Biographies and definitions contributed to the "Electrochemical dictionary" (edited by Allen J. Bard, György Inzelt, and Fritz Scholz).

PLEASE CITE THE PUBLISHED VERSION

PUBLISHER

© Springer Verlag

VERSION

AM (Accepted Manuscript)

LICENCE

REPOSITORY RECORD

Title: Biographies and definitions contributed to the "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz).

Author: Fletcher, Stephen

Keywords: Biographies, definitions, electrochemistry.

Issue Date: 2008

Publisher: © Springer

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Abstract: This document contains biographies of people who have made significant contributions to electrochemistry, including Boltzmann (Ludwig Eduard), Born (Max), Clark (Leland Charles), Coulomb (Charles Augustin de), Gauss (Carl Friedrich), Gray (Stephen), Gurney (Ronald Wilfrid), Henry (Joseph), Kelvin (William Thomson, Baron Kelvin of Largs), Mott, (Nevill Francis), Randles (John Edward Brough), Siemens (Ernst Werner von), Tesla (Nikola), Whewell, (William), Wilhelmy (Ludwig Ferdinand), and Wollaston (William Hyde). The document also contains definitions of some diverse terms used in electrochemistry and related fields, including Accumulation region, Adiabatic process, Band bending, Boltzmann constant, Boltzmann distribution, Capacitive deionization, Clausius-Mossotti equation, Contact angle, Coulomb force, Depletion region, Diffuse layer capacitance, DLVO theory, Electricity, Electroconvection, Electrocrystallization, Electrolysis Cell, Electron, Electron Transfer, Electron work function, Electroporation, Galvanic, Galvanoglyphy, Galvanize, Hydrated electron, Non-adiabatic (diabatic) process (quantum mechanics), Nucleation, Nucleation and growth, Nucleation overpotential, Open circuit potential, Permittivity (relative), Phase transition, Phospholipids, Polarizability (of a molecule), Polarization (of an electrode), Polarization density (of a dielectric medium), Pole, The Randles semicircle, Randles-Ershler impedance, Template synthesis, Thermodynamic temperature, Vesicles, Work (electrical).

Description: The Electrochemical Dictionary is intended to provide authoritative definitions of terms used in electrochemistry and related fields. The Dictionary also contains biographies of people who have made significant contributions to electrochemistry.

ISBN-10: 3540745971, **ISBN**-13: 978-3540745976.

Appears in Collections: Book Chapters (Chemistry)

	Biographies
1	Boltzmann, Ludwig Eduard
2	Born, Max
3	Clark, Leland Charles
4	Coulomb, Charles Augustin de
5	Gauss, Carl Friedrich
6	Gray, Stephen
7	Gurney, Ronald Wilfrid
8	Henry, Joseph
9	Kelvin (William Thomson, Baron Kelvin of Largs)
10	Mott, Nevill Francis
11	Randles, John
12	Siemens, Ernst Werner von
13	Tesla, Nikola
14	Whewell, William
15	Wilhelmy, Ludwig Ferdinand
16	Wollaston, William Hyde

	Definitions
17	Accumulation region
18	Adiabatic process (thermodynamics)
19	Adiabatic process (quantum mechanics)
20	Band bending
21	The Boltzmann constant
22	The Boltzmann distribution
23	Capacitive deionization
24	Clausius-Mossotti equation
25	Contact angle
26	Coulomb force
27	Depletion region
28	Diffuse layer capacitance
29	DLVO theory
30	Electricity
31	Electroconvection
32	Electrocrystallization
33	Electrolysis Cell
34	Electron
35	Electron Transfer
36	Electron work function
37	Electroporation
38	Galvanic
39	Galvanoglyphy
40	Galvanize
41	Hydrated electron
42	Non-adiabatic (diabatic) process (quantum mechanics)
43	Nucleation

Boltzmann, Ludwig Eduard

(February 20, 1844, Vienna, Austria - September 5, 1906 in Duino, Austria, 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
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Born, Max

(December 11, 1882, Breslau, Germany (now Wrocław, Poland) – January 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 PhD 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 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 → *Born equation*, → *Born-Haber cycle*, → *Born-Mayer equation*, and → *Born solvation energy*.

Refs.: [i] Born M (1920) Z Phys 1:45; [ii] Born M, Oppenheimer JR (1927) Ann Phys 84:457; [iii] M. Born, "The statistical interpretation of quantum mechanics" Nobel Lecture, 1954; [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 GmbH, München*

SF, FS
stephen.fletcher@lboro.ac.uk

Clark, Leland Charles

(Dec 04, 1918, Rochester, N.Y., USA - 25 Sept 2005, Cincinnati, OH, USA.) One of the few students ever to make a perfect score of 100 on the New York State Regents science exam, Clark earned a bachelor's degree in chemistry from Antioch College in 1941. He subsequently graduated from the University of Rochester School of Medicine and Dentistry with a Ph.D. in biochemistry and physiology in 1944. After graduation, he returned to the Antioch College campus to form a biochemistry department at the newly opened Fels Research Institute. In 1955 he moved to Cincinnati as a senior research associate of pediatrics and surgery. From 1958 to 1968 he was a professor in the department of surgery at the University of Alabama College of Medicine. In 1968, he returned to Cincinnati and served as Head of the Division of Neurophysiology at the Children's Hospital Medical Center until 1991. He is best known for the invention of the voltammetric membrane oxygen electrode to measure levels of dissolved oxygen in blood ($\rightarrow$ *Clark oxygen sensor*) [i]. Prior to that, the only way to measure oxygen in blood was to draw a sample, take it to the lab, and analyze it. Clark's electrode allowed oxygen to be monitored actually during surgery, an invention that has saved millions of lives over the past half century. Today, the oxygen electrode also provides the basis of a series of non-medical technologies, ranging from the detection of oxygen in oceans and rivers to the successful manufacture of beer and wine. After becoming a Professor of Surgery, Clark continued his research to increase the number of analytes that could be measured in the human body. In a presentation at the New York Academy of Sciences in 1962 he showed how this could be done, by immobilizing enzymes on top of his basic oxygen electrode design using a dialysis membrane [ii]. Using this approach, various substrates (such as glucose) could freely interact with the enzymes to create peroxide, and then the peroxide could be detected by the electrode. In that way, the first generation of $\rightarrow$ *biosensors* was created.
Refs.: [i] Clark LC (1959) US Patent 2,913,386 (1959), [ii] Clark LC and Lyons C (1962) Ann NY Acad Sci 102, 29.

SF
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Coulomb, Charles Augustin de

(14 June 1736, Angoulême, France – 23 Aug 1806, Paris, France) The son of Henry Coulomb and Catherine Bajet, he was raised in Angoulême and later in Paris. As a young man he received a classical education at the Collège Mazarin (one of the historic colleges of the University of Paris). Following the estrangement of his parents, he moved to Montpellier in March 1757 to live with his father. However, in October 1758, he returned to Paris to prepare for the entrance examinations for the elite Royal Military Engineering College at Mézières (L'École Royale du Génie de Mézières). He gained entry in February 1760. Its engineering course was notoriously difficult: the first year was devoted to theory, the second year to military exercises. Each student then spent two years allocated to a Regiment and two further years as an intern under a Senior Officer, working on a major project. In February 1764 he was duly posted to Martinique as a second lieutenant, but instead of the projected two-year tour of duty, he actually labored for eight years on the construction of Fort Bourbon. His health deteriorated, and he did not return to France until 1772. Thus, it was not until the age of 37 that he was able to present his first paper to the Académie des Sciences in Paris (in 1773). But it was also an extraordinary paper – it contained solutions to a range of unsolved problems in structural mechanics, mostly obtained by the calculus of variations. A few years later, in 1777, he shared with Jan Hendrik van Swinden (1746-1823) the Grand Prix of the Académie des Sciences for his work on the manufacture and properties of magnetic compass needles. Finally, in 1781, he won the Grand Prix outright for his perceptive study of friction forces, entitled "Théorie des Machines Simples". He was elected Adjoint Mécanicien of the Académie des Sciences on 14 December 1781. His scientific career then reached its pinnacle in 1785, when he reported his famous experiments on electricity and magnetism [i]. These involved the use of a high-precision torsion balance "based on the property of metal wires that have a torsion force proportional to torsion angle". Having successfully developed a means of obtaining highly precise data, he was able to confirm the laws by which both the "magnetic and the electric fluids acted", whether by repulsion or by attraction. He also realized that electrostatic charges leaked away from seemingly isolated bodies in humid air. In his two most famous experiments, he provided a direct confirmation of the inverse square law for electrical forces, proposed twenty years earlier by Joseph Priestley (13 March 1733 – 06 February 1804) [ii], and he also confirmed the inverse square law for magnetic forces, which had been suggested by John Michell (25 December 1724 – 29 April 1793) in 1750 [iii]. Coulomb remained a prominent member of the Corps du Génie until 1791, but within two years he was forced into internal exile near Blois after the Académie des Sciences

was abolished by the revolutionary National Convention on 08 August 1793. (Lavoisier, who remained in Paris, was guillotined 08 May 1794.) However, after the National Convention was replaced by the *Directoire*, Coulomb felt confident enough to return to Paris, and was elected Resident Member (1st Class) in the new "Institut de France" on 09 December 1795. He married Louise Françoise LeProust Desormeaux in 1802, and died in 1806. Today, the → *SI unit* of electrical charge, the coulomb (symbol C) is named in his honor.

Refs.: [i] Coulomb, Charles Augustin (1785) Premier Mémoire, Sécond Mémoire, Troisième Mémoire sur l'Electricité et le Magnétisme, Histoire de l'Académie Royale des Sciences, 569, 578, 612. [ii] Priestley, Joseph (1767) "The History and Present State of Electricity, with Original Experiments." Printed for J. Dodsley et al. (London). [iii] Rivoire, Antoine (1752) Traités des Aimans Artificiels [...] (Fr. translation of Michell's "A Treatise of Artificial Magnets, etc" Chez Hippolyte-Louis Guérin l'aîné, Paris. See also, Michell, John (1750) A Treatise of Artificial Magnets, etc. Printed by Joseph Bentham, and sold by W. and J. Mount et al., Cambridge (UK).

SF
stephen.fletcher@lboro.ac.uk

Gauss, Carl Friedrich

(April 30, 1777, Brunswick, Duchy of Brunswick (now Lower Saxony, Germany)–February 23, 1855, Göttingen, Hanover (now Lower Saxony, Germany).) Gauss (Gauß) was a polymath who made profound contributions to many fields, including number theory, analysis, differential geometry, geodesy, magnetism, astronomy and optics. He was the son of Gebhard Dietrich Gauss (1744–1808) and Dorothea Benze (1743–1830). As a child, Gauss attended the Katharinen-Volksschule (1784–1788) and the Gymnasium Catharineum in Braunschweig (1788–1792). His extraordinary mathematical abilities were drawn to the attention of The Duke of Brunswick (Karl Wilhelm Ferdinand, Herzog zu Braunschweig-Lüneburg), whose patronage enabled Gauss to attend the Collegium Carolinum (1792–1795) and the "Georgia Augusta" (Georg-August-Universität) in Göttingen (1795–1798). Gauss was awarded a doctorate from the Universität Helmstedt on July 16, 1799.

While still in college, Gauss proved that any regular polygon whose number of sides is a Fermat prime can (in principle!) be constructed by compass and straight edge. This extended the list of constructible regular polygons for the first time since antiquity, famously including the case n=17 (the heptadecagon). Then, in his 1799 dissertation, Gauss gave a proof of the fundamental theorem of algebra, which states that every polynomial has a root of the form $a+bi$. This was followed in 1801 with his fundamental theorem of arithmetic, which states that every natural number can be represented as the product of primes in just one way. Finally, at age 24, Gauss published one of the greatest achievements in the history of mathematics, his *Disquisitiones Arithmeticae*, in which number theory was systematized for the first time [i]. In 1801, Gauss also developed the method of least squares fitting, some years before Legendre, but unaccountably did not publish it. The method did, however, enable him to calculate the orbit of the asteroid Ceres. This was the start of a life-long pattern. Among several major discoveries that he failed to publish were the concept of non-Euclidean geometry, and the Cauchy integral theorem. Any one of those would have made an ordinary mathematician immortal. Financial insecurity after 1806 (caused by the death of his patron) caused Gauss to seek more regular employment, and in 1807 he was appointed Professor of Astronomy and Director of the astronomical observatory at Göttingen, a post he retained for the rest of his life. In 1831 Gauss began a collaboration with Wilhelm Weber (1804–1891) that involved a thorough investigation of magnetic fields. This led Gauss into a period of practical invention, including an electric telegraph in 1833, and the bifilar magnetometer in 1836. Meanwhile, in 1835, Gauss had formulated his famous law – but did not publish it. Indeed, it did not emerge into the light of day until published by James Clerk Maxwell in 1865 [ii]. In physical chemistry, Gauss's law gives the relation between the electric flux flowing through a closed surface and the electric charge enclosed by the surface. (The electric flux is equal to the charge divided by the permittivity.) Oddly, the mathematical function most closely associated with Gauss today – the Gaussian Distribution – was actually introduced by Abraham de Moivre in 1734 (in the context of approximating certain binomial distributions for large n). However, Gauss used the distribution in 1809 in his celebrated proof of the method of least squares, and the name has stuck ever since. Gauss died in Göttingen in 1855 and is buried in the Albanifriedhof cemetery there. He asked for a heptadecagon on his gravestone, but the stonemason balked! Among his many international honors were Fellowship of the Royal Society (1807), Knight of the Order of the Westphalian Crown (1810), Fellow of the American Academy of Arts and Sciences (1822), Chevalier de Légion d'Honneur (1837), and the Copley Medal (1838).

Refs.: [i] Gauss CF (1801) Disquisitiones Arithmeticae, Ger. trans.(1889) "Untersuchungen über höhere arithmetik" Springer, Berlin. Reprinted (1965) by Chelsea NY. [ii] Maxwell JC (1865) "A Dynamical Theory of the Electromagnetic Field", Phil Trans Roy Soc (Lond) 155; 459.

