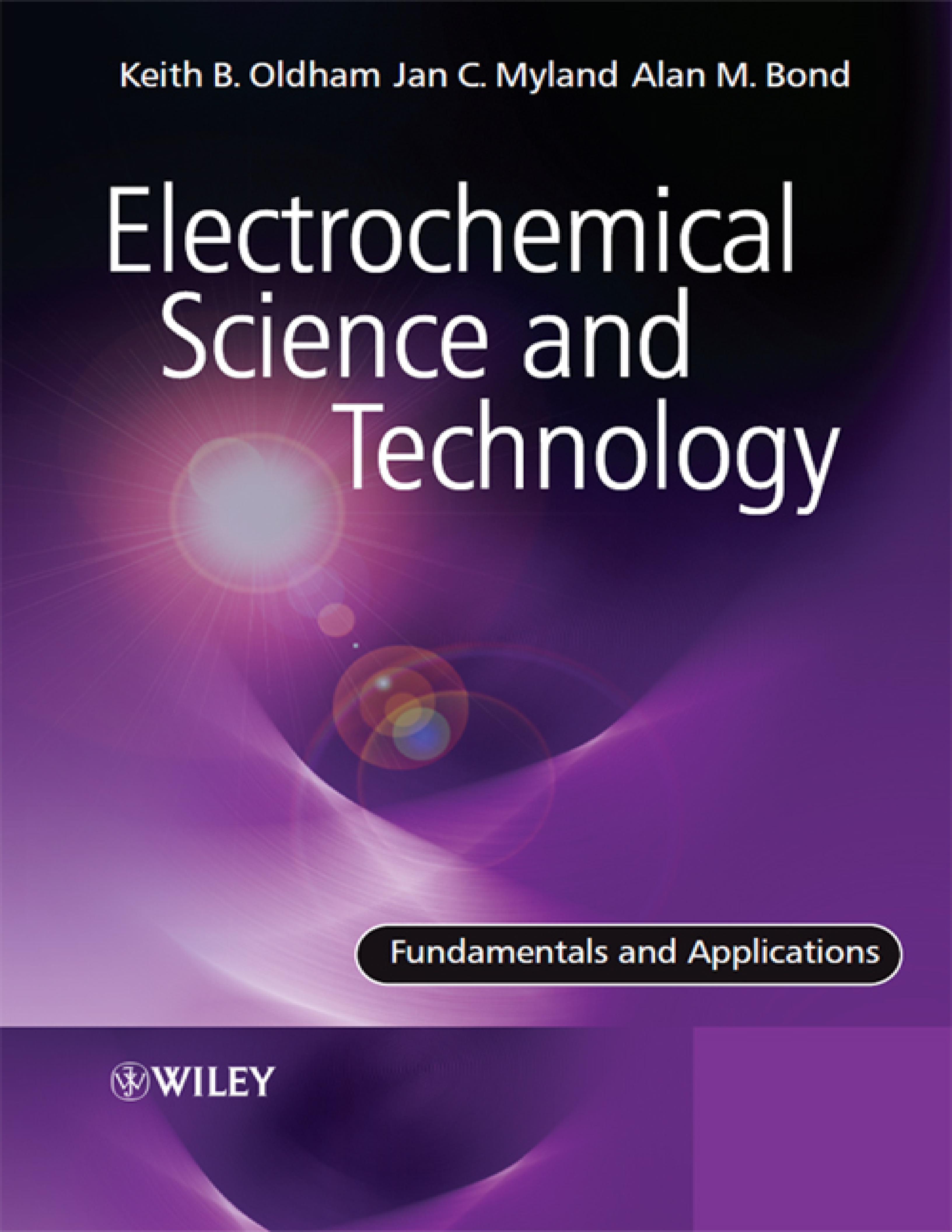
Keith B. Oldham Jan C. Myland Alan M. Bond

Electrochemical Science and Technology

Fundamentals and Applications



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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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Chapter 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 ca **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.

