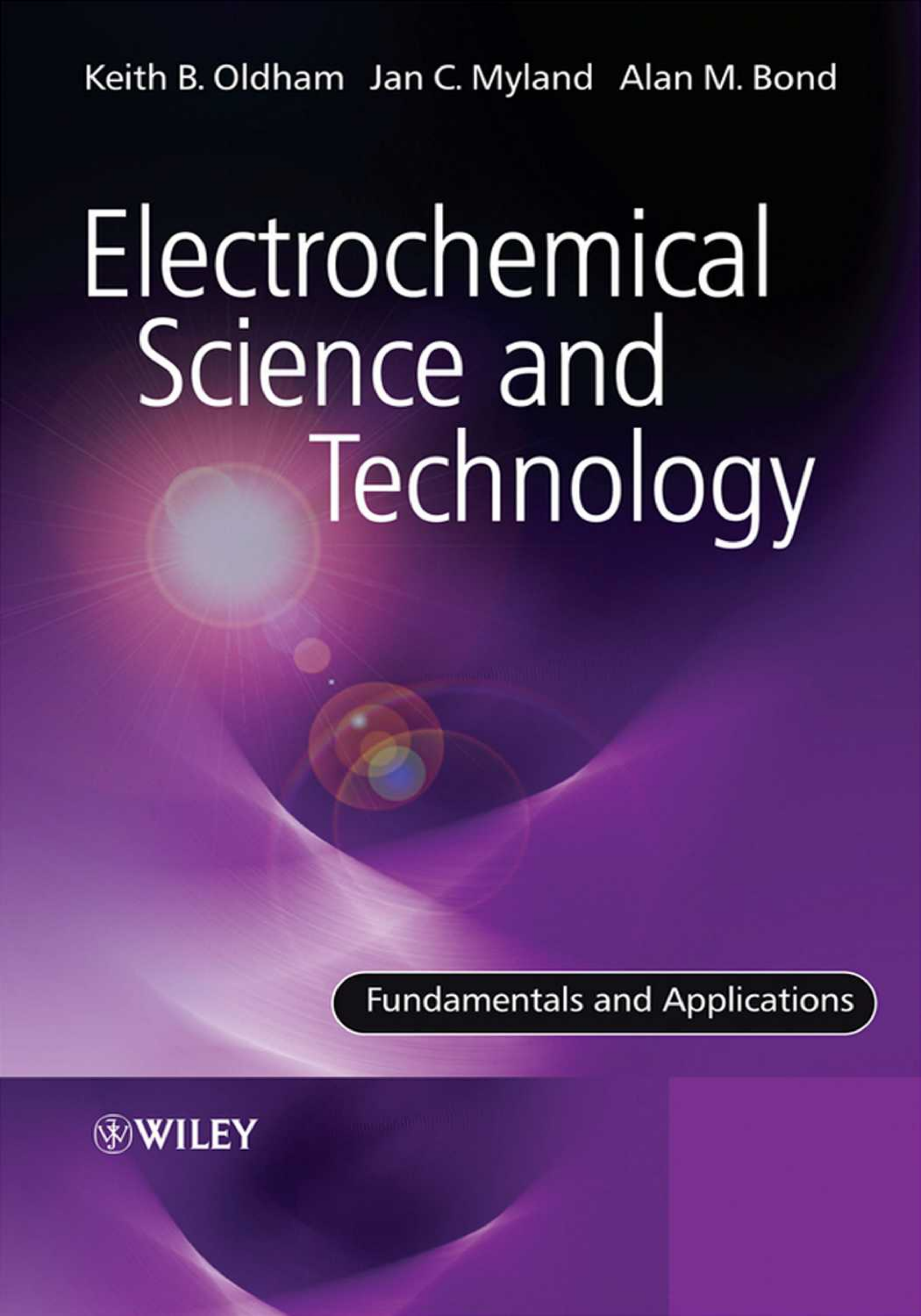
Keith B. Oldham   Jan C. Myland   Alan M. Bond

Electrochemical Science and Technology

Fundamentals and Applications



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ELECTROCHEMICAL SCIENCE AND TECHNOLOGY

Fundamentals and Applications

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WILEY
A John Wiley & Sons, Ltd., Publication

This edition first published 2012
© 2012 John Wiley & Sons, Ltd
Reprinted with corrections 2013

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data

Oldham, Keith B.
Electrochemical science and technology: fundamentals and applications / Keith B. Oldham, Jan C. Myland, Alan M. Bond.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-71085-2 (cloth) -- ISBN 978-0-470-71084-5 (pbk.) -- ISBN 978-1-119-96588-6 (ePDF) -- ISBN 978-1-119-96599-2 (oBook) -- ISBN 978-1-119-96684-5 (ePub.) -- ISBN 978-1-119-96685-2 (Mobi)
1. Electrochemistry. I. Myland, Jan C. II. Bond, A. M. (Alan Maxwell), 1946- III. Title.
QD553.O42 2011
541'.37--dc23
2011037230

A catalogue record for this book is available from the British Library.

Print ISBN: 9780470710852 (HB)

Print ISBN: 9780470710845 (PB)

Set in 11pt Times New Roman by the authors using WordPerfect

Printed and bound in Singapore by Markono Print Media Pte Ltd

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Preface

This book is addressed to all who have a need to come to grips with the fundamentals of electrochemistry and to learn about some of its applications. It could serve as a text for a graduate, or senior undergraduate, course in electrochemistry at a university or college, but this is not the book's sole purpose.

The text treats electrochemistry as a scientific discipline in its own right, not as an offshoot of physical or analytical chemistry. Though the majority of its readers will probably be chemists, the book has been carefully written to serve the needs of scientists and technologists whose background is in a discipline other than chemistry. Electrochemistry is a quantitative science with a strong reliance on mathematics, and this text does not shy away from the mathematical underpinnings of the subject.

To keep the size and cost of the book within reasonable bounds, much of the more tangential material has been relegated to "Webs" – internet documents devoted to a single topic – that are freely accessible from the publisher's website at www.wiley.com/go/EST. By this device, we have managed largely to avoid the "it can be shown that" statements that frustrate readers of many textbooks. Other Webs house worked solutions to the many problems that you will find as footnotes scattered throughout the pages of *Electrochemical Science and Technology*. Another innovation is the provision of Excel® spreadsheets to enable the reader to construct accurate cyclic (and other) voltammograms; see Web#1604 and Web#1635 for details.