SF
stephen.fletcher@lboro.ac.uk

**Gray, Stephen** (_b_.1666 Canterbury, England – 15 February 1736 London, England). Stephen Gray was baptized in Canterbury, Kent, England on 26 December 1666 (St Stephen's day – hence possibly his name). Little is known about his education, though like Shakespeare he probably acquired rudimentary Latin at school. He first came to the attention of the Royal Society in 1696, when he published the design of a novel magnifying lens. This greatly interested the Astronomer Royal, John Flamsteed, and the two soon became firm friends. For a decade afterwards Gray applied his energies to the quantitative observations of astronomical phenomena such as sunspots and solar eclipses, but after 1706 his astronomical work petered out as he became increasingly troubled by an arthritic hip. He then found it difficult to earn a living, a problem exacerbated by his natural shyness [i]. Fortunately, he was rescued by the good offices of Flamsteed and Sir Hans Sloane (later President of the Royal Society), who arranged for him to be admitted as a Poor Brother into the Charterhouse (a well-endowed almshouse for "gentlemen by descent and in poverty") in Clerkenwell, London, in 1718. It was at this point that Gray began his epochal experiments on electricity, sometimes carried out at friend's houses. In 1732 (at the age of sixty five!) Gray announced the discovery of electrical conduction in the following words [ii];

 "Sir, in the Year 1729 I communicated to Dr. Desaguliers [iii], and some other Gentlemen, a Discovery I had then made, showing that the Electric Virtue of a Glass Tube may be conveyed to other Bodies so as to give them the same Property of attracting and repelling Light Bodies as the Tube does, when excited by rubbing; and that this attractive Virtue might be carried to Bodies that were many Feet distant from the Tube…" [iv]

No other method of electrification (other than by friction) had previously been known. After Hans Sloane had taken over the Presidency of the Royal Society in 1727, Gray belatedly began to receive the recognition that his electrical researches deserved. He was awarded the Royal Society's first Copley Medal in 1731 for his discovery of conduction, and the second in 1732 for his work on electrostatic induction. Despite his high voltage experiments, and a fondness for tobacco, he survived until 1736. He has no monument in stone, but was memorialized in verse by "Dictionary Johnson" (Samuel Johnson 1709-1784) [v]. He received the Copley Medal twice (in 1731 and 1732) and became FRS in 1733.

Refs.: [i] An observation of Brook Taylor (originator of Taylor's theorem) in a letter to John Keill, 03 July 1713. [ii] "Two letters from Gray to Mortimer, containing a farther account of his experiments concerning electricity", Philosophical Transactions No 37 (1731-32). [iii] Jean Théophile (John Theophilus) Désaguliers (12 March 1683 - 29 February 1744) was a brilliant instrument designer, the French-born son of a Huguenot who fled to England some time after the revocation of the Edict of Nantes in 1685. [iv] "Attractive virtue" may be interpreted as "electrostatic potential". Note that I have modernized the spelling, but not the punctuation! [v] "On the Death of Stephen Grey (sic), FRS" in "Miscellanies in Prose and Verse", ostensibly by Mrs. Anna Williams, but actually by Samuel Johnson, as described in Boswell's "Life of Johnson", ed Hill GB and Powell LF, Oxford, Clarendon Press, 1934.

SF

stephen.fletcher@lboro.ac.uk

Gurney, Ronald Wilfrid

Photo © Cambridge University (with permission)

(01 July 1898, Cheltenham, Gloucestershire, England–15 April 1953, New York, USA). The son of Walter Gerald Gurney, a wealthy lawyer, and Emily C. Gurney, he entered Cheltenham College in Sept 1911 and left in April 1917. He was commissioned "ensign" (2nd Lieutenant) in the 4th (City of Bristol) Battalion, The Gloucester Regiment on 3rd February 1919, but by October 1919 he had entered Trinity Hall, Cambridge, where he graduated BA in June 1922. This was followed by doctoral studies under Ernest Rutherford at the Cavendish Labs, which led to MA and PhD degrees in June 1926. Thereafter, he accepted a Visiting Fellowship at Princeton University (1926-27) that was extended into 1928 thanks to the award of a Charlotte Elizabeth Proctor Fellowship. It was during 1928 that he met Edward Uhler Condon (1902-1974). Famously, the pair published the first paper on the application of the "new" quantum mechanics to radioactive decay [i]. As recounted by Condon [ii], it was Gurney who had the key idea that the emission of alpha particles from radioactive elements could take place by "barrier penetration" (today known as → *tunneling*). Within a year, Gurney had also explained how the rate of barrier penetration could be massively enhanced if the penetrating particle had the same energy on both sides of the barrier (resonance tunneling) [iii]. This was three years before the Cockcroft-Walton experiments established that resonance tunneling could cause the artificial transmutation of chemical elements [iv]. After these early successes, it was only a matter of time before Gurney would apply his concept of resonance tunneling to electron transfer, and this duly took place back at the Cavendish Labs in 1931. Based on some experimental data of the Australian scientist Frank Philip Bowden (1903-1968), Gurney wrote the most important electrochemistry paper since → *Tafel* [v]. In the paper [vi] Gurney assembled many of the key ideas of modern electron transfer theory. In particular, he noted that electrons in electrodes occupy a distribution of states according to Fermi-Dirac statistics; he noted that ions in solution occupy a distribution of states due to their differing degrees of solvation; and he noted that electron transfer must take place preferentially between states having the same energy. He further noted that the effect of the electrode potential was to decrease the → *electron work function* of the metal; he noted that the elementary act of electron transfer must take place so quickly that nuclei are effectively stationary ("as in the Franck-Condon principle"); and he pointed out that an essential condition for large

current flow was that there must be a large overlap between the ionic and metallic orbitals. Finally, he showed that the mathematical formulation of electron transfer theory necessarily involves summations over joint distributions of ionic and electronic states. The only major feature that he didn't explain was how the conservation of energy and the Franck-Condon principle could be satisfied simultaneously. That particular conundrum was finally solved by → *Randles* in 1952 [vii]. In a final flourish to his career [viii], Gurney pointed out that the chemical potentials of non-electrolytes in various solvents should be based on their concentrations expressed as mole fractions x_k (amount fractions) rather than molalities. (The advantage of doing this is that the unit of mole fraction corresponds to 100% purity of one component, which eliminates complications from the entropy of mixing. This has proved to be very important in the study of hydrophobicity.) Gurney married Natalie Kouteinikoff on 31st August 1934, moved to the United States in 1941, and died in New York City in 1953.

[i] Gurney RW, Condon EU (1928) Nature (Lond) 122; 439. [ii] Condon EU (1969) , reprinted (1978) Am J Phys 46; 319. [iii] Gurney RW (1929) Nature (Lond) 123; 565. [iv] Cockcroft JD, Walton ETS (1932) Nature (Lond) 129; 649. [v] Tafel J (1905) Z Phys Chem 50; 641. [vi] Gurney RW (1931) Proc Roy Soc (Lond) 134; 137. [vii] Randles JEB (1952) Trans Faraday Soc 48; 828. [viii] Gurney RW, Ionic processes in solution, McGraw-Hill (NY) 1953.

SF
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Henry, Joseph

(17 December 1797, Albany, New York, USA–13 May 1878 Washington, DC, USA). Son of William Henry (1764-1811) and Ann Alexander (1760-1835) who were both immigrants to the USA from Scotland. The untimely death of his father compelled him to become apprenticed to a local watchmaker at the age of fourteen. However, between 1819 and 1822 he was able to obtain a formal education at the recently-opened Albany Academy. He was appointed Professor of Mathematics and Natural Philosophy there in 1826. In 1832 he became Professor of Natural Philosophy in the College of New Jersey (now Princeton University), where he remained until 1846. In that year the United States government received the then-astonishing sum of half a

million dollars as a bequest from the English chemist James Smithson, which they used to found the Smithsonian Institution. On 03 December 1846 Henry became its first Secretary (Director). At the height of his career he was a technical adviser to Abraham Lincoln. However, most of Henry's discoveries took place during the Albany years. In 1831, he constructed a functioning electric telegraph, though he did not patent it. Also around 1831, he improved the electromagnet design of William Sturgeon (1783-1850), which he did by insulating the windings. By 1832 he had built an electromagnet so powerful that it could lift "between six hundred and seven hundred pounds"[i]. While carrying out these experiments, Henry observed that a spark was generated when breaking a circuit containing a long wire, but not when breaking a circuit containing a short wire. He soon realized that the spark was caused by the primary current in the long wire acting upon itself. This was the first experimental observation of self-inductance [i]. Although this secured his place in history, he was careful not to extend his claim to the induction of secondary currents. "The secondary currents, as it is well known, were discovered in the induction of magnetism and electricity, by Dr Faraday, in 1831"[ii]. Thus, Henry was the discoverer of self inductance, while → *Faraday* was the discoverer of mutual inductance. Throughout his life, Henry promoted high ethical standards in scientific research. Indeed, he once remarked that, "I think that immorality and great mental power are incompatible with one another, and that more error is introduced from defect in moral sense than from want of intellectual capacity." Henry married Harriet Alexander on 03 May 1830, and died in Washington DC on 13 May 1878. He was given a state funeral. Today, the → *SI unit* of inductance the henry (symbol H) is named in his honor.

*Refs.: [i] Henry J (1832) On the Production of Currents and Sparks of Electricity from Magnetism. The American Journal of Science and Arts 22; 403; [ii] Henry J (1839) Contributions to Electricity and Magnetism, No. 3. On Electro-Dynamic Induction. Transactions of the American Philosophical Society (NS) 6; 303.*

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Kelvin (William Thomson, Baron Kelvin of Largs)
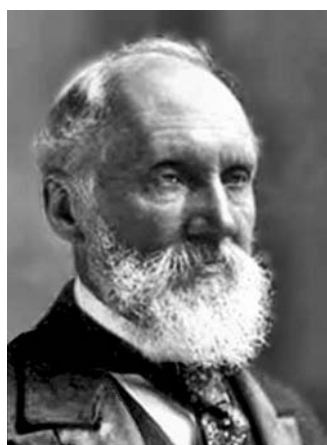
(26 June 1824, Belfast, County Antrim, Ireland (now Northern Ireland) – 17 December 1907, Largs, Ayrshire, Scotland.) The fourth child of James Thomson (1786-1849), Professor of Mathematics at the Belfast Academical Institution, and Margaret Gardner (1790-1830). Surprisingly, William was able to register at Glasgow University at the age of ten! On the 6th April 1841, the sixteen-year old William Thomson went up to the ancient college of Peterhouse, Cambridge. There he soon revealed his exceptional physical and mental powers. On leaving Cambridge in 1845 he spent some time at → *Faraday*'s laboratory at the Royal Institution in London and at Regnault's laboratory at the Collège de France in Paris. During these visits Thomson developed an interest in the theory of dielectrics, and at the age of 21 astonished the world of physics by describing his "method of images" [i], which allowed the precise determination of the electric field surrounding a point charge, even when it is perturbed by a nearby spherical or planar conductor. Shortly thereafter he announced the discovery of a mathematical technique for transforming a harmonic function inside the unit sphere into a harmonic function outside the unit sphere [ii], now generally known as the "Kelvin Transformation". These papers established his reputation. The following year (1846) he was appointed to the Chair of Natural Philosophy at the University of Glasgow. In 1848, in another *tour de force*, he proposed a thermodynamic scale of temperature [iii]. This implied the existence of an absolute zero of temperature. By February 1851 he had arrived at the second law of thermodynamics [iv], although he cannot claim sole credit for this, since the idea was "in the air". (Other versions of the second law emerged contemporaneously from the fertile minds of Clausius, → *Helmholtz*, → *Joule*, Liebig and Rankine.) In 1852 he discovered the "Joule-Thomson Effect" in collaboration with James Prescott Joule[v]. This led, ultimately, to the development of industrial-scale refrigeration. In 1855-56 he derived, and solved, the "Telegraph Equation" [vi, vii] and pointed out the "law of squares" which states that the delay in a → *transmission line* is proportional to the square of its length. This was crucially important in the design of telegraph cables. In December 1856, Thomson was invited to join the board of directors of the Atlantic Telegraph Company. Based on his theoretical insights, he eventually developed a complete electrical system for operating a submarine telegraph. This included a mirror galvanometer (1858) and a siphon recorder (1867), the latter anticipating the modern ink-jet printer. Later, he invented a balance for the precise specification of the → *Ampère*, and he investigated many aspects of hydrodynamic flow, including wave-motion and vortex-motion [viii]. Indeed, he continued to innovate mathematically

until his death in 1907. Thomson received many awards during his lifetime, including Fellowship of the Royal Society (1851), a Knighthood (1866), the Copley Medal (1883), the Prussian Orden Pour le Mérite (1884), the Barony of Largs (1892), and the Order of Merit (1902). The → *SI unit* of temperature, the kelvin (symbol K), is named in his honor.

Refs.: [i] Thomson W (1845) J Math Pure Appl 10; 364; [ii] Thomson W (1847) J Math Pure Appl.12; 256; [iii] Thomson W (1848) Math and Phys Papers, vol.1, pp100-106; [iv] Thomson W (1851) Math and Phys Papers, vol.1, p175. Ibid p.179. Ibid p.183; [v] Joule JP and Thomson W (1856) Proc Roy Soc (Lond) 78; [vi] Thomson W (1855) Proc Royal Soc (Lond) 61; [vii] Thomson W (1856) Proc Roy Soc (Lond) 299 and 303; [viii] Thomson W (1856) Math. and Phys. Papers vol.1, pp333-455.

