → *carbon electrode* [i]. The Bunsen battery contained a zinc electrode in sulfuric acid and a carbon electrode in nitric acid. The two electrode compartments were separated by a ceramic pot. Bunsen discovered a way to carbonize a mixture of powdered coke and hard coal by strong heating; thus foreshadowing the later used graphitizing process [ii, iii].

*Refs.: [i] Bunsen R (1841) Annal Chem Pharm 38:311 (DOI: 10.1002/jlac.18410380306); [ii] Hauck WP (1883)*

*Die Galvanischen Batterien, Accumulatoren und Thermosäulen, 2*$^{nd}$ *edn. Hartleben's Verlag, Wien; [iii] Roscoe H (1901) Bunsen memorial lecture. In: Memorial lectures delivered before the Chemical Society 1893–1900. Gurney and Jackson, London, pp 513*

FS

**Bunsen's chromic acid battery** → *Bunsen* constructed a → *chromic acid battery* with zinc anodes for the purpose of producing electric sparks for spectral analysis [i]. The electrodes (carbon and zinc) could be immersed in the electrolyte in a controlled way as to regulate the current [ii–iv].

See also → *Daniell cell*, → *zinc*, → *$Zn^{2+}$/Zn electrodes*, → *$Zn^{2+}$/Zn(Hg) electrodes*, → *zinc–air batteries (cell)*, and → *Leclanché cell*.

*Refs.: [i] Bunsen R (1875) Ann Phys 231:230; [ii] Hauck WP (1883) Die Galvanischen Batterien, Accumulatoren und Thermosäulen. 2*$^{nd}$ *edn. Hartleben's Verlag, Wien; [iii] Pfaundler L (1888–1890) Müller-Pouillet's Lehrbuch der Physik und Meteorologie, 9*$^{th}$ *edn., vol 3. Vieweg und Sohn, Braunschweig, p 381; [iv] Roscoe H (1901) Bunsen memorial lecture. In: Memorial lectures delivered before the Chemical Society 1893–1900. Gurney and Jackson, London, pp 513*

FS

**Burger's vector** is used to characterize dislocations, a very important class of extended → *defects in solids*. Dislocations are stoichiometric line imperfections, with two extreme cases: edge and screw [i]. An edge dislocation can be visualized as an extra half-plane of atoms, i.e., one plane that only passes a part of the way through a crystal lattice. The center of the distorted region where the extra half-plane terminates, is the so-called line of the dislocation. The Burger's vector is perpendicular to this line; its magnitude corresponds to the distance between the extra and regular planes. A screw dislocation transforms successive atom planes into a helix surface; the Burger's vector has the same physical meaning, but is parallel to the dislocation line. Other forms of dislocations may be constructed from segments of these two extreme forms. As for other extended defects, dislocations may affect mechanical behavior, ion intercalation and transport at low temperatures, grain-growth and texturing

in ceramic materials, electronic conduction, and other properties of → *solid materials*.

*Refs.: [i] West AR (1984) Solid state chemistry and its applications. Wiley, Chichester; [ii] Bacon DJ, Hull D (1984) Introduction to dislocations, 3*$^{rd}$ *edn. Pergamon, New York*

VK

**Butler, John Alfred Valentine**



(Courtesy of
W.V. Mayneord)

(Feb. 14, 1899, Winchcombe, Gloucestershire, England – July 16, 1977). Butler was English scientist [i] greatly contributed to chemical thermodynamics [ii] and theoretical electrochemistry, particularly to connection of electrochemical kinetics and thermodynamics [iii]. The famous → *Butler–Volmer equation* (1924) showing the exponential relation between current and potential was named after him (and → *Volmer*) [iv–vii]. It should be noted that → *Erdey-Gruz* (Volmer's student at that time) significantly contributed to this work, but his name is, unfortunately, almost forgotten now. Butler also introduced (along with → *Gurney*) the energy-level thinking into electrochemistry (1951) similarly to → *photochemistry* [viii]. His interests were later shifted to biophysics where he introduced physical and chemical approach to biological problems [ix-x].