It was in 1960 that IUPAC (the International Union of Pure and Applied Chemistry) officially adopted the *SI* system of units, but electrochemists have been reluctant to abandon centimeters, grams and liters. Here, with some concessions to the familiar units of concentration, density and molar mass, we adopt the *SI* system almost exclusively. IUPAC's recommendations for symbols are not always adhered to, but (on pages 195 and 196) we explain how our symbols differ from those that you may encounter elsewhere. On the same pages, we also address the thorny issue of signs.

Few references to the original literature will be found in this book, but we frequently refer to monographs and reviews, in which literature citations are given. We recommend Chapter IV of F. Scholz (Ed.), *Electroanalytical Methods: guide to experiments and* *applications 2E*, Springer, 2010, for a comprehensive listing of the major textbooks, monographs and journals that serve electrochemistry.

The manuscript has been carefully proofread but, nevertheless, errors and obscurities doubtless remain. If you discover any such anomalies, we would appreciate your bringing it to our attention by emailing Alan.Bond@monash.edu. A list of errata will be maintained on the book's website, www.wiley.com/go/EST.

Electrochemical Science and Technology: fundamentals and applications has many shortcomings of which we are aware, and doubtless others of which we are ignorant, and for which we apologize. We are pleased to acknowledge the help and support that we have received from Tunde Bond, Steve Feldberg, Hubert Girault, Bob de Levie, Florian Mansfeld, David Rand, members of the Electrochemistry Group at Monash University, the Natural Sciences and Engineering Research Council of Canada, the Australian Research Council, and the staff at Wiley's Chichester office.

July 2011

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1

Electricity

At the heart of electrochemistry lies the coupling of chemical changes to the passage of electricity. The science of electricity is a branch of physics, but here we start our study of electrochemistry by reviewing the principles of electricity from a more chemical perspective.

Electric Charge: the basis of electricity

Charge is a property possessed by matter. It comes in two varieties that we call **positive charge** and **negative charge**. The salient property of electric charges is that those of opposite sign attract each other, while charges of like sign repel, as illustrated.

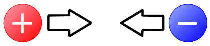

Figure 1-1 Charges of unlike sign attract each other, those of like sign repel.

Charge is measured in **coulombs** and it occurs as multiples of the **elementary charge**

1:1 $$Q_0 = 1.6022 \times 10^{-19}\ \text{C}$$ elementary charge

Charge is not found in isolation, it always accompanies matter. Such fundamental particles as the proton H^+ and the electron e^- possess single charges, that is $\pm Q_0$, as do many **ions**[101] such as the sodium Na^+, chloride Cl^-, and hydronium H_3O^+ ions. Other ions, such as the magnesium Mg^{2+} cation and phosphate PO_4^{3-} anion are multiply charged. Even neutral molecules, which have no net charge, are held together electrically and frequently have charges on their surfaces. For example, one side of the water molecule pictured in Figure 1-2 has a negative region, the other side being positively charged. Such structures,

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[101] Ions are charged atoms or groups of atoms; if positively charged, they are called **cations**, whereas **anion** is the name given to a negative ion.

Electrochemical Science and Technology: Fundamentals and Applications Keith B. Oldham, Jan C. Myland, and Alan M. Bond

called **dipoles**[102], behave as if they contain small (generally less than Q_0) localized positive and negative charges separated by a small distance.

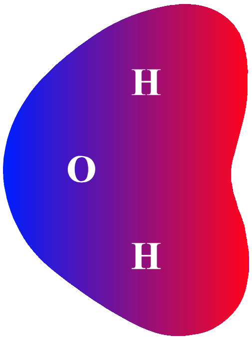

Figure 1-2 The architecture of the **dipolar** water molecule. The red and blue surface regions are charged positively and negatively respectively.

Ions and electrons are the actors in the drama of electrochemistry, as are molecules. Most often these charged particles share the stage and interact with each other, but in this chapter we mostly consider them in isolation. The electrical **force** f between two charges Q_1 and Q_2 is independent of the nature of the particles on which the charges reside. With r_{12} as the distance between the two charges, the force[103] obeys a law

1:2 $$f = \frac{Q_1 Q_2}{4\pi\varepsilon r_{12}^2}$$ Coulomb's law

attributed to Coulomb[104]. The *SI* unit of force is the **newton**[105], N. Here ε is the **permittivity** of the medium, a quantity that will be discussed further on page 13 and which takes the value

1:3 $$\varepsilon_0 = 8.8542\times10^{-12}\ \mathrm{C^2\ N^{-1}\ m^{-2}}$$ permittivity of free space

when the medium is free space[106]. The force is repulsive if the Q's have the same sign, attractive otherwise. To give you an idea of the strong forces involved, imagine that all the Na^+ cations from 100 grams of sodium chloride were sent to the moon, then their attractive force towards the earthbound chloride anions probably exceeds your weight[107].

A consequence of the mutual repulsion of two or more similar charges is that they try to get as far from each other as possible. For this reason, the interior of a phase[108] is usually free of net charge. Any excess charge present will be found on the surface of the phase, or very close to it. This is one expression of the **principle of electroneutrality**.

---

[102] Read more at Web#102 about the water dipole and **dipole moments**.

[103] Calculate the repulsive force (in newtons) between two protons separated by 74.14 pm, the internuclear distance in the H_2 molecule. See Web#103 to check your result.

[104] Frenchman Charles Augustin de Coulomb, 1736 – 1806, first confirmed the law experimentally.

[105] Sir Isaac Newton, 1643 – 1727, renowned English scientist.

[106] The permittivity of free space, ε_0, is also known as the **electric constant**.

[107] Justify this statement. See Web#107.

[108] A **phase** is a region of uniform chemical composition and uniform physical properties.

Charges at Rest: electric field and electrical potential[109]

Coulomb’s law tells us that an electric charge can make its presence felt at points remote from its site. An **electric field** is said to exist around each charge. The electric field is a vector; that is, it has both direction and strength. Figure 1-3 shows that the field around an isolated positive charge points away from the charge, at all solid angles.

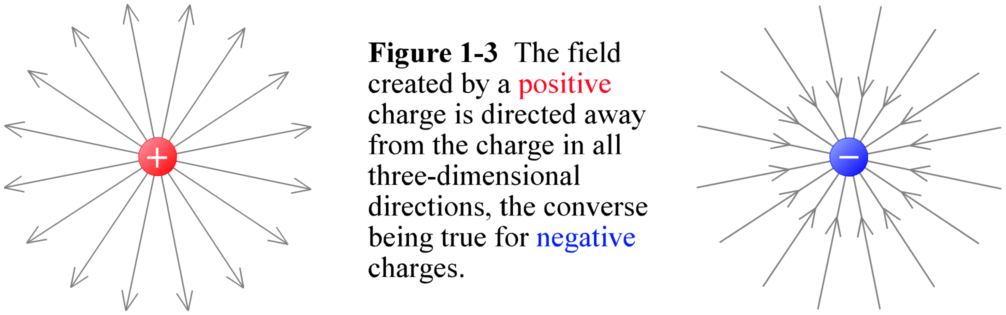

Figure 1-3 The field created by a positive charge is directed away from the charge in all three-dimensional directions, the converse being true for negative charges.