SF
stephen.fletcher@lboro.ac.uk

Mott, Nevill Francis
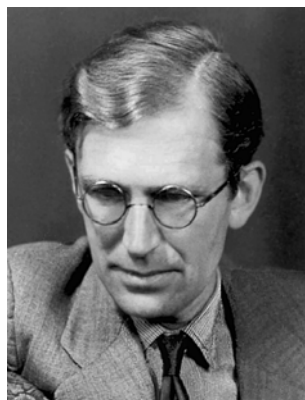
(30 September 1905, Leeds, England – 08 August 1996, Milton Keynes, England.) Nevill Francis Mott was the first child of Charles Francis Mott and Lilian Mary Reynolds, both of whom worked at the Cavendish Laboratory under J. J. Thomson (1856-1940), the discoverer of the → e*lectron*. He was educated at home until the age of ten, when he was finally sent to Baswich House (a preparatory school in Stafford) and then Clifton College in Bristol. In 1923 he won a scholarship to St. John's College, Cambridge, from where he graduated BA in 1927. After spending part of 1928 in Copenhagen with Niels Bohr (1885-1962), he was appointed lecturer at Manchester University in 1929. In 1930, Mott returned to Cambridge, received a master's degree, and became a lecturer at the college of Gonville and Caius (pronounced *kees*). In 1933 he moved to Bristol University as Melville Wills Professor in Theoretical Physics. After a period of military research in London during WWII, he became Director of the Henry Herbert Wills Physical Laboratory at Bristol. In 1954 he was appointed Cavendish Professor of Physics at Cambridge, a post he

held until 1971. During the period 1929-33 he applied the "new" quantum mechanics to electron scattering. In particular, he was interested in the case where a high energy electron is passing by an atom, and is deflected by its electric field. During such a process the electron is often decelerated, causing it to emit a type of radiation called "bremsstrahlung". When quantum effects dominate over classical coulombic effects, this interaction is now referred to as "Mott Scattering". After his move to Bristol, Mott decided to investigate the behavior of electrons in solids. Before WWII, solid-state science was regarded as a risky area for theoreticians, with too many free parameters to yield elegant results, and of course no-one could foresee how important the subject would become towards the end of the century. Mott, nevertheless, embraced solid-state science after his move to Bristol. Over a decade, he gradually built up a store of knowledge, and eventually collaborated with → *Gurney* to create the classic solid-state textbook "Electronic Processes in Ionic Crystals"[i]. Together, they also formulated a theory explaining the effect of light on photographic emulsions (the theory of the latent image). After these early successes, Mott's interest in the behavior of electrons in solids never wavered. By the mid-1940s he had turned his attention to doped magnetic oxides, which were puzzling everyone because they should have been conducting, but weren't. These materials are now known as "Mott Insulators", in recognition of his remarkable discovery that, for partially filled bands, electron-electron correlations tend to localize the electrons and thus drive the whole system into an insulating state [ii]. Finally, in the mid-1960s, Mott switched his attention to non-crystalline, or amorphous, semiconductors, a research shift that brought him the Nobel Prize in 1977, shared with Philip Warren Anderson (b.1923) and John Hasbrouck van Vleck (1899-1980). Once again Mott focused on the interaction between the motions of electrons and the motions of atomic nuclei, but this time at low energies where localized electronic states are formed. In particular, Mott and his contemporaries realized that in any non-crystalline material the states at the bottom of the conduction band were localized (that is to say, they were actually electron traps) and that there was a distribution of such traps as a function of energy, up to a certain "mobility edge" [iii]. Most importantly, the existence of a mobility edge implied two different mechanisms of conduction, which were soon found by experimentalists. At high temperature, the electrons had enough energy to become delocalized above the mobility edge, and thus conducted normally, whereas at low temperature the electrons remained localized below the mobility edge, and could move only by "hopping" (tunneling) between the localized states. This overall picture, which Mott helped to develop, is widely applied today in such diverse areas as computer memory, photocopying machines, and the theory of → *conducting polymers*. Mott's ideas on non-crystalline materials are beautifully summarized in his book with Edward Arthur Davis (b.1936) published in 1979 [iv]. Mott married Ruth Eleanor Horder in 1930, and had two daughters. He died in 1996. Among many honors received during his lifetime were Fellowship of the Royal Society (1936), a Knighthood (1962), the Copley Medal (1972), and the Nobel Prize for Physics (1977). He was also made Chevalier de l'Ordre National du Mérite (1977) and Companion of Honour (1995).

Refs.: [i] Mott NF and Gurney RW (1948) Electronic Processes in Ionic Crystals, Clarendon Press, Oxford. [ii] Mott NF (1949) Proc Phys Soc (Lond) A62; 416. [iii] Mott NF (reprinted 1992) Electrons in Glass, Nobel Lectures, Physics 1971-1980 Editor Stig Lundqvist, World Scientific Publishing Co., Singapore. [iv] Mott NF and

Davis EA (1979) Electronic Processes in Non-Crystalline Materials, Clarendon Press, Oxford.

SF

stephen.fletcher@lboro.ac.uk

Randles, John

John Edward Brough Randles (*b*. 26th August 1912, England, *d*. February 13, 1998, England) was one of the founders of dynamic electrochemistry. He was educated at Derby School and Cambridge University. During the second world war, Randles was a conscientious objector, and was allocated to a research establishment. In 1945 he was appointed Lecturer at Birmingham University (U.K.), and remained there for the rest of his scientific career. Archie Hickling had invented the → *potentiostat* in 1942, but it was an essentially static device. John Randles built a dynamic version which he reported in 1947 *[i]*. This was a cathode ray polarograph that had a synchronizing circuit to give exact control of the time lag between the fall of a mercury drop and the start of a linear voltage sweep. Within a year, Randles in England *[ii]* and Augustin → *Ševčík* in Czechoslovakia *[iii]* had independently developed linear sweep voltammetry and derived an expression for the current-voltage response of a diffusion controlled electrode reaction. Today, this landmark result is known as the → *Randles-Ševčík equation*. Many modern techniques of electrochemistry are descended from this work, including → *cyclic voltammetry*, → *anodic stripping voltammetry*, and various types of → *hydrodynamic voltammetry*. At the Faraday Discussion of 1947 Randles described the impedance of a circuit containing both diffusion and interfacial electron transfer, and showed that the mathematical couplings between diffusion, electron transfer, and solution resistance could be represented by an equivalent circuit of linear components *[iv]*. This opened the way to the study of fast electrode reactions, and laid the groundwork for the future field of → *a.c. impedance*. At the same meeting, a communication from Boris Ershler *[v]* revealed that parallel developments were in progress in the Soviet Union. Today, the "Randles-Ershler equivalent circuit" (→ *Randles-Ershler impedance*) remains one of the most widely used models of electrochemical impedance, typically including a double layer

capacitor and a charge transfer resistance in parallel, and a solution resistance in series. In 1952, Randles realized that thermal fluctuations were required in the atomic coordinates of reactant species and their solvation shells, before $\rightarrow$ *electron transfer* could take place *[vi]*. This epochal idea was illustrated with a plot of potential energy versus reaction coordinate, and remains today as the cornerstone of modern electron transfer theory. Besides his theoretical insights, Randles was a first-class experimentalist. His measurement of the $\rightarrow$ *Volta potential* difference between mercury and aqueous solution remains a classic *[vii]*. This experiment generated estimates of the absolute hydration enthalpy of the proton, $\Delta H_{aq}°[H^+]$, which averaged about -1131 kJ/mol. Modern estimates (Tissandier et al., *[viii]*) place the true value at -1150 ± 10 kJ/mol, remarkably close to Randles' value.

Refs.: [i] Randles JEB (1947) Analyst 72:301; [ii] Randles JEB (1948) Trans Faraday Soc 44:327; [iii] Ševčík A (1948) Coll Czech Chem Comm 13:349; [iv] Randles JEB (1947) Discuss Faraday Soc 1:11; [v] Ershler BV (1947) Discuss Faraday Soc 1:269; [vi] Randles JEB (1952) Trans Faraday Soc 48:828; [vii] Randles JEB (1956) Trans Faraday Soc 52:1573; [viii] Tissandier MD, Cowen KA, Feng WY, Gundlach E, Cohen MJ, Earhart AD, Coe JV (1998) J Phys Chem A 102:7787

SF
stephen.fletcher@lboro.ac.uk

Siemens, Ernst Werner von

(13 December 1816 Poggenhagen, Hannover – 06 December 1892 Charlottenburg, Berlin, Germany.) The son of Christian Ferdinand Siemens (1787-1840), an estate manager, and Eleonore Henriette Deichmann (1792-1839). When he was eight years old his family moved to Menzendorf, a small municipality in Western Pomerania. After 1829 he was educated at home by a tutor. From 1832 to 1834 he attended the Katharinen Gymnasium in Lübeck, but left without completing his examinations. Unable to afford a University education, he joined the Prussian Army's Engineering Corps as a cadet. This gave him access to the Artillery school in Magdeburg, where he began studies at the end of 1834. By autumn 1835 he had transferred to the

prestigious Royal Artillery and Engineering School in Berlin, where he remained until 1838. In that year he was commissioned second lieutenant in the Prussian Army.

Following a short prison sentence (for acting as a second in a duel) he produced his first invention, a silver plating process, in 1842. A few years later, in collaboration with another engineer called Johann Georg Halske (1814-1890), he developed a "needle-pointer" telegraph (1847). Based on this invention, the pair founded the company Telegraphen Bau-Anstalt von Siemens & Halske on 01 October 1847. This company was an instant success. By 1848 they had built a 500km underground telegraph line between Berlin and Frankfurt am Main. Shortly thereafter the Company expanded to London, Paris, St. Petersburg, and Vienna. Though he now found himself the head of a multinational enterprise, Siemens continued to carry out fundamental research. In January 1850 he published a paper in which he discussed methods of locating faults in underground wires. In 1855 he was granted a patent on a method of transmitting telegraph messages in opposite directions at the same time. (This doubled the value of his telegraph lines overnight!) Having often complained about the lack of a reproducible standard of electrical resistance, he then solved the problem himself by using a column of pure mercury one metre high and one square millimetre in cross-section, at a temperature of 0°C. In 1875-77 he developed the selenium photometer, whose response depended on changes in electrical conductance as a function of light intensity.

Meanwhile, the company of Siemens & Halske prospered. In 1866 they manufactured a dynamo that could be set in motion by the residual magnetism of its electromagnet, thus removing the need for a separate exciting current. This new generation of dynamos made "Siemens" a household name. Among his further engineering successes were the completion of an 11,000km telegraph line between London and Calcutta (now Kolkata, West Bengal) in 1870, the patenting of a moving-coil transducer (1877), which later formed the basis of the loudspeaker, the demonstration of the first electrically-driven railway (1879), and the illumination of a boulevard in Berlin using arc lamps (1882). He also coined the word "Elektrotechnik" in German, meaning "electrical engineering".

Siemens received many honors during his lifetime, including an honorary doctorate from the University of Berlin (1860), membership of the Royal Prussian Academy of Sciences (1873), and election to the Prussian Orden Pour le Mérite (1886). In 1888 he was raised to the nobility by Kaiser Friedrich III (1831-88). He married his cousin Mathilde Drumann (1824-1865) in 1852; after her untimely death he married another cousin, Antonie Sophie Siemens (1840-1900) in 1869. He died from pneumonia on 06 December 1892. Today, the → *SI unit* of electrical conductance, the siemens (symbol S) is named in his honor.

Refs.: Scientific & Technical Papers of Werner von Siemens. Vol. 1: Scientific Papers and Addresses, London, 1892; Vol. 2: Technical Papers, London, 1895.

SF
stephen.fletcher@lboro.ac.uk

Tesla, Nikola

(10 July 1856, Smiljan, near Gospić, Lika, Austria-Hungary (now Croatia) – 07 January 1943, New York City, New York, USA.) Fourth child of Rev. Milutin Tesla, a priest of the Serbian Orthodox Church, and Đuka Mandić. Primary education at the Gospić normal school (1862-66), the Gymnasium in Gospić (1866-70), and finally the Gimnazija Karlovac (1870-73). Studied physics and maths at the Joanneum (Technische Hochschule) Graz (1875-77) but left without taking a degree. He also, briefly, attended the Karl-Ferdinand University in Prague (then Bohemia, now Czech Republic) as an external student (1880). After terminating his formal studies he had a severe nervous breakdown. His scientific career was rescued by a family friend, Ferenc Puskás (1848–1884) whose older brother Tivadar Puskás (1844-93) was Thomas Alva Edison's European agent. Under their mentorship, Tesla became established as an electrical engineer, first in Budapest, then Paris, and finally New York (1884), where he worked briefly for Edison. After some initial struggles he formed his own company, Tesla Electric Co., in 1887. While in New York he met the famous industrialist George Westinghouse (06 October 1846-12 March 1914) who was in the throes of forming the Westinghouse Electric Company to distribute electric power (1886). For long-distance power transmission, it was becoming clear that high voltage and alternating current would probably be most efficient. However, such a system would not be safe without a transformer to decrease the voltage to an acceptable level at the receiving end of the line. Lucien Gaulard and John Dixon Gibbs had demonstrated a successful transformer in 1883 in London. Westinghouse therefore licensed the Gaulard-Gibbs transformers and, after some modifications, funded a successful demonstration of electrical lighting in Great Barrington, Massachusetts in 1886. But as far as industry was concerned, a key component was still missing – a motor that would run efficiently on the ac power supply. Tesla provided the solution. In June 1888, George Westinghouse bought all of Tesla's patents related to induction motors [i,ii,iii]. Tesla's induction motor was based on the principle that a magnetic field would rotate if two coils at right angles were supplied with AC currents that were 90 degrees out-of-phase. In one of those curious coincidences that abound in the history of science, the same principle had occurred to Galileo Ferraris (03 Oct 1847- 07 Feb 1897) who disclosed the idea to the Turin Academy of Science on 18 March 1888 [ii]. However, he does not appear to have

patented it. The resulting coupling of AC transmission with high efficiency electric motors would, within a few decades, revolutionize industrial production, and bring an end to the age of steam. With the profits from the Westinghouse deal, Tesla was able to expand his own electrical researches, and a remarkable period of activity followed. He patented the idea of the "Tesla coil" in March 1891 [v], and the first practical RF power supply in June 1891 [vi]. In that *annus mirabilis*, he also became an American Citizen. He then set about applying these devices to the solution of many technical problems, such as spark generation, power transmission, and even radio-controlled automata(!). Eventually, more than 100 patents would be granted in the US alone. A noteworthy excursion into chemistry occurred in 1896, when he patented an ozone generator [vii]. In 1900, he patented yet more circuits (in addition to the tesla coil) that helped make radio transmission a practical proposition [viii,ix]. Eventually, he also created man-made lightning flashes more than 10 meters long. But here the scientific part of the story ends. Sadly, his mental health deteriorated after 1900 and he became obsessed with the notion that the Earth could act as a giant conductor. His financial backers gradually withdrew, and by 1917 Tesla had fallen into bankruptcy. After a long mental decline he died alone in a New York City hotel room on 07 January 1943. He never married. In his honor, the SI unit of magnetic flux density is today called the *tesla* (symbol T).

[i] US Patent 381968, Electro-Magnetic Motor, 01 May1888. [ii] US Patent 381969, Electro-Magnetic Motor, 01 May1888. [iii] US Patent 382279, Electro-Magnetic Motor, 01 May1888. [iv] G. Ferraris, Rotazioni elettrodinamiche prodotte per mezzo di correnti alternate, Atti dell'Accademia delle Scienze di Torino 23; 360 (1887-88). [v] US Patent 447921, Alternating Electric Current Generator, 10 March 1891. [vi] US Patent 454622, System of Electric Lighting, 23 June 1891.[vii] US Patent 568177, Apparatus for Producing Ozone, 22 September 1896. [viii] US Patent 645576, System of Transmission of Electrical Energy, 20 March 1900. [ix] US Patent 649621, Apparatus for Transmission of Electrical Energy, 15 May 1900.