*Refs.: [i] Mayneord WV (1979) Biographical Memoirs of Fellows of the Royal Society, 25:145; [ii] Butler JAV (1928) Chemical thermodynamics. Macmillan, London; [iii] Bockris JO'M, Reddy AKN, Gamboa-AldecoM (2000) Modern electrochemistry, fundamentals of electrodics, 2*$^{nd}$ *ed, vol 2A. Kluwer, New York, p 1048; [iv] Butler JAV (1924) Trans Faraday Soc 19:729; [v] Butler JAV (1924) Trans Faraday Soc 19:734; [vi] Erdey-*

*Gruz T, Volmer M (1930) Z phys Chem 150A:203; [vii] Delahay P (1965) Double layer and electrode kinetics. Interscience, New York, pp 154–159; [viii] Butler JAV (1951) (ed) Electrical phenomena at interfaces, in chemistry, physics and biology. Methuen, London; [ix] Butler JAV (1959) Inside the living cell. Allen & Unwin. London; [x] Butler JAV (1964) The life of the cell. Allen & Unwin, London*

EK

**Butler–Volmer equation**  The Butler–Volmer or → *Erdey-Grúz*–Volmer or Butler–Erdey-Grúz–Volmer equation is the fundamental equation of → *electrode kinetics* that describes the exponential relationship between the → *current density* and the → *electrode potential*. Based on this model the → *equilibrium electrode potential* (or the reversible electrode potential) can also be interpreted.

The seminal paper by → *Erdey-Grúz* and → *Volmer* appeared in 1930 [i] in that the "hydrogen overpotential" was elucidated by using a kinetic model for the → *electrode processes* when the → *charge transfer* step, i.e., the → *electrode reaction* is the → *rate-determining step*.

Although such terms as Butler–Volmer equation or Butler–Volmer expression or Butler–Volmer kinetics or Butler–Volmer model are widely used in the literature, see e.g., Refs. [ii–xii], its definition is ambiguous and even the name is questionable in the light of the historical facts [viii, xiii, xiv, xv].

Nevertheless, the most acceptable form of the current–electrode potential equation that may be called Butler–Volmer equation for a one-step, one-electron process (O + e⁻ ⇌ R⁻) is as follows:

$$j = k^{\ominus} F \left[ -c_O(x = 0) \exp\left( -\frac{\alpha_c F(E - E_c^{\ominus\prime})}{RT} \right) + c_R(x = 0) \exp\left( \frac{\alpha_a F(E - E_c^{\ominus\prime})}{RT} \right) \right], \quad (1)$$

where $j$ is the → *current density*, $k^{\ominus}$ is the standard rate coefficient, $F$ is the → *Faraday constant*, $c_O(x = 0)$ and $c_R(x = 0)$ are the concentrations of the oxidized and reduced forms of the species at the site of the reaction (at

the electrode surface) taking part in the electron exchange process, respectively, $\alpha_a$ and $\alpha_c$ are the anodic and cathodic → *transfer coefficients*, respectively, $R$ is the → *gas constant*, $T$ is the thermodynamic temperature, $E$ is the electrode potential, and $E_c^{\ominus\prime}$ is the → *formal potential*.

In the other version of the Butler–Volmer equation the potential term is expressed by using the → *overpotential* ($\eta$) and the → *exchange current density* ($j_o$) instead of $E$, $E_c^{\ominus\prime}$, and $k^{\ominus}$, respectively:

$$j = j_o \left[ -\frac{c_O(x = 0)}{c_O^*} \exp\left( -\frac{\alpha_c F \eta}{RT} \right) + \frac{c_R(x = 0)}{c_R^*} \exp\left( \frac{\alpha_a F \eta}{RT} \right) \right], \quad (2)$$

where $c_O^*$ and $c_R^*$ are the bulk concentration of the respective species.

The two equations are equivalent and easy to transform Eq. (1) into Eq. (2) by using the appropriate → *Nernst equation*

$$E_e = E_c^{\ominus\prime} + \frac{RT}{F} \ln \frac{c_O^*}{c_R^*}, \quad (3)$$

the definition of the overpotential

$$\eta = E - E_e \quad (4)$$

and the relationship between the exchange current density and the standard rate coefficient

$$j_o = k^{\ominus} F c_O^* \exp\left[ -\frac{\alpha_c F \left( E_e - E_c^{\ominus\prime} \right)}{RT} \right]. \quad (5)$$

If the solution is well stirred and the currents are kept so low that the concentrations at the site of the reactions (at the electrode surface) do not differ substantially from the bulk values, i.e., the difference between $c_O^*$ and $c_O(x = 0)$ and $c_R^*$ and $c_R(x = 0)$ is less than 10%, Eq. (2) becomes

$$j = j_o \left[ -\exp\left( -\frac{\alpha_c F \eta}{RT} \right) + \exp\left( \frac{\alpha_a F \eta}{RT} \right) \right]. \quad (6)$$

In many cases Eq. (6) is called the Butler–Volmer equation since it describes the case when the charge-transfer step exclusively determines the rate of the reaction (current), i.e., the rate of mass transport is very high in comparison with the rate of the charge transfer.