The strength of an electric field at a point can, in principle, be assessed by placing a very small positive “test charge” Q_{test} at the point. The choice of a sufficiently *small* test charge ensures that the preexisting field is not disturbed. The test charge will experience a small **coulombic force**. The **electric field strength**[110], or more simply the **field**, X, is then defined as the quotient of the force by the test charge:

1:4 $$X = \frac{f}{Q_{\text{test}}}$$ definition of field

and therefore it has the unit[111] of newtons per coulomb, $\mathrm{N\,C^{-1}}$. Thus, for any static charge distribution, it is possible to calculate field strengths using Coulomb’s law[112].

Force, and therefore also electric field, is a vector quantity. In this book, however, we shall avoid the need to use vector algebra by addressing only the two geometries that are of paramount importance in electrochemistry. These two geometries are illustrated in Figures 1-4 and 1-5. The first has **spherical symmetry**, which means that all properties are uniform on any sphere centered at the point $r = 0$. Thus, there is only one spatial coordinate to consider; any property depends only on the distance r, where $0 \le r < \infty$. The

---

[109] “Electric” and “electrical” are adjectives of identical meaning. A quirk of usage is that we usually speak of electric field and electric charge but electrical potential and electrical conductivity.

[110] Physicists use E for field strength, but traditionally electrochemists reserve that symbol for potential, a holdover from the antiquated term “electromotive force”.

[111] or, equivalently and more commonly, volt per meter, $\mathrm{V\,m^{-1}}$. See equation 1:9 for the reason.

[112] Consider two protons separated by 74.14 pm, the internuclear distance in the H_2 molecule. Find the field strength and direction at points 25%, 50% and 75% along the line connecting the protons. For a greater challenge, find the field at some point not on the line of centers. See Web#112.

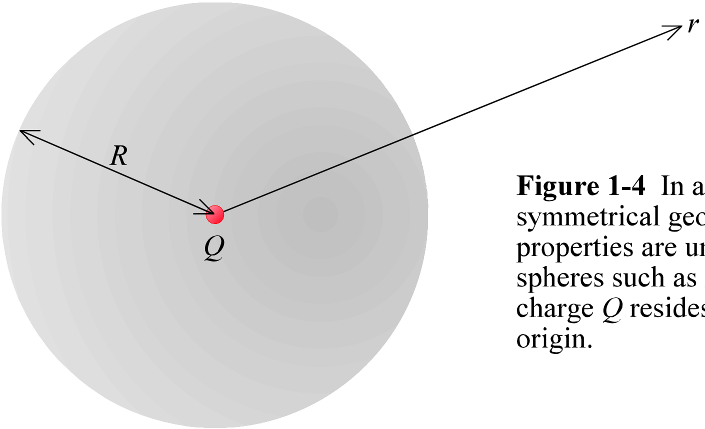

Figure 1-4 In a spherically symmetrical geometry, all properties are uniform on spheres such as $r = R$. Here a charge Q resides at the $r = 0$ origin.

second geometry of prime electrochemical concern has **planar symmetry**, meaning that uniformity of properties exists in planes. The space of interest lies between two parallel planes separated by a distance L, the planes being very much larger than L in their linear dimensions. Again, there is only one coordinate to consider, now represented by x, where $0 \leq x \leq L$. Each of these two geometries is simple in that there is only one relevant distance coordinate. Thus, when we discuss the field, we mean implicitly the field strength in the direction of increasing r or x.

Coulomb's law tells us that the electric field strength falls off with distance according to the **inverse-square law**: at double the distance from a point source the field is

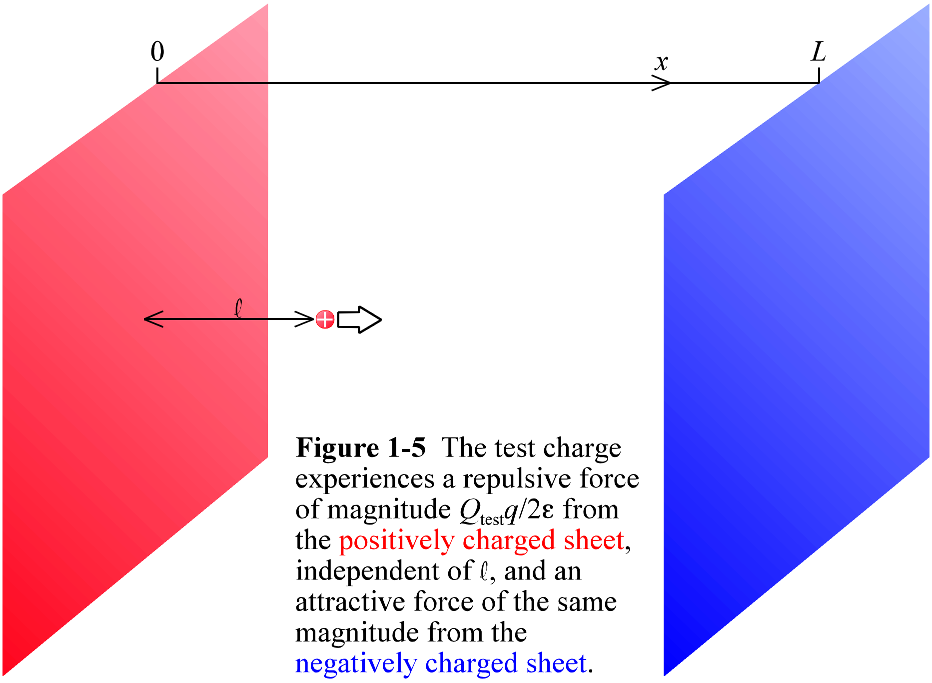

Figure 1-5 The test charge experiences a repulsive force of magnitude $Q_{\text{test}}q/2\varepsilon$ from the positively charged sheet, independent of ℓ, and an attractive force of the same magnitude from the negatively charged sheet.

one-fourth. Thus, it is evident that at a distance R from the point charge Q

1:5 $$X(R) = \frac{f}{Q_{\text{test}}} = \frac{Q}{4\pi\varepsilon R^2}$$ inverse-square law

The field is uniform at all points on the sphere shown in Figure 1-4, falling off as $1/R^2$. The inverse-square law does not apply to the field in planar symmetry. In that geometry, electrochemists are interested in the field between two charged planes, such as electrodes. In Figure 1-5 the left-hand plane is uniformly charged such that the **charge density** (measured in coulombs per square meter, C m^{-2}) is q. The field strength caused by that plane, at a distance ℓ, can be shown[113] to be simply $X(\ell) = q/[2\varepsilon]$. Taking into account the second, oppositely charged, plane, the total field is

1:6 $$X(\ell) = \frac{q}{\varepsilon}$$ planar symmetry

Provided that the charged sheets are large enough and parallel, the adjacent field doesn't depend on location. The field strength[114] is constant!