SF

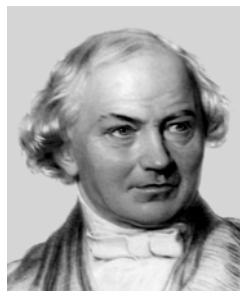**stephen.fletcher@lboro.ac.uk**

Whewell, William

Photo © Lancaster City Museums (with permission)

(May 24, 1794, Lancaster, England, – March 6, 1866, Cambridge, England.) English polymath, neologist, and philosopher of science. Educated at Heversham Grammar School (Westmoreland) and Trinity College (Cambridge). Ordained 1825. Professor of Mineralogy at Cambridge University 1828-32; Knightbridge Professor of Moral Philosophy at Cambridge University 1838-1855; Master of Trinity College 1841-66. Whewell (pronounced "yule") had a strong intellectual influence on several giants of nineteenth century science, including → *Faraday*, Darwin, Lyell and Airy. Faraday, in particular, often turned to Whewell for philosophical and terminological assistance. Among the electrochemical terms suggested to Faraday by Whewell were → *anode[i]*, → *cathode[i]*, and → *ion[ii]*. Other useful words included Eocene, Miocene and Pliocene for Lyell; diamagnetic and paramagnetic for Faraday, biometry for Lubbock, and astigmatic for Airy. Remarkably, he also invented the words scientist, physicist, and radiative, and, in the philosophy of science, introduced the terms consilience, Catastrophist, and Uniformitarian. Throughout his life he championed the concept that correct nomenclature was vital to the progress of science.
Refs.: [i] Lett. to M. Faraday, 25 April 1834, in Todhunter, I. (1876) William Whewell, D.D., Master of Trinity College, Cambridge. An Account of His Writings with Selections from His Literary and Scientific Correspondence. 2 vols. London. [ii] Lett. to M. Faraday, 5 May 1834, ibid.

<div align="right">

SF
stephen.fletcher@lboro.ac.uk

</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Wilhelmy, Ludwig Ferdinand
(December 25, 1812, Stargard, Prussia (now Poland) – February 18, 1864, Berlin Germany) Wilhelmy studied pharmacy in Berlin, and opened an apothecary in Stargard. However, he sold the apothecary in 1843 in order to study physics and chemistry in Berlin, Gießen, and Heidelberg. In 1846 he received his Ph.D. for a thesis entitled "Die Wärme als Maas der Cohäsion" ("Heat as a measure of cohesion"). Thereafter he traveled to Italy and Paris for further studies, and finally habilitated in Heidelberg in 1849 [i] with a thesis entitled "Versuch einer mathematisch-physikalischen Wärme-Theorie" ("Towards a mathematical-physical theory of heat") [ii]. In 1852 he published a book on the physical basis of physiology and psychology [iii]. He was a Privatdozent in Heidelberg from 1849 to 1854. Thereafter he lived privately in Berlin. He was the first person to formulate chemical rate laws as differential equations. The first reaction studied this way was the inversion of sucrose by acid [iv, v]. In 1863 he published his famous paper on the Wilhelmy plate method for measuring the → *interfacial tension* [vi, vii] of liquids.

Refs.: [i] Deutsche Biographische Enzyklopädie (DBE) (1999) Killy W, Viehaus R (eds), vol 10, p 507, KG Saur, München; [ii] Wilhelmy L (1851) Versuch einer mathematisch-physikalischen Wärme-Theorie , Akademische Anstalt für Literatur und Kunst (Karl Groos), Heidelberg; [iii] Wilhelmy L (1852) Zur physikalischen Begründung der Physiologie und Psychologie. Akademische Anstalt für Literatur und Kunst (Karl Groos), Heidelberg; [iv] Wilhelmy L (1850) Ann Phys 81:413, 499; [v]

Wilhelmy L, (1891) Über das Gesetz, nach welchem die Einwirkung der Säuren auf den Rohrzucker stattfindet. In: Ostwalds Klassiker der exakten Wissenschaften No 29. W Engelmann, Leipzig; [vi] Wilhelmy L (1863) Ann Phys 119:177; [vii] Wilhelmy L (1864) Ann Phys 122:1

SF, FS

stephen.fletcher@lboro.ac.uk

Wollaston, William Hyde

(August 6, 1766, East Dereham (Norfolk, England) – December 22, 1828, London, England.) Educated at Charterhouse, 1774-1778 and Gonville and Caius College (pronounced "Kees" College), Cambridge, 1782-1787. MD, 1793; Fellow of the Royal Society 1793. English physician who made important contributions to electrochemistry, metallurgy, mineralogy and optics (despite transient partial blindness in both eyes from 1800 onwards). In 1801 he showed that electricity from a Voltaic pile arose from the metal/solution interface not the metal/metal interface, thus presaging modern electrochemistry. He also explained the differences between the new galvanic electricity and the old frictional electricity. In particular, he showed that the pile of → Volta delivered less tension (later called → voltage) and more quantity (later called → current) than frictional devices [i]. In the same year he perfected a powder method of preparing platinum in malleable form, and thus established the platinum metals industry [ii]. Shortly thereafter, he reported the discovery of the elements Rhodium [iii] and Palladium [iv]. In 1813 he invented a robust method of producing extremely fine (1 micrometer diameter) platinum wire, today known as "Wollaston wire" [v]. His final contribution to electrochemistry was to explain the behavior of → *Ampère'*s magnetically interacting wires "upon the supposition of an electromagnetic current passing round the axis of [each]" [vi]. In addition to his electrochemical achievements, Wollaston developed the refractometer (1802), discovered the dark lines in the solar spectrum (1802), invented the reflecting goniometer (1809), discovered the first amino acid (cystine) to be found in the human body (1810), proposed the concept of equivalent weight (1813), and invented the "Wollaston Doublet" lens for microscopy, with which "Dr Wollaston saw the finest striae and serratures... upon the scales of a gnat's wing" [vii].

[i] Wollaston WH (1801), Phil Trans Roy Soc Lond 91, 427. [ii] Wollaston WH (1801), Cambridge University Library, Private Notebook G, p23. [iii] Wollaston WH (1804), Phil Trans Roy Soc Lond 94, 419. [iv] ibid 95, 316. [v] ibid 103, 114. [vi] Heilbron JL (1981) "The Electrical Field before Faraday", in Conceptions of Ether: Studies in the History of Ether Theories 1740-1900. Cantor GN, Hodge MJS (eds) Cambridge University Press. [vii] Brewster D (1831). A Treatise On Optics. Longman, Rees, Orme, Brown and Green; and John Taylor, London. p342.

<div align="right">SF, FS

stephen.fletcher@lboro.ac.uk</div>

Citation: S. Fletcher and F. Scholz, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Accumulation region An accumulation region is any part of a → *semiconductor* device that has an increased concentration of majority carriers due to the presence of an electric field, so that it becomes nearly metallic in its conductivity. The electric field may arise from an externally applied bias, the presence of a nearby interface composed of a differently doped semiconductor material (as in a p-n junction), or the presence of a nearby interface composed of a metal (as in a → *Schottky barrier*). Because an accumulation region contains majority carriers (which are mobile) it tends to be very thin (<10nm, say). This is in contrast to a → *depletion region*, which typically contains minority carriers arising from immobile donors, and which therefore tends to be relatively thick (20-200nm, say). Under external illumination, accumulation regions readily interact with photons, but any electron-hole pairs that are generated rapidly undergo recombination. Thus, no photocurrents are seen in the external circuit when a semiconductor material is under accumulation.

<div align="right">SF

stephen.fletcher@lboro.ac.uk</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Adiabatic process (thermodynamics)

In → *thermodynamics* a process is called adiabatic (or isocaloric) if no exchange (gain or loss) of heat occurs between the system and its environment. The word was first used by W.J.M. Rankine in 1859 as a synonym for "non-crossing", being derived from the classical greek word *adiabatos*, meaning something like "(it is) forbidden to cross" [i].

Ref.: [i] Rankine WJM (1859) A Manual of Applied Mechanics. Charles Griffin and Co, London

<div align="right">FS, SF

fscholz@uni-greifswald.de</div>

Adiabatic process (quantum mechanics)

In quantum mechanics a process is called adiabatic if electrons equilibrate with nuclei as the nuclei move. The concept of quantum adiabaticity was introduced by Paul Ehrenfest (1880-1933) as early as 1917, using pre-Heisenberg quantum mechanics [i]. The idea survived the advent of post-Heisenberg quantum mechanics, and was brought into its modern form by → *Born* [ii]. The existence of adiabatic processes is readily proved by considering the Hamiltonian of any system. It can be shown that if a system starts out in an eigenstate H_1, and changes very slowly, it will not cross into any other state, but will end up in a related eigenstate H_2, which, though it has a different value than H_1, is nevertheless connected to H_1 via a unique and continuous pathway. In brief, an adiabatic process is one that produces changes in eigenvalues, but does not produce changes in eigenstates. In the theory of electron transfer, adiabatic transformations are associated with slowly moving nuclei. These do not rapidly break up transition states, leaving plenty of time for electron transfer to occur. For this reason, adiabatic electron transfer processes occur with high probability, greatly simplifying the kinetic analysis. Indeed, in many cases, the rate of an adiabatic electron transfer process is just the rate of formation of the transition state [iii, iv].

There is a tradition in electrochemistry, exemplified by the work of Marcus, that pictures electron transfer processes in terms of potential energy profiles of reactant and product sub-systems. In general, a multi-dimensional plot of the potential energy of a chemical system as a function of the coordinates of its constituent nuclei (assumed stationary) is called a potential energy surface. And the one-dimensional minimum energy route from reactants to products across such a surface is called the "potential energy profile". For classical systems (i.e. for systems that do not participate in nuclear tunneling) potential energy profiles indicate the most probable route that a system will take while transforming from reactant to product. The concept of a potential energy profile was first suggested by René Marcelin (1885-1914) [v].

In the case of adiabatic electron transfer reactions, it is found that the potential energy profiles of the reactant and product sub-systems merge smoothly in the vicinity of the transition state, due to the resonance stabilization of electrons in the transition state. Resonance stabilization occurs because the electrons have sufficient time to explore all the available superposed states. The net result is the attainment of a steady, high, probability of electron transfer. By contrast, in the case of → *non-adiabatic* (*diabatic*) electron transfer reactions, resonance stabilization of the transition state does not occur to any great extent. The result is a transient, low, probability of electron transfer.

See → *Non-adiabatic (diabatic) process,* → *Marcus theory,* → *Randles,* and → *Gurney*.

Refs.: [i] Ehrenfest P (1917) Philos Mag 33:500; [ii] Born M (1926) Z Physik 40:167; [iii] Marcus RA (1964) Annu Rev Phys Chem 15:155; [iv] Hush NS (1999) J Electroanal Chem 460: 5; [v] Marcelin R (1913) J Chim Phys 10 :1913

<div align="right">

SF

stephen.fletcher@lboro.ac.uk

</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Band bending "Band bending" is an example of laboratory jargon, and refers to the occurrence of internal electric fields inside 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 thermodynamic equilibrium, band bending manifests spontaneously at the interface between two semiconductors, or at the interface between a semiconductor and a metal, if the → *electron work function* of each phase is different. Away from thermodynamic equilibrium, band bending can be increased or decreased by applying an electric potential difference of appropriate sign and magnitude between the two phases.

<div align="right">

SF

stephen.fletcher@lboro.ac.uk

</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

The 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 6504(24) $\times 10^{-23}$ J K^{-1}.
Refs.: [i] Planck, M (1901) Annalen der Physik, 4:553. [ii] Mohr PJ, Taylor BN, and Newell DB (2007) The 2006 CODATA Recommended Values of the Fundamental Physical Constants (Web Version 5.0).

<div align="right">

SF

stephen.fletcher@lboro.ac.uk

</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

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

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

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.

SF

stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Capacitive deionization. In capacitive deionization technology, CDT, water flows between parallel pairs of porous carbon electrodes (such as carbon aerogel electrodes) that are maintained at a potential difference greater than 1.0 V. Ions (and other charged particles such as colloids and microorganisms) become electrostatically immobilized on the charged surfaces, thus allowing pure water to pass through. When the electrodes become blocked, they are regenerated simply by removing the potential difference, thus allowing the charged impurities to flow away.

[i] Farmer, JC (1995) "Method and apparatus for capacitive deionization, electrochemical purification, and regeneration of electrodes", U.S. Patent # 5,425,858. [ii] Farmer, J.C., D.V. Fix, G.V. Mack, R.W. Pekala and J.F. Poco (1996), "Capacitive Deionization of NaCl and NaNO$_3$ Solutions with Carbon Aerogel Electrodes," J Electrochem. Soc. 143, 159-169.

SF

stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Clausius-Mossotti equation Named after Rudolf Julius Emanuel Clausius (1822-1888) and Ottaviano Fabrizio Mossotti (1791-1863). It relates the electron polarizability α of an individual molecule to the optical dielectric constant (relative permittivity) ε_r of the bulk material.

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{N\alpha}{3\varepsilon_0}$$

Here N is the number of molecules per unit volume and ε_0 is the vacuum permittivity (8.854×10^{-12} F/m). The same formula applies if the electron polarizability is replaced by the total polarizability, and the optical dielectric constant is replaced by the static dielectric constant, provided attention is then restricted to non-polar materials.

Refs.: [i] Mossotti OF (1850) Memorie di Mathematica e di Fisica della Società Italiana della Scienza Residente in Modena 24; 49. [ii] Clausius R (1879) Die Mechanische Wärmetheorie, Vieweg & Sohn, Braunschweig,. vol2; 62.