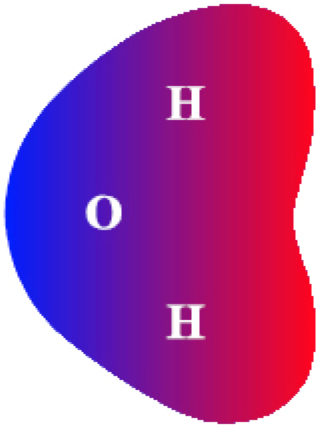
Charge is measured in **coulombs** and it occurs as multiples of the **elementary charge**

$$Q_0 = 1.6022\times10^{-19}\ \text{C} \qquad \text{elementary charge} \tag{1:1}$$

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^{3-}_4 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, 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

$$f = \frac{Q_1Q_2}{4\pi\varepsilon r_{12}^2} \qquad \text{Coulomb's law} \tag{1:2}$$

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

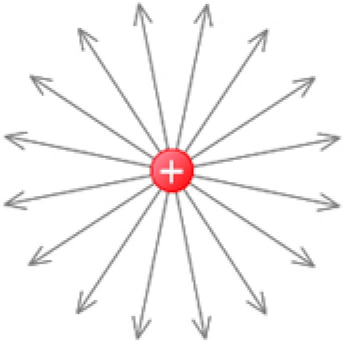
when the medium is free space[106]. The force is repulsive if the Q's have the same sign, attractive otherwise. To give you an idea of the strong forces involved, imagine that all the Na^+ cations from 100 grams of sodium chloride were sent to the moon, then their attractive force towards the earthbound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

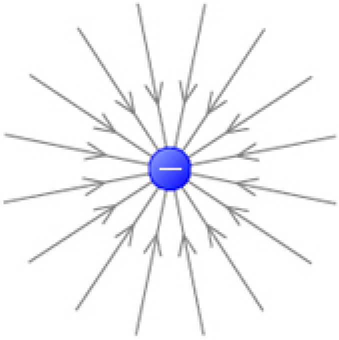
A consequence of the mutual repulsion of two or more similar charges is that they try to get as far from each other as possible. For this reason, the interior of a phase[108] is usually free of net charge. Any excess charge present will be found on the surface of the phase, or very close to it. This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

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:

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

and therefore it has the unit[111] of newtons per coulomb, NC^{-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 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 $0 \le x \le L$. 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 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 $X(l) = q/[2\varepsilon]$. Taking into account the second, oppositely charged, plane, the total field is

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.