It usually happens when the charge transfer step is very sluggish ($k^\ominus$ and $j_o$ are very small), and large → *activation overpotential* is needed to drive the reaction in any direction. In this case, the anodic and cathodic reactions are never simultaneously significant.

This type of kinetics is called → *irreversible* or *quasireversible* in electrochemistry.

It is easy the recognize that a linear → *Tafel plot* can be obtained only in this case. This formalism can also be applied for more complex reaction mechanisms when the rate-determining step is the charge transfer reaction, e.g., when the overall process involving a change of $n$ electrons, i.e., the → *charge number* of the electrode reaction ($n$) differs from one. In this case Eq. (6) can be written as follows:

$$j = j_o \left[ -\exp\left( -\frac{\alpha_c nF\eta}{RT} \right) + \exp\left( \frac{\alpha_a nF\eta}{RT} \right) \right] \tag{7}$$

and Eqs. (1) and (2) can also be rewritten in a similar manner. A more complicated case is when the order of the reaction with respect of species $i$ ($v_i$) differs from unity, i.e., the → *partial currents* are related to a product of $\Pi_i c_i^{v_i}$. For this case it is difficult to give a general definition since not all reaction rates can be expressed in this form, e.g., the rate of multistep reaction or reactions involving adsorbed species may not be expressible [xv, xvi]. By using the → *stoichiometric number* ($v$) Eq. (6) becomes

$$j = j_o \left[ -\exp\left( -\frac{\alpha_c F\eta}{vRT} \right) + \exp\left( \frac{\alpha_a F\eta}{vRT} \right) \right] \tag{8}$$

and $j_o = (n/v)Fk^\ominus \Pi_i c_i^{v_i}$ where $v_i = \alpha_c v_{i,a} + \alpha_a v_{i,c}$.

When reactants or intermediates are adsorbed, the rate of the reaction may no longer be related to the concentration by a simple law. This situation is best understood where a reactant is nonspecifically adsorbed in the outer → *Helmholtz plane*. The effect of such adsorption on the electrode kinetics is usually termed the → *Frumkin* effect. Physical and chemical adsorption on the electrode surface is usually described by means of an → *adsorption isotherm* and kinetic equations compatible with various isotherms such as the → *Langmuir*, → *Temkin*, → *Frumkin isotherms* are known.

*Refs.: [i] Erdey-Grúz T, Volmer M (1930) Z phys Chem A150:203; [ii] Bard AJ, Faulkner LR (2001) Electrochemical methods. 2nd edn. Wiley, New York, pp 87–135; [iii] Inzelt G (2010) Kinetics of electrochemical reactions. In: Scholz F (ed) Electroanalytical methods, 2nd edn, Springer, Berlin, pp 33–53; [iv] Brett CMA, Oliveira Brett AM (1993) Electrochemistry. Oxford University Press, Oxford, pp 70–81, 104–105; [v] Bockris JO'M, Razumney GA (1967) Electrocrystallization. Plenum, New York, p 11; [vi] Bockris JO'M, Reddy AKN (1970) Modern electrochemistry. Plenum, New York; [vii] Bockris JO'M, Rand DAJ, Welch BJ (1977) Trends in electrochemistry. Plenum, New York, p 10; [viii] Bockris JO'M, Khan SUM (1993) Surface electrochemistry. Plenum, New York, pp 213–215; [ix] Christensen PA, Hamnett A (1994) Techniques and mechanism in electrochemistry. Blackie Academic & Professional, London, pp 16–18; [x] Oldham KB, Myland JC (1994) Fundamentals of electrochemical science. Academic Press, San Diego, pp 167–186; [xi] Hamann CH, Hamnett A, Vielstich W (1998) Electrochemistry. Wiley-VCH, Weinheim, pp 152–168; [xii] Rieger PH (1994) Electrochemistry. Chapman & Hall, New York, p 318; [xiii] Erdey-Grúz T (1972) Kinetics of electrode processes. Akadémiai Kiadó, Budapest, pp 22–79, 150–202; [xiv] De Levie R (2000) J Chem Educ 77:610; [xv] Parsons R (1974) Manual of symbols and terminology for physicochemical quantities and units, Appendix III. Electrochemical nomenclature. Pure Appl Chem 37:503; [xvi] Parsons R (1979) Pure Appl Chem 52:233; [xv] Inzelt G (2011) J Solid State Electrochem 15:1373–1389; [xvi] Parsons R (1974) Manual of symbols and terminology for physicochemical quantities and units, Appendix III. Electrochemical nomenclature. Pure Appl Chem 37:503; [xvii] Parsons R (1979) Pure Appl Chem 52:233*