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Contact angle The contact angle is the angle of contact between a droplet of liquid and a flat rigid solid, measured within the liquid and perpendicular to the contact line where three phases (liquid, solid, vapor) meet. The simplest theoretical model of contact angle assumes thermodynamic equilibrium between three pure phases at constant temperature and pressure *[i,ii]*. Also, the droplet is assumed to be so small that the force of gravity does not distort its shape. If we denote the interfacial tension of the solid-vapor interface as γ_{SV}, the interfacial tension of the solid-liquid interface as γ_{SL} and the interfacial tension of the liquid-vapor interface as γ_{LV}, then by a horizontal balance of mechanical forces ($\theta < 90^{o}$)

$$0 = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos\theta$$

where θ is the contact angle. This equation is known as $\rightarrow$ *Young's equation*, and was derived in 1805 *[iii]*. Thus the contact angle is a measure of the wettability of a solid by a liquid phase; the smaller the contact angle the larger the wettability. An important subset of cases arises when the liquid is water. If the contact angle approaches 0° then the solid is said to be hydrophilic. This commonly occurs on surfaces that form hydrogen bonds with water. If the contact angle is greater than 90° then the solid is said to be hydrophobic. Finally, if the contact angle is greater than ~150° then the surface is said to be superhydrophobic. In case of a droplet of oil on the surface of water, Young's equation becomes:

$$\gamma_{WV} \cos\theta_3 = \gamma_{OV} \cos\theta_1 + \gamma_{WO} \cos\theta_2$$

where each γ term denotes the interfacial tension between adjacent phases. In this three-fluid case (water, vapor, oil) the oil droplet becomes lens-shaped.

Although contact angle is theoretically a function of state (meaning that its value is independent of system history) experimentally it is often found that the system history has a measurable effect. This has led to the pragmatic definition of *advancing* and *receding* contact angles. Typically, advancing contact angles are measured by dipping a solid into a liquid, whereas receding contact angles are measured by withdrawing them again. The different values of contact angle observed are frequently attributed to non-homogeneities on the solid surface. Contact angles are principally measured by two techniques: a static method based on the imaging of sessile drops, and a dynamic (receding) method *[iv]* based on weighing a vertical plate as it is withdrawn from the liquid of interest.

Refs. : [i] de Gennes PG (1985) Rev Mod Phys 57:827 ; [ii] Israelachvili JN (1985) Intermolecular and Surface Forces. Academic Press, New York; [iii] Young T (1805) Phil Trans Roy Soc (London) 95:65; [iv] Wilhelmy LF (1863) Ann Phys Chem (Leipzig) 119:177

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Coulomb force The Coulomb force is the electrostatic force. That is, the Coulomb force is the force that exists between two or more charged bodies. If the bodies are both positively or both negatively charged, the force is repulsive; if they are of opposite charge, the force is attractive. The force is named after Charles Augustin de → Coulomb (1736-1806), who made some early measurements of electrostatic forces using a torsion balance [i]. The magnitude of the Coulomb force F on a point particle of constant charge q_1 due to another point particle of constant charge q_2 may be obtained by multiplying the electric field caused by q_2 by the charge q_1,

$$F = \frac{q_1 q_2}{4\pi\varepsilon_r\varepsilon_0 d^2}$$

where ε_r is the relative permittivity (static dielectric constant) of the surrounding medium, ε_0 is the permittivity of free space (8.854×10^{-12} F/m), and d is the distance between the particles. This is an example of an *inverse square law*. The corresponding electrostatic potential energy is

$$U = \frac{q_1 q_2}{4\pi\varepsilon_r\varepsilon_0 d}$$

In many chemical systems, how the electrostatic potential energy varies with respect to the nuclear coordinates has a strong influence on the rates of electron transfer. All intermolecular forces are electrostatic in origin. This includes all the "named" forces, such as Debye forces, Keesom forces, London forces, and van der Waals forces. These secondary forces arise from spatial distributions of charge (as opposed to point

charges), or from temporal fluctuations of charge (as opposed to constant charges), or from combinations of both. In computer simulations of chemical systems, an important adjunct to Coulomb's Law is the Hellman-Feynman theorem [ii,iii]. This states that, once the spatial distribution of electrons has been determined by solving the Schrödinger equation, the intermolecular forces may be calculated by classical electrostatics. This theorem removes the need for programming secondary forces, but at high computational cost.

Refs.: [i] Société Française de Physique. Mémoires relatifs à la Physique, tome 1: Mémoires de Coulomb. Paris: Gauthier-Villars, 1884; [ii] Hellman H (1937) Einführung in die Quantenchemie. F. Deuticke, Leipzig, p 285; [iii] Feynman RP (1939) Phys Rev 56:340

<div align="right">

SF

stephen.fletcher@lboro.ac.uk
</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Depletion region A depletion region is any part of a → *semiconductor* device that has been depleted of majority carriers due to the presence of an electric field, so that it becomes nearly insulating. The electric field may arise from an externally applied bias, the presence of a nearby interface composed of a differently doped semiconductor material (as in a p-n junction), or the presence of a nearby interface composed of a metal (as in a → *Schottky barrier*). In the presence of light, photons may interact with matter inside a depletion region, creating electron-hole pairs that are then rapidly separated by the electric field. Efficient separation permits the electrons and holes to do useful work in an external circuit. This is the basis of many photoelectrochemical devices. The differential capacity C_{SC} of the depletion region (also called the space charge region) in a semiconductor is related to the potential drop $\Delta\varphi_{SC}$ across it by the → *Mott-Schottky* equation.

<div align="right">

SF

stephen.fletcher@lboro.ac.uk
</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Diabatic process: See → *Non-adiabatic (diabatic) process*

Diffuse layer capacitance The diffuse layer is the outermost part of the electrical double layer *[i]*. The electrical → *double layer* is the generic name for the spatial

distribution of charge (electronic or ionic) in the neighborhood of a phase boundary. Typically, the phase boundary of most interest is an electrode/solution interface, but may also be the surface of a colloid or the interior of a membrane. For simplicity, we here focus on the metal/solution interface. The charge carriers inside the metal are → *electrons*, which are confined to the metallic phase. The charge carriers inside the solution are ions, which are confined to the solution phase. Due to the differences in → *electron work function* between the two phases, the different charge carriers in the different phases accumulate in the vicinity of the interface, in an attempt to maintain overall → *electroneutrality*. Due to the high concentration and small size of electrons in the metal, the excess charge on the metal is localized at its surface. But due to the low concentration and large size of ions in solution, any neutralizing charge in the solution is distributed over a finite region of space. This region of space may be imagined as consisting of three zones of different character. There is a near-field region in which desolvated ions are essentially immobilized in contact with the metal surface. The forces involved are both electrostatic and quantum in character. There is an intermediate-field region in which ions are continuously undergoing solvation/desolvation processes driven by electrostatic forces, and finally there is a far-field region in which fully solvated ions are undergoing continuous place-exchange with ions from the bulk of solution. This latter region is known as the → *diffuse layer*. There is some experimental support for the idea that the total capacitance of the three regions of solution adjacent to an electrode surface may be treated as three capacitors in series:

$$1/C_T \;=\; 1/C_1 \;+\; 1/C_2 \;+\; 1/C_d$$

where the diffuse layer capacitance C_d is given by *Chapman's formula*

$$C_d \;=\; A\left(\frac{2\varepsilon_r\varepsilon_0\,e^2 z_i^2 c_i}{kT}\right)^{1/2} \cosh\left(\frac{ez<V(a)>}{2kT}\right)$$

Here ε_r is the relative permittivity (static dielectric constant) of the solution, ε_0 is the → *permittivity* of free space, e is the unit charge on the electron (→ *elementary electric charge*), z_i is the valence of the ionic species i, c_i is the bulk concentration of the adsorbing species i, k is the → *Boltzmann constant*, T is the absolute temperature, and $<V(a)>$ is the time-averaged value of the electric potential difference across the diffuse layer. The diffuse layer capacitance is (very roughly) of the order of $10\mu F/cm^2$. The "thickness" of the diffuse layer is essentially the → *Debye length* L_D,

$$L_D \;=\; \left(\frac{\varepsilon_r\varepsilon_0\,RT}{F^2\sum_i c_i z_i^2}\right)^{1/2}$$

where ε_r is the relative permittivity (static dielectric constant) of the solution, ε_0 is the permittivity of free space, R is the gas constant, T is the absolute temperature, F is the Faraday constant, c_i is the bulk concentration of species i, and z_i is the valence of species i.

Ref.: [i] Parsons R (1954) in Modern Aspects of Electrochemistry, Academic Press, New York

SF

stephen.fletcher@lboro.ac.uk

DLVO theory The DLVO theory is named after Derjaguin and Landau *[i]*, and Verwey and Overbeek *[ii]*. It describes the forces acting between colloidal particles in ionic solutions. The theory builds on an idea of Chapman *[iii]*, who assumed that, everywhere throughout an ionic solution, the local concentration of electrolyte ions was determined by the local time-averaged value of the electric potential $<V(r)>$ according to a Boltzmann-like formula. Thus, the local population of ions of species i was assumed to take the form

$$n_i(r) = n_i^0 \exp\left(-\frac{\Delta G_i}{kT}\right)$$

so that

$$n_i(r) = n_i^0 \exp\left(-\frac{ez_i <V(r)>}{kT}\right)$$

where ΔG_i is the molar $\rightarrow$ *Gibbs energy* of the ionic species i, $n_i(r)$ is the concentration of the ionic species i at location r, n_i^0 is the concentration of ionic species i far from the reactant, e is the unit charge on the electron ($\rightarrow$ *elementary electric charge*), z_i is the valence of the ionic species i, k is the $\rightarrow$ *Boltzmann constant*, T is the absolute temperature, and $<V(r)>$ is the time-averaged value of the electric potential at location r. The Chapman model works reasonably well, at least at low concentrations (<0.01M). Assuming that there are only two types of ions, having equal and opposite valences (z_+ and z_-), one finds

$$\sum_i^N ez_i n_i(r) = ez_+ n_+(r) - ez_- n_-(r)$$

$$= ez_i n_i^0 \left[\exp\left(-\frac{ez_i <V(r)>}{kT}\right) - \exp\left(+\frac{ez_i <V(r)>}{kT}\right)\right]$$

$$= -2ez_in_i^0 \sinh\left(\frac{ez_i <V(r)>}{kT}\right)$$

Hence

$$\nabla^2 <V(r)> = \frac{2ez_in_i^0}{\varepsilon_r\varepsilon_0}\sinh\left(\frac{ez_i <V(r)>}{kT}\right)$$

where ε_r is the relative → *permittivity* (static dielectric constant) of the solution, ε_0 is the permittivity of free space, and $e/kT = F/RT = 25.7\text{mV}$ at room temperature. This non-linear partial differential equation in $<V(r)>$ is very well known and is called the → *Poisson-Boltzmann equation*. But it is very badly named. Neither Poisson nor Boltzmann advocated it, and neither lived to see it! Still, it is the equation that needs to be solved. Despite all the simplifications used in its derivation, no general solution of the Poisson-Boltzmann equation has ever been found. Indeed, only the particular case of planar co-ordinates has been solved exactly, by Chapman himself, yielding his celebrated formula for the diffuse layer capacitance of a planar electrode

$$C_{\text{DIFF}} = A\left(\frac{2\varepsilon_r\varepsilon_0 e^2 z_i^2 n_i^0}{kT}\right)^{1/2}\cosh\left(\frac{ez <V>}{2kT}\right)$$

To make headway with the colloidal problem, the Poisson-Boltzmann equation must be solved in *spherical* co-ordinates. → *Peter Debye* and → *Erich Hückel [iv]* introduced the following approximation into the spherical case,

$$\sinh\left(\frac{ez_i <V(r)>}{kT}\right) \approx \frac{ez_i <V(r)>}{kT}$$

This transformed the non-linear Poisson-Boltzmann equation into the linear Helmholtz-type equation

$$\nabla^2 <V(r)> \approx \kappa^2 <V(r)>$$

where κ was the reciprocal → *Debye length*

$$\kappa = \left(\frac{2e^2 z_i^2 n_i^0}{\varepsilon_r\varepsilon_0 kT}\right)^{1/2}$$

Based on this idea, Derjaguin and Landau, and Verwey and Overbeek, found the pair potential for the electrostatic repulsion of two identical spherical particles in an electrolyte solution to be

$$U_1(x) = \frac{(Ze)^2}{\varepsilon_r\varepsilon_0}\left[\frac{e^{\kappa a}}{1+\kappa a}\right]^2\frac{e^{-\kappa x}}{x}$$

where (Ze) is the effective surface charge on the particles, e is the unit charge on the electron, ε_r is the relative permittivity (static dielectric constant) of the solution, ε_0 is the permittivity of free space, κ is the reciprocal Debye length (determined by the electrolyte concentration), a is the radius of the spheres, and x is the centre-to-centre distance between the spheres. The full DLVO pair potential can also be extended to take into account an attractive van der Waals term $U_2(x)$, so that

$$U_{\text{DLVO}} \; = \; U_1(x) \; + \; U_2(x)$$

where

$$U_2 \; = \; -\frac{A_{\text{H}}}{6} \left[\frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln\left(\frac{r^2 - 4a^2}{r^2} \right) \right]$$

and A_{H} is the Hamaker constant. The van der Waals term creates a minimum in U_{DLVO} at very small inter-particle separations *[v]*. However, in many practical applications this can be ignored

Refs.: [i] Derjaguin B, Landau L (1941) Acta Physicochim URSS 14:633; [ii] Verwey EJW, Overbeek JThG (1948) Theory of the Stability of Lyophobic Colloids. Elsevier, New York; [iii] Chapman DL (1913) Phil Mag 25:475; [iv] Debye P, Hückel E (1923) Physik Z 24:185; [v] Lyklema J (1991) Fundamentals of Interface and Colloid Science (5 vols), Academic Press, New York

<div align="right">

SF

stephen.fletcher@lboro.ac.uk

</div>

Electricity Electricity is the name given to any macroscopic manifestation of electric → *charge*, whether static or dynamic. For historical reasons, bulk quantities of electric charge have traditionally been classified in terms of their motion. Thus, bulk quantities of electric charge are commonly described as either "static electricity" or "dynamic electricity". Static electricity refers to electric charges at rest, and these can manifest on the surface of either → *insulators* or → *conductors*. By contrast, dynamic electricity refers to electric charges in motion, and those can flow only through conductors or → *semiconductors*. Although static electricity was known to the ancients, the modern study of static electricity is usually traced to the experiments of William Gilbert (1544-1603). Indeed, it was he who coined the word "electric" (in Latin, in the form 'Electrica Effluvia' [i]). Dynamic electricity was first observed by → *Gray* in 1729 [ii]. Experimentally, a free electric charge has never been observed. Instead, charge is always associated with a → *charge carrier*, which may be a fundamental particle (a quark; or a lepton such as an → *electron*), a composite particle (a baryon such as a → *proton*), a lattice-stabilized entity (such as a → *hole*, or →

polaron), or a chemical species (such as an → *ion*). On the Standard Model of particle physics, "charge" is one of the four irreducible properties of matter (the other three being "color", "mass" and "spin") and therefore, at the current state of knowledge, it is not capable of further definition.