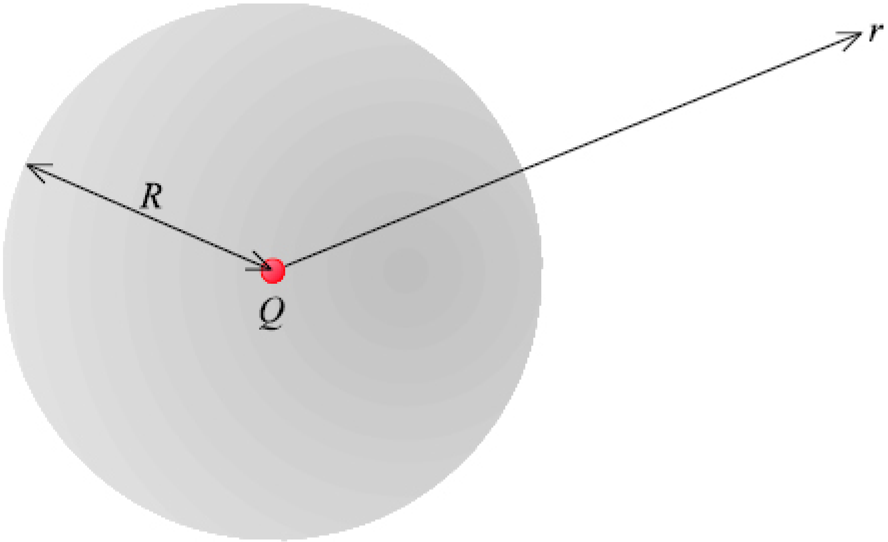
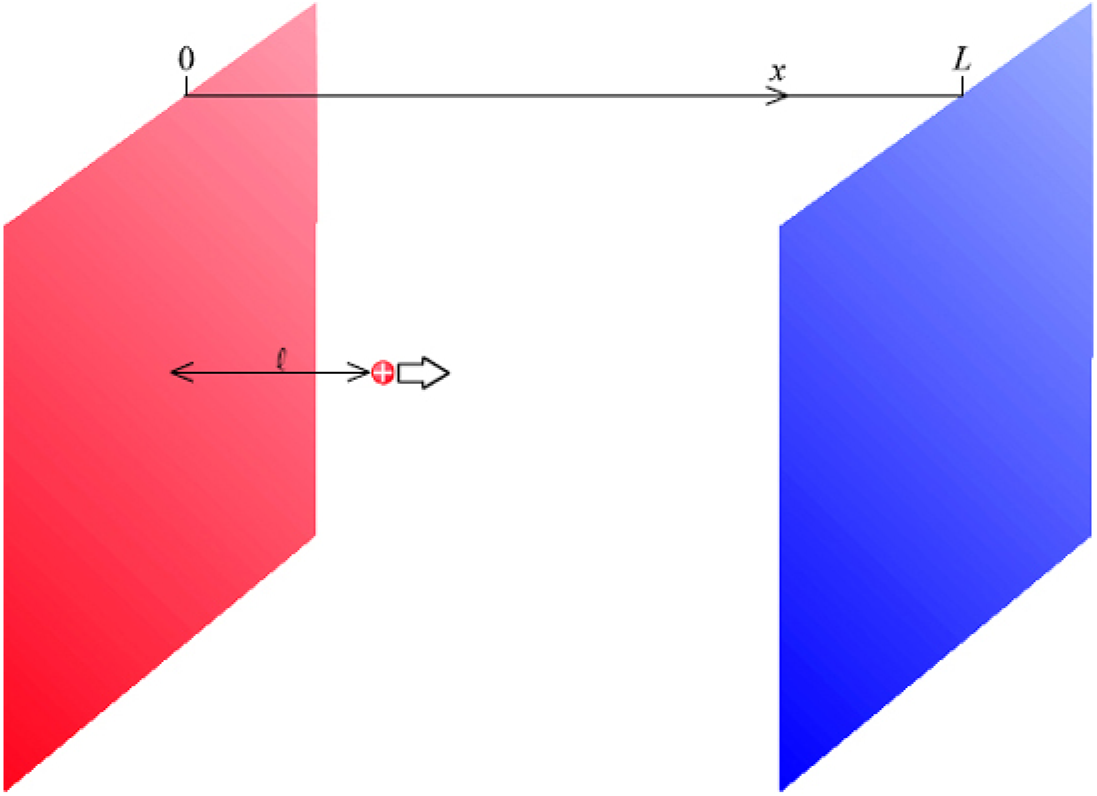


Figure 1-5 The test charge experiences a repulsive force of magnitude $Q_{test}q/2\varepsilon$ from the positively charged sheet, independent of *l*, and an attractive force of the same magnitude from the negatively charged sheet.

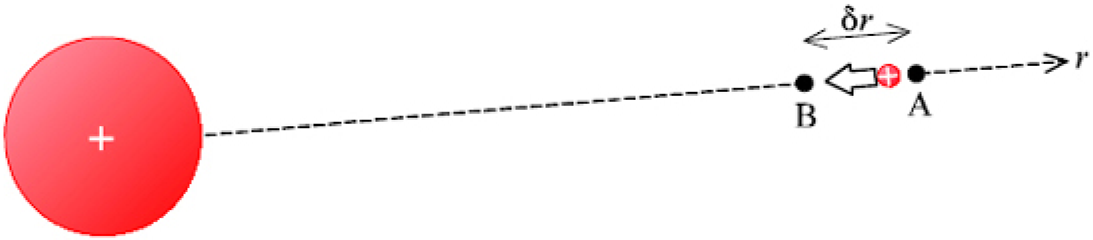


1:6 $X(\ell) = \dfrac{q}{\varepsilon}$ planar symmetry

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** $w_{A\to B}$ for the test charge to reach its destination, point B. Work (measured in **joules**[115], J) can be calculated as *force* x *distance* or, in this case:

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.