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**Butyronitrile —
Table.** Comparison of low-temperature electrochemical solvent systems employing $NBu_4ClO_4$ electrolyte [ii]

| Solvent system | Temperature threshold for electrochemical experiments/$°C$ |
|---|---|
| butyronitrile | −105 |
| 69 wt % butyronitrile/31 wt % propionitrile | −118 |
| 50 wt % butyronitrile/50 wt % ethylbromide | −145 |
| 33 wt % butyronitrile/33 wt % ethylbromide/ 17 wt % isopentane/17 wt % methylcyclopentane | −158 |
| 50 wt % butyronitrile/50 wt % ethylchloride | −185 |

**Button cell** Type of button-shaped cell construction most frequently employed with small cells as used in watches, hearing-aid devices, and other small electronic appliances.

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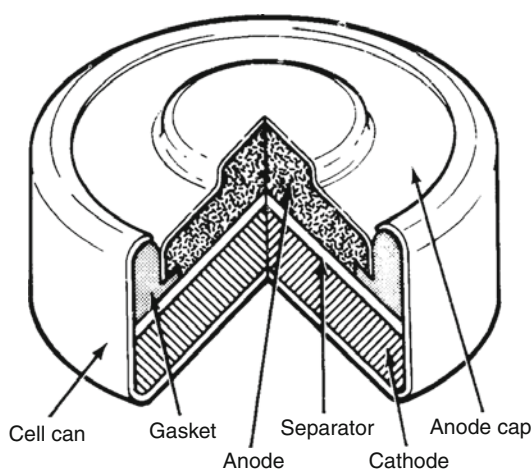


**Button cell — Figure.** Schematic design of a button cell (alkali-manganese type)

**Butyronitrile** Propyl cyanide, $(CH_3CH_2CH_2CN)$, organic solvent, melting point $-112\,°C$, boiling point $117.5\,°C$ with a density $(0.795\,g\,cm^{-3}$

at $15\,°C)$ lighter than water and somewhat soluble in water $(3\,g$ in $100\,cm^3$ water at $25\,°C)$. Butyronitrile is readily purified and dried over neutral activated alumina or molecular sieves similar to acetonitrile [i]. Due to its low melting point, butyronitrile is an excellent solvent for low temperature studies [ii]. Solvent mixtures containing butyronitrile can be employed to reach extremely low temperatures.

*Refs.: [i] Reichardt C (2003) Solvents and solvent effects in organic chemistry. Wiley-VCH, Weinheim; [ii] McDevitt, Ching S, Sullivan M, Murray RW (1989) J Am Chem Soc 111:4528*

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**Byrne cell** This was a chromic acid–zinc $\rightarrow$ *battery* where the inert electrode was made from copper with a lead coverage on which the platinum electrode was soldered. The copper and lead base was used to reduce the resistance of the, usually, thin platinum wires.

See also $\rightarrow$ *chromic acid battery*, $\rightarrow$ *Daniell cell*, $\rightarrow$ *zinc*, $\rightarrow$ *$Zn^{2+}$/Zn electrodes*, $\rightarrow$ *$Zn^{2+}$/Zn(Hg) electrodes*, $\rightarrow$ *zinc–air batteries (cell)*, and $\rightarrow$ *Leclanché cell*.

*Ref.: [i] Hauck WP (1883) Die Galvanischen Batterien, Accumulatoren und Thermosäulen, 2$^{nd}$ edn. Hartleben's Verlag, Wien*

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