Ref.: [i] William Gilbert, De Magnete, Magneticisque Corporibus, et de Magno Magnete Tellure, (On the Magnet, Magnetic Bodies and the Great Magnet, the Earth) pub. Petrus Short (London) 1600. [ii] Stephen Gray, "Two letters from Gray to Mortimer, containing a farther account of his experiments concerning electricity", Philosophical Transactions No 37 (1731-32)

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

<div align="right">\textbf{stephen.fletcher@lboro.ac.uk}</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Electroconvection

(a) is the macroscopic motion of a solution resulting from the effect of gravity on non-equilibrium density gradients caused by potential differences (→ *electric field*). The density changes are generated by → *electrostriction*. In practice, electroconvection is largely confined to solutions near charged interfaces, because that is where the electric fields are largest. (b) (also called electrohydrodynamic): This is an → *electrokinetic effect*. When an ac field is applied across nematic and smectic liquid crystals [i], or across a colloidal suspension [ii], convection is caused and specific convection patterns are induced. The phenomenon belongs to the pattern formation due to the non-linear response of dissipative media to external fields. Thus electroconvection bears some similarity to Bénard [iii] and Bénard-Marangoni [iv] convection caused by a temperature gradient. (See also → *Marangoni streaming*). See also → *electrorheological fluid* for liquids with a high contents of dispersed particles. See also → *Quincke* rotation).

[i] Blinov LM (1998) Behaviour of Liquid Crystals in Electric and Magnetic Fields. In: Handbook of Liquid Crystals. Demus D, Goodby J, Gray GW, Spiess HW, Vill V (eds), vol 1, Wiley-VCH, Weinheim, pp 477
[ii] Han Y, Grier DG (2005) J Chem Phys 122:164701 (DOI: 10.1063/1.1884599)
[iii] Bénard H (1900) Rev Gén Sci Pure Appl 11:1261
[iv] Tokaruk WA, Molteno TCA, Morris SW (2000) Phys Rev Lett 84:3590

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

<div align="right">\textbf{stephen.fletcher@lboro.ac.uk}</div>

Citation: S. Fletcher and F. Scholz, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Electrocrystallization   A term first coined by Fischer [i] to describe a crystallization process in which the electrode potential provides the driving force, either directly in the form of a → *crystallization overpotential*, or indirectly in the form of a → *supersaturation*. (A solution is said to be "supersaturated" if it contains a concentration of a dissolved substance that is greater than the equilibrium concentration.)

See also → *nucleation and growth kinetics*, → *nucleation overpotential*, → *electrodeposition*, → *Stranski*,→ *Kaishev*.

Ref.: Fischer HJ (1954) Elektrolytische Abscheidung und Elektrokristallisation von Metallen. Springer, Berlin

SF
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Electrolysis cell (electrolytic cell):

An electrolysis cell typically consists of an inert vessel containing a supporting → *electrolyte* solution, a reactant, an → *anode* and a → *cathode*, and a → *separator*. The reactant is typically un-reactive at the → *open circuit potential* of the cell, but becomes reactive upon application of an → *overpotential* to either the anode or the cathode (or both). In general there is sufficient volume inside the cell to contain the product formed, which is removed on a batch basis. (*cf.* A flow cell, in which the product is collected elsewhere.) At constant temperature and pressure, the → *Gibbs energy* of the electrolysis reaction is positive, which means that energy must be supplied from the surroundings to make the reaction proceed. This contrasts with reactions inside a → *galvanic cell*, for which the Gibbs energy is negative, and which therefore proceed spontaneously.

SF
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Electrolytic cell: See → *Electrolysis cell*

Electron   The electron was the first elementary particle to be discovered, by J. J. Thomson in 1897. It has a very low rest mass m_e of $9.109\,3826(16){\times}10^{-31}$ kg, and an elementary charge e of $1.602\,176\,53(14){\times}10^{-19}$ C *[i]*. Electric charge is conserved. Thus, in chemistry, where electrons are not annihilated by other nuclear particles, we

can assume that electrons themselves are conserved. (This explains why chemical reactions "have to balance".) Electrons have two spin states. The number of spin states for any particle of non-zero rest mass is $2s+1$, so the electron has spin quantum number $s = \frac{1}{2}$. This means that electrons are fermions – their wavefunctions are anti-symmetric, and they obey the exclusion principle. The exclusion principle states that two electrons in an atom are excluded from occupying the same energy level, unless they have opposite spin. Inside a substance, electrons populate energy levels according to the → *Fermi-Dirac Function $F(E_i)$* . This tells us what the probability is that a selected energy level i is occupied by an electron. (Assuming the energy level exists, and assuming the energy level lies inside a system that is in thermal equilibrium with a large reservoir of heat). In its electrochemical form

$$F(E_i) \;=\; \cfrac{1}{1 + \exp\left(\cfrac{E_i - E_F}{kT}\right)}$$

Here k is the → *Boltzmann constant*, T is the absolute temperature, E_i is the energy of the ith energy level, and E_F is the → *Fermi Energy*. The Fermi Energy of a system is simply the energy at which the Fermi-Dirac function equals one half. There is not necessarily an energy level that corresponds with it. For most metals, the Fermi energy lies about (4 ± 2) eV below the vacuum energy. Note that the Fermi-Dirac function is not a density-of-states. That is, it does not tell us anything about whether a particular energy level actually exists. It merely tells us what the probability of occupancy would be, if indeed the state did exist. In a → *semiconductor*, which by definition has a gap in its distribution of energy levels, it often happens that no such level exists. However, in a metal, there is a nearly continuous distribution of energy levels. Thus, in a metal, it is virtually certain that a real energy level (called the → *Fermi Level*) will be found at the → *Fermi Energy*. The existence (or otherwise) of energy levels in a substance may be inferred from its *density of states* function $f(E)$. Disregarding the complications caused by d-orbitals, an approximate formula for the density of states in a metal is available from free electron theory. The result is

$$f(E) \;=\; \frac{4\pi(2m^*)^{3/2}}{\hbar^3}\sqrt{E}$$

where $f(E)$ is the number of electron states per unit volume per unit energy at energy E, and m^* is the effective mass of the electron. Note that this result is independent of the linear dimension L, or area A, of the metal, as it should be.

Wave/particle duality is the postulate that all objects of physical reality possess both localized (particle) and distributed (wave) properties. Due to their low rest mass, electrons exhibit both particle and wave behavior on the scale of length of atoms (nanometers). Thus, every electron has a wavelength associated with it. This wavelength is called the de Broglie wavelength λ_{DB},

$$\lambda_{DB} \;=\; \frac{h}{p}$$

Here h is → *Planck's constant* and p is the electron's momentum. For an electron traveling at non-relativistic velocities, this can be written

$$\lambda_{DB} = \frac{h}{mv}$$

where m is the electron mass and v is the electron velocity, or

$$\lambda_{DB} \approx \frac{1.23}{\sqrt{V}} \text{ nm}$$

which is dimensionally sound provided the voltage V is expressed in volts. Thus, for an electron accelerated through 1 volt, the de Broglie wavelength is 1.23 nm. Most importantly, the wave character of electrons allows them to pass through electrostatic potential barriers that would block classical particles *[ii]*. This leads to the phenomenon of electron → *tunneling* at interfaces *[ii, iii]*. It is interesting to determine what fraction of incident electrons is actually transmitted through a potential barrier, so that they emerge on the other side. This fraction is called the transmission probability T. For a rectangular barrier of width L and height Φ, and for an electron of energy E, the result is

$$T = \left[1 + \frac{(e^{\kappa L} - e^{-\kappa L})^2}{16\varepsilon(1-\varepsilon)} \right]^{-1}$$

where $\varepsilon = E/\Phi$, and Φ is the electron work function. Assuming the barrier is high and wide so that $\kappa L \gg 1$, this simplifies to

$$T = 16\varepsilon(1-\varepsilon)\exp(-2\kappa L)$$

Thus the transmission probability T decays exponentially with barrier thickness L. Indeed, it decreases by a factor of ~10 for every 0.1nm of barrier thickness, indicating that electron tunneling is very short range indeed.

Refs.: [i] Mohr PJ, Taylor BN (2005) Reviews of Modern Physics 77:1. [ii] Hund FH (1927), Z Phys 40:742, 42:93, 43:805. [iii] Fowler RH, Nordheim LW (1928) Proc Roy Soc Lond A 119:173

SF
stephen.fletcher@lboro.ac.uk

Electron Transfer

Electron transfer is the process by which an electron is transported into (or out of) an otherwise closed system, thereby inducing a change in the occupation number of at least one electronic state.

See → *Charge transfer,* → *Electron transfer at liquid-liquid interfaces,* →
Marcus theory, → *adiabatic process,* → *non-adiabatic process*

SF
stephen.fletcher@lboro.ac.uk

Electron work function   The electron work function Φ deep inside a substance is the
work required to raise the energy of a stationary → *electron* from the substance's →
Fermi energy to the vacuum energy *[i]*. In the absence of intervening electric fields,
the electron work function also corresponds to the work required to transfer an
electron from the Fermi energy inside the substance to infinity. The electron work
function is important in the theory of thermionic emission. It is also important in the
theory of metal-semiconductor junctions (Schottky diodes). This is because the
difference in electron work function between a metal and a semiconductor determines
if their contact is ohmic or rectifying. An ohmic contact is simply one that has been
prepared so that the current-voltage (*I-V*) curve of the interface is linear and
symmetric. Ohmic contacts are formed when a metal and an *n*-type semiconductor are
brought into ideal contact, whereas rectifying contacts are formed when a metal and a
p-type semiconductor are brought into ideal contact. However, in the presence of
surface states caused by defects etc, all contacts tend to be ohmic.

Substance	Work Function (eV)
Sodium	2.3
Potassium	2.3
Calcium	2.9
Uranium	3.6
Magnesium	3.7
Cadmium	4.1
Aluminum	4.1
Lead	4.1
Niobium	4.3
Zinc	4.3
Iron	4.5
Mercury	4.5
ITO	4.7
Copper	4.7
Silver	4.7
Carbon	4.8
Cobalt	5.0
Nickel	5.0
Gold	5.1
Platinum	6.3

Ref.: [i] Woodruff DP and Delchar TA (1994) Modern Techniques of Surface Science.
Cambridge University Press, Cambridge (UK)

SF

stephen.fletcher@lboro.ac.uk

Electroporation A technique in which a brief (sub-millisecond) electric pulse is used to stimulate a transient increase in the solute permeability of a bilayer membrane. The process is referred to as electroporation because it is thought that micropores form in the membranes above some threshold value of membrane potential. In the case of suspensions of living cells, electric fields as high as 35 kV/cm and durations as low as 1μs have been used. Typically, a suspension of cells is prepared in a 1mL electroporation cuvette containing parallel plate aluminum electrodes. Once formed, the micropores allow some of the cell contents (cytoplasm) to escape into solution, whilst also allowing some of the solution species to penetrate the cell interior. These solution species may include drugs, molecular probes, and even DNA. Although microinjection into cells is known to have a higher individual success rate, electroporation is able to target 10^7 cells in a single experiment, with as little as 100μg of double-stranded DNA per mL, thus making it ideal for scale-up. Doevenspecki first proposed the use of pulsed electric fields to kill microorganisms in 1961 [i]. Later, in 1968, Sale and Hamilton described the lethal effects of high electric fields on microorganisms such as erythrocytes and protoplasts [ii]. Then, in a landmark paper of 1982, Neumann et al. reported successful gene transfer into living mouse lyoma cells by electroporation using sub-lethal electric pulses of 5μs duration and 8 kV/cm field strength [iii]. Today, electroporation is widely used for the introduction of foreign genes into tissue culture cells, especially mammalian cells. For example, it is used in the process of producing knockout mice (which lack a specific gene), as well as in gene therapy, cell therapy, and tumor treatment.

[i] Doevenspeck H (1961) Fleischwirtschaft, 13: 986.
[ii] Sale AJH and Hamilton WA (1968) Biochimica and Biophysica Acta, 163: 37.
[iii] Neumann E, Schaefer-Ridder M, Wang Y, and Hofschneider PH (1982) EMBO Journal 1:841.

SF
stephen.fletcher@lboro.ac.uk

Galvanic

Following the epochal experiments of $\rightarrow$ *Galvani*, in which electric discharges were shown to activate the dissected muscles of a frog [i], the word "galvanic" was adopted by a small group of scientists to describe this particular effect. However, shortly thereafter, $\rightarrow$ *Volta* announced the invention of his eponymous pile (which consisted of alternating disks of zinc and copper separated by brine-soaked cloth), and with this new source of electricity it became possible to carry out galvanic

experiments for longer periods, and on a much wider range of materials, than previously. As a result, the word "galvanic" rapidly spread into much wider usage. Today, the word "galvanic" has entered most languages in the world, and remains in regular use in three principal areas of science: (a) to describe electricity generated spontaneously from a voltaic pile ($\rightarrow$ *galvanic cell*) (b) to describe phenomena occurring at the junction of two dissimilar metals (galvanic contact, galvanic corrosion), and (c) to describe phenomena occurring at the interface between an electrode and living cells (galvanic skin response).

Refs. : [i] Aloysii (Luigi) Galvani, De viribus electricitatis in motu musculari, pub. Accademia delle Scienze, Bologna, 1791. [ii] Alessandro Volta, On the Electricity Excited by the Mere Contact of Conducting Substances of Different Kinds, Philosophical Transactions of the Royal Society (London), Vol. 2, pp 403-431, 1800.

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Galvanoglyphy

An electrotype process in which a copy of an engraved plate is produced with a raised surface, suitable for letter-press printing. The term originated in the Victorian era, and is synonymous with glyphography, electrotint, cerography, etc. In the first stage of the process, an artist incised a design into the surface of a wax-coated plate by means of a hand tool. After dusting with graphite, the remaining wax was then electroplated with copper, filling the incised lines and forming the master plate for printing. After the invention of the $\rightarrow$ *Daniell* cell in 1836, which provided a stable electrical current for several hours, galvanoglyphy based on thick copper plating became technologically feasible, and a number of practical processes soon emerged. These provided an inexpensive means of making durable printing plates for mass production. Early success was achieved by C J Jordan [i], Thomas Spencer and John Wilson [ii], Sidney Edwards Morse (1794-1871) [iii], and Moritz Hermann Jacobi (1801-1874) [iv]. However, many others developed similar processes around the same time, but withheld the details as trade secrets.