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

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,

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

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

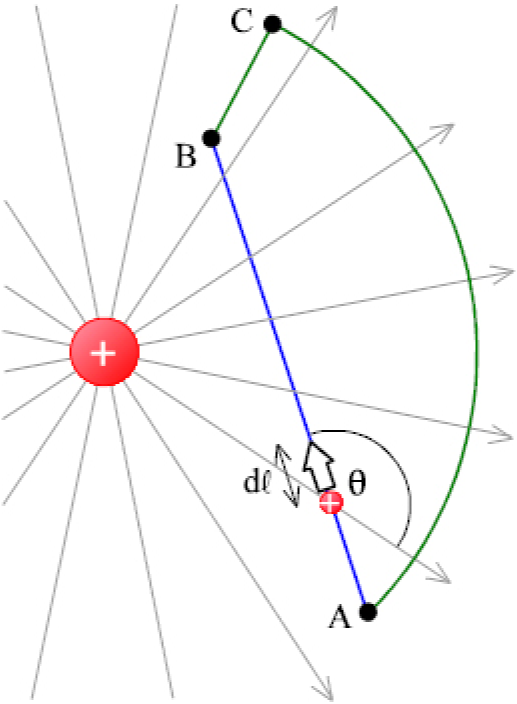
The unit of electrical potential is the **volt**[119]. The first equality in 1:8 shows that one volt equals one joule per coulomb (V = J C^{-1}).

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 $$\phi_{\mathrm{B}} - \phi_{\mathrm{A}} = -\int_{\mathrm{A}}^{\mathrm{B}} X(r)\,\mathrm{d}r = \frac{-Q}{4\pi\varepsilon}\int_{r_{\mathrm{A}}}^{r_{\mathrm{B}}} \frac{\mathrm{d}r}{r^2} = \frac{Q}{4\pi\varepsilon}\left(\frac{1}{r_{\mathrm{B}}} - \frac{1}{r_{\mathrm{A}}}\right) \qquad \text{spherical symmetry}$$

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

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.



$$\phi_{\mathrm{B}} - \phi_{\mathrm{A}} = \frac{w_{\mathrm{A}\to\mathrm{B}}}{Q_{\mathrm{test}}} = \frac{-1}{Q_{\mathrm{test}}}\int_{\mathrm{A}}^{\mathrm{B}} f\cos\{\theta\}\,\mathrm{d}\ell = -\int_{\mathrm{A}}^{\mathrm{B}} X\cos\{\theta\}\,\mathrm{d}\ell \qquad 1{:}11$$

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, 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 ρ(x) at any distance x from the left-hand plate. We seek the field at some point $x = l$. The space charge can be regarded as being made up of many thin wafers, each of areal charge density ρ(x)dx. Each of these will contribute to the field, positively for the thin wafers to the left of $x = l$, negatively (think of the effect on a test charge) when $x > l$. Following the discussion surrounding Figure 1-5, it follows that the total field at the point of interest is

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

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

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

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

$$1{:}14 \quad \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2} = \frac{-\rho(x)}{\varepsilon} \qquad \text{Poisson's equation planar symmetry}$$

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

$$1{:}15 \quad \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left\{r^2\frac{\mathrm{d}\phi}{\mathrm{d}r}\right\} = \frac{-\rho(r)}{\varepsilon} \qquad \text{Poisson's equation spherical symmetry}$$

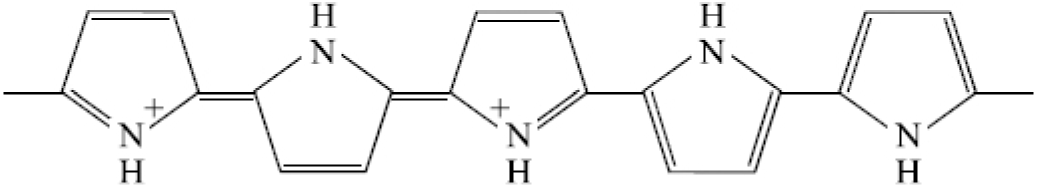
This law finds application in the Debye-Hückel theory discussed in the next chapter.