The concept of a small "test charge" is a valuable fiction; it is also used to define electrical potential. Imagine that we place a test charge at point A, and move it a small distance δr towards a much larger fixed charge as in Figure 1-6. It needs the expenditure of **work** $w_{\text{A}\to\text{B}}$ for the test charge to reach its destination, point B. Work (measured in **joules**[115], J) can be calculated as *force* × *distance* or, in this case:

1:7 $$w_{\text{A}\to\text{B}} = f \times [-\delta r] = -Q_{\text{test}} X \delta r$$

The negative sign arises because the journey occurs in the negative r direction. It is said that an **electrical potential** exists at each of points A and B and we define the difference between these potentials as the coulombic work needed to carry a test charge between the two points divided by the magnitude of the test charge. Hence,

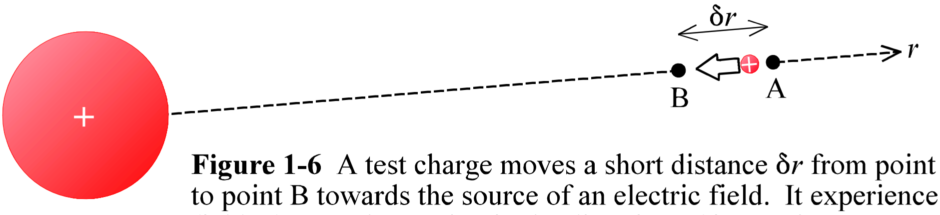

Figure 1-6 A test charge moves a short distance δr from point A to point B towards the source of an electric field. It experiences a field of strength X acting in the direction of increasing r.

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[113] See Web#113 for the derivation from Coulomb's law. It involves an integration in polar coordinates.

[114] Two square metal plates, each of an area of 6.25 cm^2 are separated by 1.09 cm. They are oppositely charged, each carrying 2.67 nC. The pair is immersed in acetonitrile, a liquid of permittivity 3.32×10^{-10} $\text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$. Calculate the field (strength and direction) at a point 500 μm from the negatively charged surface. Check your answer at Web#114.

[115] James Prescott Joule, 1818 – 1889, English scientist and brewer.

1:8 $$\phi_B - \phi_A = \frac{w_{A\to B}}{Q_{\text{test}}} = -X\delta r$$

Notice that the definition defines only the *difference* between two potentials, and not the potential ϕ itself[116,117]. In differential notation, the equation becomes[118]

1:9 $$\frac{d\phi}{dr} = -X \qquad \text{definition of potential}$$

The unit of electrical potential is the **volt[119]**. The first equality in 1:8 shows that one volt equals one joule per coulomb ($V = J\ C^{-1}$).

The situation depicted in Figure 1-6 is simple because the distance moved, in that case, was small enough that the field could be treated as constant. For a longer journey one finds, making use of equation 1:5,

1:10 $$\phi_B - \phi_A = -\int_A^B X(r)dr = \frac{-Q}{4\pi\varepsilon}\int_{r_A}^{r_B}\frac{dr}{r^2} = \frac{Q}{4\pi\varepsilon}\left(\frac{1}{r_B} - \frac{1}{r_A}\right) \qquad \text{spherical symmetry}$$

Moreover, the situation depicted in Figure 1-6 is especially simple in that the journey was along a radial direction. A geometry like that in Figure 1-7 is more general. The force on the moving test charge now varies along the journey, not only because the field strength changes, but also because the angle θ constantly alters as the charge moves. The potential difference between points A and B in this geometry can be calculated from the following chain of equalities

1:11 $$\phi_B - \phi_A = \frac{w_{A\to B}}{Q_{\text{test}}} = \frac{-1}{Q_{\text{test}}}\int_A^B f\cos\{\theta\}\,d\ell = -\int_A^B X\cos\{\theta\}\,d\ell$$

Both X and θ change as the distance ℓ traveled by the test charge increases. Remarkably, the result of the integration does not depend on the route that the test charge travels on its journey from A to B. The work, and therefore the potential change, is exactly the same for the direct route as for the circuitous path via point C in Figure 1-7, and this fact greatly simplifies the calculation of the potential difference[120]. In fact, equation 1:10 applies.

Equation 1:9 shows the electric field strength to be the negative of the gradient of the electrical potential. In electrochemistry, electrical potential is a more convenient quantity than electric field, in part because it is not a vector. It does have the disadvantage, though,

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[116] Calculate the electrical potential difference between the 75% and 50% points in the problem cited in Footnote 112. Which is the more positive? Check your answer at Web#116.

[117] Refer to the problem in Footnote 114 and find the potential difference between the point cited and a point at the surface of the nearby electrode. Web#117 has the answer.

[118] From Coulomb's law derive an expression for the electrical potential difference between a point at a distance r from an isolated proton and a point at infinity. Our derivation will be found at Web#118.

[119] Alessandro Guiseppe Antonio Anastasio Volta, 1745 – 1827, Italian scientist.

[120] See Web#120 for the derivation of the potential change accompanying the A → B journey in Figure 1-7.

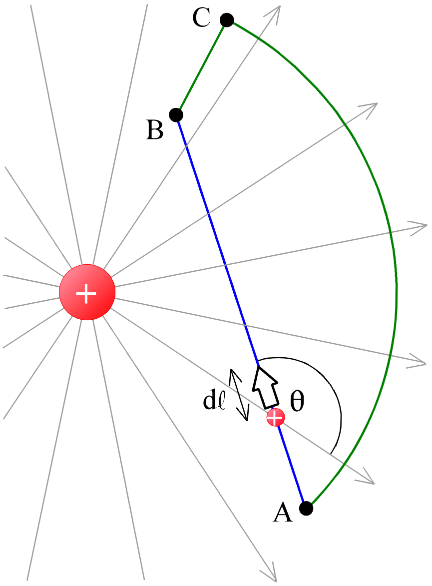


Figure 1-7 A test charge journeying by the direct A → B route encounters a field that is constantly changing in both strength and direction. However, the work involved is the same as via the route A → C → B. No work accompanies the A → C journey along the circular arc.

of being a relative, rather than an absolute quantity. For this reason we more often encounter the symbol $\Delta\phi$ rather than ϕ itself. In this book the phrase **electrical potential difference** will often be replaced by the briefer term **voltage**.