Refs.: [i] C J Jordan, Engraving by Galvanism, Mechanics Magazine, 08 June 1839. [ii] Thomas Spencer and John Wilson, Certain Improvements in the Process of Engraving upon Metals by Means of Voltaic Electricity, British Patent No 8656, 7th October 1840. [iii] Sidney Edwards Morse, Cerographic Atlas, New York: S.E. Morse & Samuel Breese, 1843. [iv] Moritz Hermann Jacobi, Bericht über die Entwicklung der Galvanoplastik. Bulletin de la Classe Physico-Mathématique de l'Académie Impériale des Sciences de Saint-Pétersbourg 1. Sp.65-71, 1843.

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Galvanize (1) To stimulate living cells by means of an electric current. (2) To electroplate a metal surface with a dissimilar metal; in particular, to electroplate iron with zinc. In the latter case, the term is also commonly misapplied to iron that has been dip-coated with zinc. (3) Figuratively, to restore something to life from a dormant state.

<div align="right">

SF

stephen.fletcher@lboro.ac.uk

</div>

Hydrated electron When a free electron is injected into water, it localizes in a cavity (electrostatic potential well) between two water molecules within less than 1 ps:

$$e^-(vac) \; + \; H_2O(aq) \; \rightarrow \;\; e^-(aq)$$
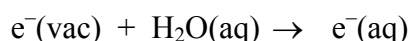
There it forms two slightly asymmetric H-bonds with neighboring water molecules, and survives for about 1ms at pH 7. During its brief lifetime it exists in an s-like (near-spherical) ground state. After formation, the equivalent radius of the hydrated electron is about 200 pm. Ultimately it decomposes by reaction with a proton to create a hydrogen atom:

$$e^-(aq) \; + \; H^+(aq) \;\; \rightarrow \;\; H^\bullet(aq)$$
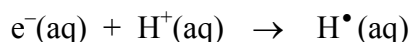
Electrochemically, "hydrated electrons" require ultra-negative electrode potentials for their formation in the dark (more negative than –2.87V *vs* SHE), corresponding to +1.57V *vs* a stationary electron in the vacuum *[i]*. Accordingly, they are not formed spontaneously in the conventional range of electrode potentials in water. The thermodynamic properties of hydrated electrons may be estimated by a →*Born-Haber cycle*. Thus the Gibbs energy of hydration of the electron is $\Delta G_{hyd} \approx -149$ kJ/mol, the enthalpy of hydration of the electron is $\Delta H_{hyd} \approx -166$ kJ/mol, and the entropy of hydration of the electron is $\Delta S_{hyd} \approx -58$ J/K/mol. Analogous to hydrated electrons, ammoniated electrons can be prepared in liquid ammonia. These are stable for several days, forming a characteristic blue solution.
Ref.: [i] Trasatti S (1986) Pure Appl Chem 58:955

<div align="right">

SF

stephen.fletcher@lboro.ac.uk

</div>

Non-adiabatic (diabatic) process (quantum mechanics)

In quantum mechanics a process is called non-adiabatic (diabatic) if one or more electrons fails to equilibrate with nuclei as they move. In a widely-used extension of this terminology, non-adiabatic electron transfer is said to occur when an electron tunnels out of one electronically non-equilibrated state into another. Due to the requirement of energy conservation, such tunneling also requires a random fluctuation inside the system to equalize the energies of the two states. In principle this fluctuation can be provided by any suitable degree of freedom, but in practice it is usually assumed to be due to electrostatic polarization of the reaction center by the motion of one or more nearby solvent molecules. A characteristic feature of non-adiabatic electron transfer is that the transition state assembles and disassembles many times before an electron finally tunnels into the new state.

Unfortunately, the mathematical modeling of non-adiabatic electron transfer requires the solution of the fully time-dependent Schrödinger equation, something generally considered impossible except at the very lowest levels of system complexity. To overcome this difficulty, Paul Dirac (1902-1984) developed a brilliant extension of quantum mechanics called "time-dependent perturbation theory", which yields good approximate solutions to many practical problems. The only limitation on Dirac's method is that the coupling (orbital overlap) between the donor states and the acceptor states should be weak [i]. → *Fermi* was so impressed with Dirac's solution that he famously referred to it as a "Golden Rule", and the name has stuck [ii]. The Golden Rule formula for the electron transition rate from a near-continuum of donor states to a near-continuum of acceptor states is

$$\langle \lambda_{\mathrm{MDMA}} \rangle \approx \frac{2\pi}{\hbar} \int_{-\infty}^{\infty} \left\langle \left| M_{\mathrm{DA}}(E) \right|^2 \right\rangle \varphi_{\mathrm{DA}}(E) \, \mathrm{d}E$$

where $\lambda_{\mathrm{MDMA}} \, (\mathrm{s}^{-1})$ is the multiple-donor multiple-acceptor rate constant for electron transfer, $\hbar$ is the reduced Planck constant (1.055×10^{-34} Js), M_{DA} is the coupling energy (matrix element) between the donor and acceptor states (joules), and $\varphi_{\mathrm{DA}}(E)$ is the joint density of donor and acceptor states through which electron transfer may occur (joules^{-2}). The term $\left\langle \left| M_{\mathrm{DA}}(E_{\mathrm{D}}) \right|^2 \right\rangle$ denotes the value of $\left| M_{\mathrm{DA}}(E_{\mathrm{D}}) \right|^2$ averaged over all the paired states, and by "joint density" we simply mean the number of donor states whose energies actually coincide with the energies of acceptor states.

Three landmark papers on the application of time-dependent perturbation theory to electrochemical problems were published in rapid succession by → *Levich* and → *Dogonadze* in 1959 [iii], → *Gerischer* in 1960 [iv], and McConnell in 1961 [v]. A very large literature has subsequently sprung from these works, driven by developments in scanning tunneling microscopy, molecular electronics, and biological electron transfer.

Compared with the adiabatic case, the visualization of non-adiabatic electron transfer in terms of potential energy profiles is much simpler. Because resonance does not

occur in the transition state, the potential energy surfaces of the reactant and product states (considered independently of each other) simply superpose.

See also → *adiabatic process,* → *Marcus theory,* → *Randles,* and → *Gurney.*

Refs.: [i] Dirac PAM (1927) Proc Roy Soc (Lond) A114:243; [ii] Nuclear Physics. A Course Given by Enrico Fermi at the University of Chicago. Notes compiled by Orear J, Rosenfeld AH, and Schluter RA, Univ Chicago Press, 1950; [iii] Levich V, Dogonadze RR (1959) Dokl Akad Nauk SSR 124:123; [iv] Gerischer H (1960) Z Physik Chem 26:223; [v] McConnell HM (1961) J Chem Phys 35:508.

<div align="right">

SF
stephen.fletcher@lboro.ac.uk

</div>

Nucleation is the commonest mechanism by which first order → *phase transitions* are initiated. The nucleation mechanism involves the creation of domains of a new phase, together with their phase boundaries, somewhere inside an existing system. In many cases the new domains are crystals, in which case the process is also referred to as crystallization. If the phase transition occurs at an electrode, the process is referred to as → *electrocrystallization*. When the domains are small, their interfacial excess → *Gibbs energy* is a substantial fraction of their total Gibbs energy. As a result, there is a Gibbs energy barrier separating the reactant state from the product state. The magnitude of this barrier depends on domain size, but has a local maximum at a certain critical size. Domains that are comparable in size with this critical size are called nuclei. After the initiation of a nucleation process (typically by changing the electrode potential) thermal fluctuations create a steady state population of nuclei around the critical size. Macroscopic domains then grow out of this seed population. The time delay required to form the seed population is known as the time-lag. Time lags are the signature feature of nucleation processes — all nucleation processes exhibit them. If we denote the solution or ambient phase as phase 1, the electrode as phase 2, and the new phase as phase 3, then we may define three interfacial excess free energy densities between them, namely γ_{12}, γ_{13}, and γ_{23}. The steady state rate of nucleation on the electrode surface may then be written *[i]*

$$\alpha = \alpha_0 \exp\left(\frac{-4\pi[\gamma_{13} - \gamma_{12} + \gamma_{23}]^2 [2\gamma_{13} + \gamma_{12} - \gamma_{23}]}{3RT[nF\rho_m\eta]^2} \right)$$

where α is the steady state rate of nucleation, α_0 is a constant, R is the gas constant, T is the absolute temperature, n is the number of electrons in the total reaction, F is the Faraday constant, ρ_m is the molar density of the depositing phase, and η is the overpotential. Inspection of the above equation reveals that the steady state rate of nucleation is a highly non-linear function of both overpotential and interfacial excess

free energy density. This accounts for the observation that nucleation rates are different on different parts of electrode surfaces (nucleation rate dispersion), the appearance of long-range order among nucleated crystals (decoration of scratches, defects, etc), and the very poor level of experimental reproducibility between ostensibly identical electrodes. In theory, the equilibrium shape of crystals in solution can be determined from knowledge of their Gibbs energies and their interfacial excess free energy densities. In practice, however, the interfacial excess free energy densities are so dependent on the molecular properties of solvents that the construction of the equilibrium shapes of crystals remains a difficult problem.
Ref.: [i] Deutscher RL, Fletcher S (1990) J Electroanal Chem 277: 1

<div style="text-align:right">SF</div>

<div style="text-align:right">**stephen.fletcher@lboro.ac.uk**</div>

__Nucleation and growth__ Nucleation-and-growth is the principal mechanism of phase transformation in electrochemical systems, widely seen in gas evolution, metal deposition, anodic film formation reactions, and polymer film deposition, etc. It is also seen in solid state phase transformations (e.g., battery materials). It is characterized by the complex coupling of two processes (nucleation and phase growth of the new phase, typically a crystal), and may also involve a third process (diffusion) at high rates of reaction. In the absence of diffusion, the observed electric current due to the nucleation and growth of a large number of independent crystals is *[i]*

$$I \;=\; \int_0^t I_1(\tau,t) N'(\tau) \, \mathrm{d}\tau$$

where I_1 is the current flowing into one crystal nucleated at time τ and observed at time t, $N(t)$ is the number of crystals at time t, and $N'(t)$ is the observed nucleation rate (appearance rate) of crystals. The superscript "primed" indicates the first derivative of N with respect to time t. The above expression for the electrical current is a Volterra integral equation of the first kind. This equation generates a number of distinctive features that are useful for diagnosing nucleation-growth kinetics, most notably a nucleation-growth loop in → *cyclic voltammetry [ii]* a U-shaped potential-time curve in → *chronamperometry [iii]*, and an inductive loop in the complex plane of → *impedance [iv]*. At constant potential, the Volterra integral may be replaced by a convolution integral, allowing simplified models to be derived, usually based on polynomial approximations for $N'(t)$ and $I_1(t)$. Often, the current flowing into one crystal is wholly determined by the rate of ion transfer at the crystal surface. But when diffusion intervenes, the mathematical analysis generally becomes intractable. One exception is the current-time behavior for the growth of a single nucleus at which hemispherical diffusion is coupled with a reversible, first order ion transfer reaction. The result is then *[v]*

$$I_1 \;=\; 2\pi n F D C_b \left[1 \,-\, \exp\!\left(\frac{-nF}{RT} \eta \right) \right] \left[\frac{r^2}{r + D/k_{\mathrm{f}}} \right]$$

$$r = \left(\left[\frac{D}{k_f} \right]^2 + \frac{2DC_b t}{\rho_m} \left[1 - \exp\left(\frac{-nF}{RT} \eta \right) \right] \right)^{1/2} - \frac{D}{k_f}$$

where n is the number of electrons transferred, F is the → *Faraday constant*, D is the → *diffusion coefficient* of the diffusing species, C_b is the bulk concentration of the diffusing species, R is the gas constant, T is the absolute temperature, η is the → *overpotential*, r is the radius of the hemispherical nucleus at time t, k_f is the rate constant of the ion transfer reaction, and ρ_m is the molar density of the material composing the nucleus. In the case of multiple nucleation, the simplest possible solution to the Volterra integral equation for the total current arises in the case of so-called progressive nucleation confined to a monolayer. Then $I_1 \approx at$ and $N(t) \approx bt$, so that $I \approx abt^2/2$. The characteristic result is an electric current that rises as the square of time.

Refs.: [i] Fletcher S (1984) J Electrochem Soc 131:251; [ii] Fletcher S, Halliday CS, Gates D, Westcott M, Lwin T, and Nelson G (1983) J Electroanal Chem 159:267; [iii] Hasse U, Fletcher S, Scholz F (2006) J Solid State Electrochem 10:833; [iv] Fletcher S, unpublished results; [v] Fletcher S (1983) J Chem Soc, Faraday Trans I, 79:467

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Nucleation overpotential In 1898 → *Fritz Haber* showed that different reaction products could be obtained at different electrode potentials, using the reduction of nitrobenzene as an example *[i]*. However, a further forty four years would elapse before the invention of the → *potentiostat* by Hickling (1942), which finally made the control of the electrode potential routine *[ii]*. In the interim, a tradition developed of describing the mechanisms of electrode reactions in terms of current as input and "overpotential" as output. The culmination of this tradition was Vetter's magnum opus of 1961 which summarized much of the theory of → *overpotentials [iii]*. Today, the use of overpotentials survives only in certain specialist applications, such as in metal plating, where nucleation overpotentials continue to be routinely measured. The relation between the rate of nucleation of bulk crystals and overpotential was first derived in 1931 by → *Erdey-Gruz* and → *Volmer [iv]*. In modern terminology the result is given by Fletcher *[v]* as

$$\alpha = \alpha_0 \exp\left(\frac{-4\pi[\gamma_{13} - \gamma_{12} + \gamma_{23}]^2 [2\gamma_{13} + \gamma_{12} - \gamma_{23}]}{3RT[nF\rho_m\eta]^2} \right)$$

or

$$\ln \alpha = \ln \alpha_0 - \frac{const}{\eta^2}$$

Here we denote the solution or ambient phase as phase 1, the electrode as phase 2, and the new phase as phase 3. The three interfacial excess free energy densities between them are γ_{12}, γ_{13}, and γ_{23}, and α is the steady state rate of nucleation. In addition, α_0 is a constant, R is the $\rightarrow$ *gas constant*, T is the absolute temperature, n is the number of electrons in the total reaction, F is the $\rightarrow$ *Faraday constant*, ρ_m is the molar density of the depositing phase, and η is the overpotential.