Capacitance and Conductance: the effects of electric fields on matter

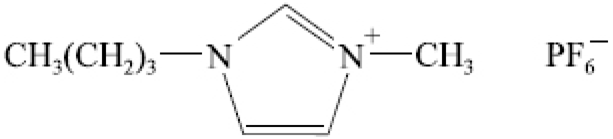
Materials may be divided loosely into two classes: electrical **conductors** that allow the passage of electricity, and **insulators** that do not. The physical state is irrelevant to this classification; both classes have examples that are solids, liquids and gases. Conductors themselves fall into two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

- materials
  - insulators
  - conductors
    - electronic conductors
    - ionic conductors

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. 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".



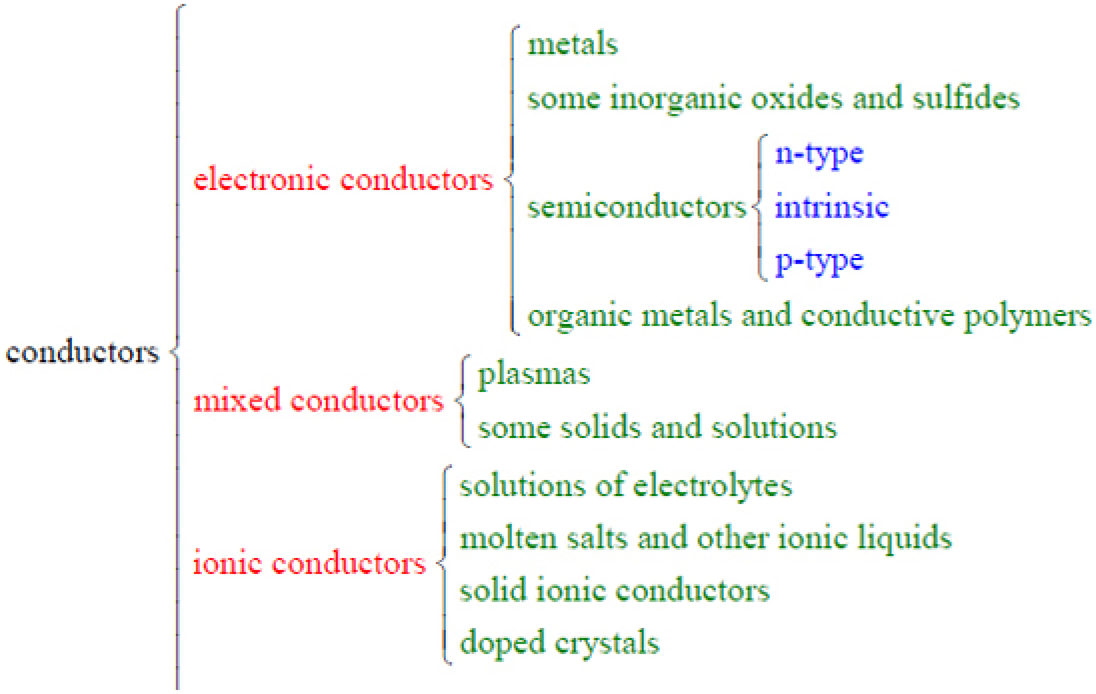
The second class of materials that conduct electricity comprises the **ionic conductors**, which possess conductivity by virtue of the motion of anions and/or cations. Solutions of electrolytes (salts, acids and bases) in water and other liquids are the most familiar examples of ionic conductors, but 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

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:



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