We can define only *differences* in electrical potential. Worse, we can define differences in the electrical potential only between points that lie within phases of the *same* (or very similar) compositions. The essential reason for this is that we do not have innocuous "test charges" at our disposal. We only have electrons, protons and ions. So when we try to measure the coulombic work in moving such charged particles from one phase to another, we inevitably encounter other energy changes arising from the change in the chemical environment in which the particle finds itself. Such **chemical work** is absent only if the departure and arrival sites have similar chemical compositions.

The electroneutrality principle prevents charges accumulating, other than near boundaries. A need exists to investigate the distribution of charge in spaces adjacent to boundaries, because it is at the junctions of phases that electrochemistry largely occurs. The symbol ρ is generally used to represent **volumetric charge density** (unit, coulombs per cubic meter, C m^{-3}). Do not confuse this quantity with q, the *areal* charge density (C m^{-2}).

Let us first consider the presence of space charge in the geometry of Figure 1-5. Imagine that, in addition to areal charge densities on the plates, there is a space charge in the region between the plates, its magnitude being $\rho(x)$ at any distance x from the left-hand plate. We seek the field at some point $x = \ell$. The space charge can be regarded as being made up of many thin wafers, each of areal charge density $\rho(x)\mathrm{d}x$. Each of these will contribute to the field, positively for the thin wafers to the left of $x = \ell$, negatively (think of the effect on a test charge) when $x > \ell$. Following the discussion surrounding Figure 1-5, it follows that the total field at the point of interest is

$$X(\ell) = \frac{q_0}{2\varepsilon} + \int_0^\ell \frac{\rho(x)}{2\varepsilon}\,\mathrm{d}x - \int_\ell^L \frac{\rho(x)}{2\varepsilon}\,\mathrm{d}x - \frac{q_L}{2\varepsilon} \tag{1:12}$$

where q_0 and q_L are the areal charge densities on the plates. This complicated formula simplifies massively on differentiating with respect to x; it becomes

$$\frac{\mathrm{d}X}{\mathrm{d}x}(\ell) = \frac{\rho(\ell)}{\varepsilon} \tag{1:13}$$

The local field gradient is simply the volumetric charge density there divided by the permittivity. In terms of the electrical potential, this may be written

$$\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{-\rho(x)}{\varepsilon} \tag{1:14}$$

Poisson's equation
planar symmetry

This is **Poisson's equation**[121] for planar geometry; it will find use in Chapter 13. For a spherically symmetric geometry, as in Figure 1-4, Poisson's equation is more complicated, but can be shown[122] to be

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left\{r^2\frac{\mathrm{d}\phi}{\mathrm{d}r}\right\} = \frac{-\rho(r)}{\varepsilon} \tag{1:15}$$

Poisson's equation
spherical symmetry

This law finds application in the Debye-Hückel theory discussed in the next chapter.

Capacitance and Conductance: the effects of electric fields on matter

Materials may be divided loosely into two classes: electrical **conductors** that allow the passage of electricity, and **insulators** that do not. The physical state is irrelevant to this classification; both classes have examples that are solids, liquids and gases. Conductors themselves fall into two main subclasses according to whether it is electrons or ions that are the **charge carriers** that move in response to an electric field.

$$\text{materials}\begin{cases}\text{insulators}\\[2ex] \text{conductors}\begin{cases}\text{electronic conductors}\\ \text{ionic conductors}\end{cases}\end{cases}$$

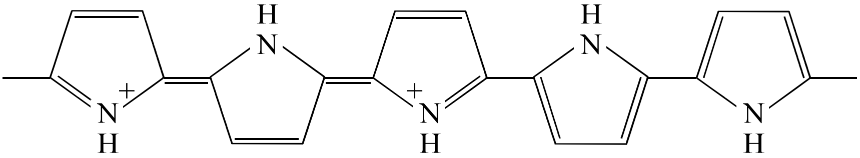
Electronic conductors owe their conductivity to the presence of **mobile electrons**. All **metals** are electronic conductors, but some solid inorganic oxides and sulfides (e.g.

---

[121] Siméon-Denis Poisson, 1781–1840, French mathematical physicist.

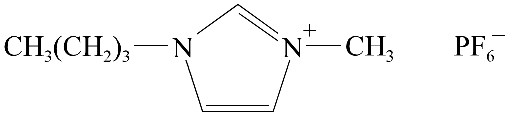
[122] This is derived in Web#122, preceded by an important lemma.

PbO_2 and[123] Ag_2S) also conduct electricity by virtue of electron flow. These, and most other **semiconductors**[124], owe their conductivity to an excess (**n-type**) or a deficit (**p-type**) of electrons compared with the number required to form the covalent bonds of the semiconductor's crystal lattice. In p-type semiconductors, the missing electrons are known as **holes** and solid-state physicists speak of the conductivity as being due to the motion of these positively-charged holes. Of course, it is actually an electron that moves into an existing hole and thereby creates a new hole at its former site. **Pi-electrons**[125] are the charge carriers in some other materials, of which graphite is the best known, but which also include newer synthetic **conductive polymers**. An example is the cationic form of polypyrrole, which conducts by motion of π-electron holes, through a structure exemplified by



Certain crystalline organic salts[126], known as **organic metals**, also conduct by virtue of π-electron motion. Yet another exotic electronic conductor is the tar-like material (see page 94 for an application) formed when the polymer of 2-vinylpyridine reacts with excess iodine to form a so-called "charge transfer compound".

The second class of materials that conduct electricity comprises the **ionic conductors**, which possess conductivity by virtue of the motion of anions and/or cations. Solutions of electrolytes (salts, acids and bases) in water and other liquids are the most familiar examples of ionic conductors, but there are several others. **Ionic liquids** resemble electrolyte solutions in that the motion of both anions and cations contributes to their electrical conductivity[127]: an example is 1-butyl-3-methylimidazolium hexafluorophosphate,



typical
ionic liquid

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[123] These two solids, and others, are slightly "nonstoichiometric". **Stoichiometric compounds** contain two or more elements in atom ratios that are stricly whole numbers. Water for example, contains *exactly* twice as many H atoms as O atoms. **Nonstoichiometric solids**, in contrast, depart often only slightly from this whole-number rule. Such an abnormality may occur naturally, being associated with defects in the crystal lattice, or be introduced artificially by admixture with a small quantity of a **dopant**.