Refs.: [i] Haber F (1898) Z Electrochem 4: 506. [ii] Hickling A. (1942) Trans Faraday Soc 38:27; [iii] Vetter KJ (1967), Electrochemical Kinetics: Theoretical and Experimental Aspects. Academic Press Inc, New York, 1967; [iv] Erdey-Gruz T and Volmer M (1931) Z Phys Chem A 157:165; [v] Fletcher S (1990) J Electroanal Chem 277:1

SF
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Open circuit potential
The electrode potential spontaneously acquired by an electrode in a particular solution, in the absence of net current flow. The units of open circuit potential are volts (V).

SF
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Permittivity (relative)
Ratio of the electric field strength in a vacuum to the electric field strength in a specified medium. Symbol ε_r, dimensionless. (Formerly called the dielectric constant.)

SF
stephen.fletcher@lboro.ac.uk

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Phase transition A phase transition occurs when the molar $\rightarrow$ *Gibbs energy* (also called free energy) of a system is non-analytic (non-smooth) over a small range of a thermodynamic variable, implying an abrupt change in the value of that variable. In many areas of science, the heat capacity is the variable of most interest. But in electrochemistry the molar density plays the central role. According to the Ehrenfests *[i]* phase transitions may be divided into two principal classes based on the type of non-analyticity involved. The most commonly observed phase transitions (such as those involving solid/liquid/gas transformations) are classified as first-order transitions because they exhibit a discontinuity in the first derivative of the molar Gibbs energy with respect to chemical potential. Some less commonly observed phase transitions are classified as second-order transitions because they exhibit a discontinuity in the second derivative of the molar Gibbs energy. For example, the ferromagnetic phase transition in iron involves a discontinuity in the second derivative of the molar Gibbs energy with respect to the magnetic field. Phase transitions are widely observed in electrochemical systems because high values of molar Gibbs energy can easily be reached by changing the electrode potential. A notable mechanism by which first order phase transitions are initiated is called nucleation. Other mechanisms include replacement (short range diffusive re-ordering), and displacement (short range non-diffusive re-ordering, also known as Martensitic re-ordering).

Ref.: [i] Ehrenfest P, Ehrenfest T (1959) The Conceptual Foundations of the Statistical Approach in Mechanics. Cornell University Press, Ithaca, New York

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Phospholipids   Phospholipids are a class of lipids containing negatively charged phosphate groups. The commonest phospholipids are phosphoglycerides (general formula $(R.COO)CH_2[(R'.COO)CH]CH_2O(PO_2^-\ X^+)$. These are biological surfactants made up of one glycerol molecule attached to two fatty acid moieties (R and R') and one phosphate group. Structurally, phosphoglycerides resemble triglycerides except that the phosphate group replaces one of the fatty acids. The alkyl chains of the fatty acids (R and R') are hydrophobic whereas the phosphate group is hydrophilic. Phosphoglycerides therefore readily self-assemble onto bilayer micelles that can solubilize organic compounds.

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Polarizability (of a molecule)

There are numerous different mechanisms that contribute to the total polarizability of a molecule. The three most important of these are termed electron polarizability, molecular-distortion polarizability, and orientation polarizability. All these parameters are measured as statistical averages over large numbers of molecules present in the bulk phase. (1) Electron polarizability α is a measure of the ease with which electrons tend to be displaced from their zero-field positions by the applied electric field. Thus, the electron polarizability of a molecule is defined as the ratio of induced dipole moment μ_{ind} (coulomb meters) to the inducing electric field E (volts per meter):

$$\alpha = \frac{\mu_{ind}}{E}$$

The SI units of polarizability are $C\,m^2\,V^{-1}$. In the older literature, electron-nucleus polarizability was often defined as

$$\alpha' = \frac{\alpha}{4\pi\varepsilon_0}$$

so that the units were cm^3. Here ε_0 is the vacuum permittivity (8.854×10^{-12} F/m).

(2) Molecular distortion polarizability is a measure of the ease with which atomic nuclei within molecules tend to be displaced from their zero-field positions by the applied electric field. (3) Orientation polarizability is a measure of the ease with which dipolar molecules tend to align against the applied electric field. The electron polarizability of an individual molecule is related to the → *permittivity (relative) of a dielectric medium* by the → *Clausius-Mossotti relation*.

<div style="text-align: right">

SF
stephen.fletcher@lboro.ac.uk

</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Polarization (of an electrode)

The difference between the closed circuit potential E_C and the → open circuit potential E_O. The units of electrode polarization are volts (V).

<div style="text-align: right">

SF
stephen.fletcher@lboro.ac.uk

</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Polarization density (of a dielectric medium)

The polarization density P is the difference between the electric displacement in a dielectric medium D_C and the electric displacement in a vacuum D_O. (Note. The electric displacement is defined as the product of the electric field strength E and the permittivity ε .) The polarization density of a dielectric medium may also be thought

of as the volume density of permanent and induced dipole moments. The units of polarization density D are therefore coulomb-meters per cubic meter, *i.e.* coulombs per square meter (C/m^2).

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Pole (i) the locus of the charge in a static electric field, or (ii) the electrically isolated terminus of a conducting path. (This latter usage, though regarded as old-fashioned, still survives in technical electrochemistry, and in circuit theory.) The inadequacy of the word in connection with electrolysis was noted by → *Faraday*, and, after conferring with → *Whewell*, he adopted the word → *electrode* [i].
Ref.: [i] Faraday M. Letter to William Whewell, 24 April 1834. In Frank A.J.L. James (ed.) The Correspondence of Michael Faraday (1993) Vol 2, 176.

<div align="right">FS, GI, SF</div>

<div align="right">**fscholz@uni-greifswald.de**</div>

Citation: F.Scholz, G.Inzelt and S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Randles semicircle When subjected to small amplitude perturbations, it is often found that electrochemical systems respond in a manner that is both linear and homogeneous. That is to say, they behave in such a way that the output from two simultaneously-applied perturbations is identical to the sum of the outputs of each perturbation applied independently. When this is the case, the "principle of superposition" is said to hold, and the electrochemical system may be modeled by a set of linear circuit elements arranged in an equivalent circuit. The special value of equivalent circuits is that they permit many of the tools of electric circuit theory (such as the Laplace transform and the Fourier transform) to be applied to the modeling process. A further advantage is that small-amplitude data may be analyzed (and visualized) in the complex plane of → *impedance*, which gives rise to the field of → *electrochemical impedance spectroscopy*. A widely applicable equivalent circuit is known as the → *Randles-Ershler impedance*. In the absence of diffusion control, the Randles-Ershler impedance generates a highly characteristic "Randles semicircle" in the first quadrant of the → *complex plane plot* (electrochemical convention), indicating the presence of a charge transfer reaction in parallel with the charging of the electrochemical → *double layer*.

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Randles-Ershler impedance An "equivalent circuit" named in honor of John E.B. Randles (1912-1998) and Boris V. Ershler (1908-1978), *[i,ii,iii]*. It consists of a parallel arrangement of a double layer capacitor and an interfacial impedance, in series with a solution resistance. Sometimes the interfacial → *impedance* is further split into a series arrangement of a charge transfer resistance and a Warburg impedance. In general, equivalent circuits consist of ideal linear circuit elements in series, parallel, or even more complex arrangements. Typical elements include resistors, inductors, and capacitors. More rarely, → *Warburg impedances*, → *transmission lines*, and → *constant phase elements* are also inserted. The principal significance of equivalent circuits is that they provide a visual representation of the mathematical couplings between different interfacial processes.

Refs.: [i] Randles JEB (1947) Discuss Faraday Soc 1:11; [ii] Ershler BV (1947) Discuss Faraday Soc 1:269; [iii] Dolin P, Ershler BV (1940) Acta Phys Chim URSS 13:747

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).

Template synthesis is the generic name for a diverse group of methods used to prepare nano-structured materials. Template synthesis typically involves the use of an inert solid phase of highly regular structure (such as a microporous membrane or a colloidal crystal) which is able to restrict the physical form of a reaction product [i]. Template methods are attractive because, in principle, they allow the size, shape, purity and chirality of nano-structured materials to be controlled experimentally. In electrochemistry, template synthesis means the preparation of electrode materials and electrode surfaces using templates to direct the deposition and patterning *[ii]*. The goal of template-synthesis is to get micro- or nano-structures, e.g., for achieving → *microelectrode* behavior, or certain catalytic activities, or to study imprints of the template material to get information on the pore structure of the template *[iii]*. In these techniques the pores of micro- or nanoporous materials, e.g., → *membranes*, are used to synthesize the particles, or to deposit material from solutions. Dissolution of the template material leaves the micro or nanoparticles or structures on the electrode surface.

*Refs.: [i] Bartlett PN, Birkin PR, and Ghanem MA (2000) J Chem Soc Chem Commun 1671; [ii] Martin CR, Mitchell DT (1999) Template-synthesized nanomaterials in electrochemistry. In Electroanal Chem, vol 21, Bard AJ, Rubinstein I (eds), Marcel Dekker, New York. [iii] Hasse U, Scholz F (2006) J Solid State Electrochem **10**:380*

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

<div align="right">**stephen.fletcher@lboro.ac.uk**</div>

Thermodynamic temperature, T

Base quantity in the system of quantities upon which SI is based. A temperature of 0 K is called "absolute zero". It coincides with the minimum molecular activity, i.e., thermal energy of matter. Thermod. temp. was formerly called "absolute temperature". In practice, the International Temperature Scale of 1990 (ITS-90) *[i]* serves as the basis for high-accuracy temperature measurements. Up to 700 K, the most accurate measurements of thermodynamic temperature are the NBS/NIST results for Constant Volume Gas Thermometry (CVGT). Above 700 K, spectral radiometry is used to measure the ratio of radiances from a reference blackbody and from a blackbody at unknown thermodynamic temperature. The idea of a thermodynamic temperature scale was first proposed in 1854 by the Scottish physicist William Thomson, Lord Kelvin. He realized that temperature could be defined *independently of the physical properties of any specific substance*. Thus, for a substance at thermal equilibrium (which can always be modeled as a system of harmonic oscillators) the thermodynamic temperature could be defined as the average energy per harmonic oscillator divided by Boltzmann's constant [iv]. Today, the unit of thermodynamic temperature is called the kelvin (K), and is defined as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

Refs.: [i], Preston-Thomas H (1990) Metrologia 27:3, errata Metrologia 27:107. [ii], Quinn TJ (1990) Temperature Academic Press, New York; [iii] Quack M, Frey J (2005) Quantities, Units and Symbols in Physical Chemistry, 3rd ed, Nov 2005, IUPAC, Pure Appl Chem.Manuscript ID PAC-REC-05-11-10; [iv] [i] Lord Kelvin (William Thomson) (1848) Phil Mag 33:313. Reprinted in: Sir William Thomson (1882) Mathematical and Physical Papers, Vol 1 , Cambridge University Press, pp. 100-106.

<div align="right">

FS, SF
stephen.fletcher@lboro.ac.uk

</div>

Vesicles

Vesicles (i) In cell biology, a vesicle is a small enclosed compartment, separated from the cytosol of a eukaryotic cell by a membrane of fatty acids. Vesicles are responsible for the transport of various compounds across cell membranes by → *endocytosis* and → *exocytosis*. (ii) In colloid chemistry, a vesicle is an assembly of surfactant molecules, about 0.1-100 μm in diameter, that contains solvent, usually water, both inside and outside. The assembled surfactant may consist of a single bi-layer or be formed of multi-layers. Good examples of vesicle-forming surfactants are provided by → *Phospholipids.* Technologically, man-made vesicles can encapsulate bio-active molecules, hence their increasing use in drug delivery. See also → *liposomes*.

FS, SF

stephen.fletcher@lboro.ac.uk

Work (electrical)

Consider a single-phase system in which there is also a finite electric potential. Further consider a point-sized charged species within that system. Then its chemical potential μ_i and electric potential ϕ_i are related by the equation

$$\mu_i = \mu_i^0 + RT \ln a_i + z_i F \phi_i$$

where μ_i^0 is the standard chemical potential in the absence of the electric potential, a_i is the activity of the charged species, z_i is its charge number, and F is the Faraday constant. We see immediately that the chemical potential μ_i is a function of ϕ_i as well as of a_i. Further, provided that the electric potential ϕ_i does not vary strongly with distance, the requirement of a point-sized charged species may be dropped, and the analysis may be applied to ions. In electrochemistry there is a convention, dating back to Guggenheim[i], of re-writing the chemical potential μ_i as the electrochemical potential $\widetilde{\mu}_i$ whenever $\phi_i > 0$, although this is, strictly speaking, un-necessary. Nevertheless, we adopt that convention here. Thus, we write

$$\widetilde{\mu}_i = \mu_i^0 + RT \ln a_i + z_i F \phi_i \qquad \text{(electrochemical convention)}$$

The corresponding equation for a system involving several phases (each one of which may have a different electric potential) is simply the sum of the equations for the various phases. Such a multiphase system might be, for example, an interface between an electrode and a solution; an interface between two immiscible electrolyte solutions (ITIES); or a solution-membrane-solution system (e.g. a cell wall). Regarding units, we note that the electric potential ϕ_i (also called the electrostatic potential) is defined as the potential energy per unit of charge placed in the electric field, and hence is measured in the electrical unit of volts. By contrast, the electrochemical potential is a thermodynamic potential and hence is measured in joules per mole. Indeed, the electrochemical potential may also be regarded as the partial molar Gibbs energy of the species i at the specified electric potential. The <u>molar electric work</u> is the triple product $z_i F \phi_i$, which is the work required to raise the electric potential of one mole of charged species i from zero to the ambient electric potential ϕ_i. Its units are joules per mole. By the second law of thermodynamics, the electrochemical potential $\widetilde{\mu}_i$ is necessarily constant and uniform across all phases in a multiphase system at equilibrium. However, no such restriction applies to the electric potential ϕ_i at

equilibrium. There may therefore be (in fact, often is) an <u>electric potential drop</u> inside a multiphase system at thermodynamic equilibrium. This accounts for the widespread existence of electrical double layers, membrane potentials, space-charge regions, etc throughout the physical world.

Refs.: [i] Guggenheim EA (1949), Thermodynamics (North-Holland Publishing Company, Amsterdam.

<div align="right">

SF
stephen.fletcher@lboro.ac.uk

</div>

Citation: S. Fletcher, in "Electrochemical Dictionary" (Edited by Allen J. Bard, György Inzelt , and Fritz Scholz). Publisher: Springer (2008).