[124] Read more about semiconductor conductivity at Web#124.

[125] In organic compounds having alternating single and double bonds in chains or rings, the electrons confer unusual properties, including abnormal electrical conductivity. Such electrons are described as "pi-electrons".

[126] Rich in π-electrons, the organic compound tetrathiafulvalene (TTF) readily forms the cation TTF^+. Another organic compound, tetracyanoquinodimethane (TCNQ), conversely forms the anion $TCNQ^-$. Accordingly, a mixture of these two compounds is in equilibrium with the salt $(TTF^+)(TCNQ^-)$ and the mixture, known as an "organic metal", has high electrical conductivity.

[127] Conductivities of various materials, including a similar ionic liquid are listed in the table on page 384.

Ionic liquids are, in fact, **molten salts**, but inorganic salts generally have much high melting points and conduct only at elevated temperatures. **Solid ionic conductors**[128], on the other hand, usually have only one mobile ionic species that may be either an anion (as in zirconia, ZrO_2, which, at high temperatures, allows oxide ions, O^{2-}, to migrate through its lattice[129]) or a cation (as in silver rubidium iodide, $RbAg_4I_5$, in which Ag^+ is mobile even at room temperature). An interesting case is provided by lanthanum fluoride, LaF_3, crystals that have been "doped" by a very small addition of europium fluoride, EuF_2. Because the **dopant** contributes fewer F^- ions to the lattice than its host, the crystal has "fluoride ion holes" which can move exactly as do electron holes in p-type semiconductors. Such crystals find applications in the fluoride ion sensor described on page 121.

A few materials permit the flow of electricity by both electronic and ionic conduction. An example of such mixed conduction is provided by the hot gases known as **plasmas**, which contain positive ions and free electrons[130]. A second example is the solution formed when sodium metal dissolves in liquid ammonia. Such a solution contains sodium Na^+ cations and solvated electrons (see page 41), both of which are mobile and share duties as charge carriers. Yet another example of mixed conduction is provided by hydrogen dissolved in palladium metal; here there is conduction by the migration of protons (hydrogen ions) as well as by electrons. In summary:

- conductors
  - electronic conductors
    - metals
    - some inorganic oxides and sulfides
    - semiconductors
      - n-type
      - intrinsic
      - p-type
    - organic metals and conductive polymers
  - mixed conductors
    - plasmas
    - some solids and solutions
  - ionic conductors
    - solutions of electrolytes
    - molten salts and other ionic liquids
    - solid ionic conductors
    - doped crystals

Though we shall not go into details, technological devices exist that produce a constant

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[128] also known as **solid electrolytes**, but this can be a misleading name.

[129] See pages 68 and 173 for an application. Zirconia exists in two forms, only one of which allows oxide ion motion; to stabilize this form, a small quantity of yttrium is added.

[130] Fluorescent lights and "neon lights" are examples.

difference of electrical potential. Such a device is called a **voltage source** and it has two terminals, one of which (often colored **red**) is at a more positive electrical potential than the other. There are other devices, named **voltmeters**, that can measure electrical potential differences. Both these devices are electronic; that is, they produce or measure an electrical potential difference by virtue of a deficit of electrons on their **red** terminals compared with the other. We do *not* have devices able directly to produce or measure deficits or excesses of other charged species, such as protons or ions, so studies on these latter charge carriers are conducted through the medium of electronic devices. Much of the later content of this book is devoted to experiments carried out to investigate the behavior of *ions*, via measurements made with *electronic* devices.

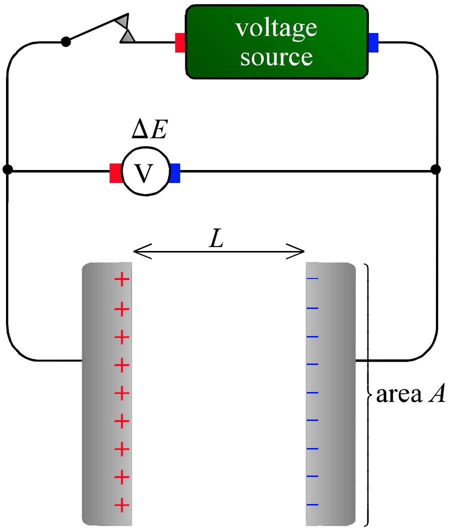

Figure 1-8 Parallel plates store electric charge, and retain the charge when the switch is opened.

Figure 1-8 shows a voltage source connected by wires and a switch to a voltmeter[131] and to a pair of parallel metal sheets, often called **plates**. On closing the switch, a brief surge of electrons occurs and causes charges to appear on the plates. Because of the electroneutrality principle, electrons arrive on the inward-facing surface of the right-hand metal plate. There is a complementary withdrawal of electrons from the inward-facing surface of the left-hand metal plate, leaving a positive charge on that surface.

We have seen in equation 1:6 that such a parallel distribution of charges produces a uniform electric field of strength $X = q/\varepsilon$ in the space between the plates. Here ε is the permittivity of the medium between the plates and, if this is air, it differs only marginally from ε_0. The direction of the field is towards the negative plate, rightwards in Figure 1-8. To carry a test charge a distance L, from a point adjacent to the negatively charged plate to a second point adjacent to the positive plate, will require work w equal to $XQ_{\text{test}}L$ or $qQ_{\text{test}}L/\varepsilon$ and, accordingly, the potential difference

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[131] An ideal voltmeter measures the voltage between its terminals while preventing any charge flow through itself. Modern voltmeters closely approach this ideal.

1:16 $$\Delta\phi = \phi_{\text{close to positive plate}} - \phi_{\text{close to negative plate}} = \frac{w}{Q_{\text{test}}} = \frac{qL}{\varepsilon}$$

exists between the destination and starting points. This shows, reasonably, that the medium close to the positive plate is at a more positive electrical potential than is the medium close to the negative plate. And of course, because the field is uniform, the potential changes linearly with distance between the two points as illustrated in Figure 1-9.

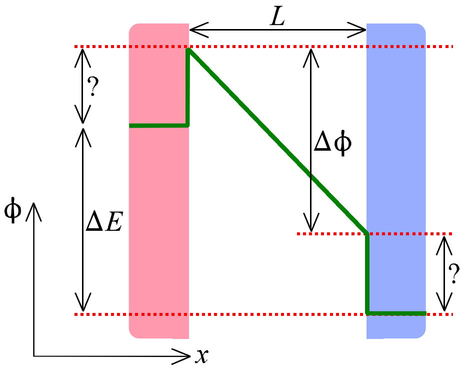

Figure 1-9 Measurable potential differences exist within the dielectric and between the metal phases, but not between points in dissimilar phases.

The $\Delta\phi$ in equation 1:16 is the potential difference between two points in the medium. The voltmeter shown in Figure 1-8 measures the difference ΔE in potential between the two metal plates. We now assert that $\Delta E = \Delta\phi$. As alluded to on page 7, we cannot measure (or even usefully define!) the potential difference between such chemically diverse media as metal and air, and so we have no information about the two potential differences labeled "?" in Figure 1-9. However, we do believe the two to be equal, because the "chemical work" in transferring any charged particle across the two interfaces will be the same. We shall continue to follow the convention that immeasurable electrical potentials that are imagined to exist within phases are symbolized ϕ, whereas electrical potential differences that can be measured by a voltmeter are denoted ΔE.

Return to Figure 1-8 and note that, on reopening the switch, the charges remain on the plates; electric charge is stored. A device, such as the parallel plates just described[132], that is able to store electric charge is called a **capacitor**. The stored charge is

1:17 $$Q = \frac{-A\varepsilon}{L}\Delta E$$

The ratio of the potential difference across a capacitor to the charge it stores is called the **capacitance** of the capacitor and is given the symbol C

1:18 $$\frac{-Q}{\Delta E} = C = \frac{\varepsilon A}{L}$$ definition of capacitance

planar symmetry

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[132] A capacitor can have a shape other than the parallel-plate configuration discussed here. Read about another important capacitor – the isolated sphere – at Web#132.

The unit of capacitance[133] is the **farad**, F. One farad equals one coulomb per volt. The negative sign in the last two equations, which you will often find missing from other texts, arises because positive charge flowing into a capacitor produces a negative charge on the remote plate.

We now turn to discuss what happens when an insulator is placed between the parallel plates of a capacitor. Equations 1:17 and 1:18 still apply, with ε becoming the permittivity[134] of the insulator. Permittivities vary greatly, as evidenced in the table on page 382. Notice that the listed permittivities[135] always exceed ε_0 so that the capacitor now has a larger capacitance and stores more charge[136] for a given voltage. The explanation for this is especially easy to understand when the insulator has a dipolar molecule, such as the organic liquid, acetonitrile, CH_3CN. Like the water molecule shown in Figure 1-2, this molecule has a positive end and a negative end and, in an electric field, such molecules tend to align themselves as illustrated in Figure 1-10. The effect is to create localized fields within the insulator that oppose, and partially neutralize, the imposed field, so that more external charge is required to reach the applied voltage ΔE. Insulators that behave in this, and similar[137], ways are often called **dielectrics**.

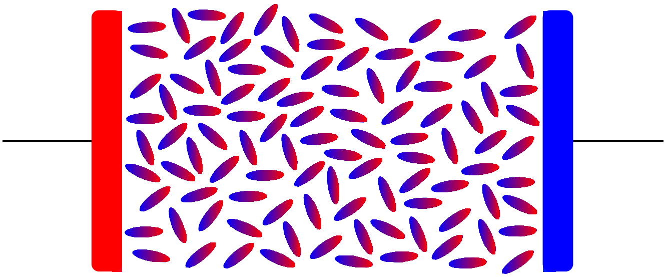

Figure 1-10 In an electric field, dipoles become aligned, to some extent, so that the dipole field opposes the field applied by the plates.

It is quite a different story if we place an electronic conductor between the plates. The electrons are now able to pass freely from the negative plate into the conductor, and from the conductor into the positive plate, as in Figure 1-11. Electrons being negative, their passage from right to left through the conductor in this figure corresponds to electric charge flowing from left to right. We say an **electric current** *I* flows through the conductor: it

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[133] Copper sheets, each of 15.0 cm^2 area are separated by an air gap of 1.00 mm. Calculate the capacitance, checking at Web#133. Also find the charge densities on the plates and the field within the capacitor, when 1000 V is applied.

[134] Confusingly ε is sometimes used to denote **relative permeability** (or **dielectric constant** or **dielectric coefficient**), which is the ratio of the permittivity of the material in question to the permittivity of free space.

[135] These are listed in farads per meter, the conventional unit of permittivity. Show that this is equivalent to the unit given in equation 1:3. See Web#135.

[136] and also more energy. The energy stored by a capacitor is $Q\Delta E/2$. Can you explain the reason for the divisor of 2? If not, consult Web#136.

[137] Even if the material is not dipolar, the presence of the imposed field can induce a temporary dipole. Such **polarizability** is how a material such as tetrachloromethane, CCl_4, exhibits an elevated permittivity.

expresses the rate at which charge passes through the conductor:

1:19 $$I = \frac{dQ}{dt}$$ definition of current

Electric current is measured in the **ampere**[138] unit, one ampere corresponding to the passage of one coulomb in a time t of one second[139] ($\text{A} = \text{C s}^{-1}$). The flow of electricity through the conductor is continuous, unlike the case of an insulator, in which there is only a brief transient passage of electricity.

Of course, the same flow of electricity that occurs in the conductor is also experienced in the wires and plates that constitute what is known as the **circuit**, the pathway through which the charge flows. That is why an **ammeter**, an electronic device[140] that measures electric current, can be positioned, as in Figure 1-11, remote from the conductor and yet measure the current flowing through it. An important quantity, equal to the current divided by the cross-sectional area through which it flows, is the **current density**, i:

1:20 $$i = \frac{I}{A}$$ definition of current density

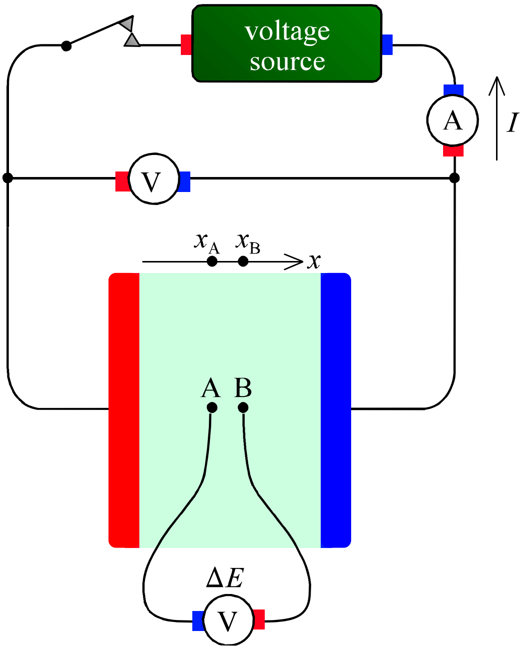

Figure 1-11 Arrangement for measuring the conductivity of an electronic conductor. The method is sometimes called the **4-terminal method** because there are four connections to the conductor. The sample of conductor is of length L and cross-sectional area A.

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[138] André Marie Ampère, 1775 – 1836, French physicist.

[139] Some pacemaker batteries (see Chapter 5) are required to generate 29 μA of electricity at 2.2 V and to operate reliably for 8 years. What is total charge delivered in the battery's lifetime? How many electrons is that? What energy is liberated? What average power? See Web#139.

[140] An ideal ammeter measures the current flow without producing any voltage across its terminals. Modern ammeters closely approach this ideal.

It is measured in amperes per square meter, A m^{-2}. Unlike the current itself, the current density does differ in different sections of a circuit.

The ratio of the current density flowing in a conductor to the field that creates it is called the **conductivity** κ of the material[141]

1:21 $$\kappa = \frac{i}{X} = \frac{I/A}{-\Delta\phi/L}$$ definition of conductivity planar symmetry

It has the unit (A m^{-2})/(V m^{-1}) = A V^{-1} m^{-1} = S m^{-1}. S symbolizes the **siemens**[142] unit.

One way in which the conductivity of an electronically conducting material can be measured[143] is illustrated in Figure 1-11. A voltmeter measures the electrical potential difference ΔE between two points A and B on the conductor, which has a uniform cross-sectional area A, and through which a known current is flowing. Then, using 1:9,

1:22 $$\kappa = \frac{i}{X} = \frac{I/A}{-\mathrm{d}\phi/\mathrm{d}x} = \frac{I(x_\mathrm{B} - x_\mathrm{A})}{-A\Delta E}$$

The relationship $i = \kappa X$ is one form of **Ohm's law**[144]. Another is $-\Delta E/I = R$ which defines the **resistance** R, measured in the **ohm** (Ω) unit, equal to S^{-1}. The second equality in the formula

1:23 $$R = \frac{-\Delta E}{I} = \frac{L}{\kappa A}$$ definition of resistance planar symmetry

applies only to conductors of a simple cuboid[145,146] or cylindrical shape. The resistances of conductors of these and some other geometries are addressed in Chapter 10.

The negative sign in the three most recent equations arose because the current flow occurred in the direction of the coordinate in use. However, Ohm's law is often used in contexts in which there is no clear coordinate direction and accordingly the equation $\Delta E = IR$ is often written, in this book and elsewhere, without a sign. The issue originates because, strictly, I is a vector whereas ΔE and R are not. Exactly the same ambiguity arises in equations 1:17 and 1:18. Just remember that the flow of current through a resistor or capacitor is accompanied by a *decrease* in electrical potential.

Thus far, we have investigated what happens when we apply an electric field to an

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[141] The reciprocal 1/κ of the conductivity is known as the **resistivity**. Conduct*ivity* and resist*ivity* are properties of a *material*. In contrast conduct*ance* and resist*ance* are properties of a particular *sample* of material.

[142] Ernst Werner von Siemens, 1816 – 1892, German engineer.

[143] Another uses alternating current, as discussed on page 104.

[144] Georg Simon Ohm, 1789 – 1854, German physicist.

[145] Show that the resistance, measured between opposite edges of a square of a thin conducting film, does not depend on the size of the square. For this reason, the resistances of thin films are often expressed in **ohms per square**. A thin copper film has a resistance of 0.6 Ω per square. Using the table entry on page 385, find its thickness. Compare you answer to that in Web#145.

[146] Find the resistance between opposite faces of a cube of pure water of edge length 1.00 cm. See Web#146.

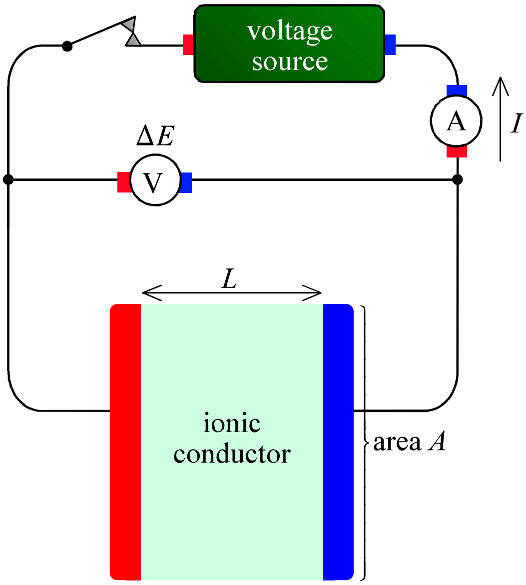

Figure 1-12 In the absence of chemical reaction, current flows transiently when a field is applied to an ionic conductor.

insulator or to an electronic conductor. What occurs when an electric field is applied to an ionic conductor, for example by applying a voltage between two plates that sandwich the conductor? Often a chemical reaction occurs and we enter the realm of electrochemistry. Sometimes, however, if the applied voltage ΔE is small enough, conditions[147] are such that no chemical reaction can occur. In such circumstances, when the switch shown in Figure 1-12 is closed, a current flows that, unlike the case of the electronic conductor, declines in magnitude and eventually becomes immeasurably small. The quantity of charge, $Q(t)$, that has passed increases with time in the manner described by the curves in Figure 1-13. As in the insulator case, the charge passed ultimately, $Q(\infty)$, is proportional to the area A of the plates and (approximately at least) to the applied voltage ΔE. However, it is entirely independent of the separation L. Evidently there are factors at play in the case of an ionic conductor that have no parallel in the other two classes of materials, but the novel behavior is readily explained.

If the ionic conductor contains mobile ions of two types, cations and anions, then the effect of the field is to cause these ions to move, anions leftwards in Figure 1-14 and cations rightwards. As the moving ions approach the impenetrable plates, they are halted and accumulate there. The two sheets of accumulating ions themselves create a field that opposes that caused by the plates, decreasing the field experienced by the moving ions and slowing their motion. Eventually the motion ceases because the two fields entirely cancel and leave the interior of the conductor field-free.

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[147] Electrochemists refer to such a circumstance as "an electrochemical cell under **totally polarized** conditions". See Chapter 10.