1
Foundations, Definitions and Concepts

1.1
Ions, Electrolytes and the Quantisation of Electrical Charge

In solid crystals such as NaCl, electrical charges are localised on those sites that form the lattice. These lattice sites are occupied not by (neutral) atoms but by negatively charged chlorine or positively charged sodium ions and the crystal is held together by the coulombic forces that exist between all electrically oppositely charged species. The energy of interaction between two particles of charge q_1 and q_2 at a distance r from one another is given by

$$U_{12} = \frac{q_1 \cdot q_2}{4\pi\varepsilon_{\mathrm{r}}\varepsilon_0 r} \tag{1.1}$$

where ε_{r} is the relative permittivity of the medium and ε_0 the permittivity of free space. The energy is positive (ie unfavourable) when q_1 and q_2 have the same sign, but is negative (implying an attractive force) when q_1 and q_2 have opposite signs. The corresponding force between the two particles is a *vector* quantity, directed along the interparticle axis, $\mathbf{r}$; if the two charges have the same sign, the force $\mathbf{F}$ is repulsive:

$$\mathbf{F}_{12} = -\frac{\partial U_{12}}{\partial \mathrm{r}} = \frac{q_1 q_2}{4\pi\varepsilon_r\varepsilon_0 r^2}\frac{\mathbf{r}}{r} \tag{1.1a}$$

These coulombic forces are very powerful, and ions are drawn close together before short-range repulsive forces come into play and an equilibrium interionic distance is established. The result that very large amounts of energy are needed to break down the lattice, leading, for example, to the familiar observation of high melting points in ionic crystals. The actual calculation of the energy required completely to break up the crystal lattice can be carried out provided some analytical form for the ionic repulsion can be written down. Commonly this repulsion is deemed to take the form $R_{12} = B/r^n$, where B depends on the relative extension of valence and core-electron clouds. The total interaction energy between pairs of ions can then be written $E_{12} = U_{12} + R_{12}$, and by summing over all pairs of ionic sites in the lattice, the total crystal can be calculated. In general this is difficult to do mathematically, since the sum will obviously consists of a very large number of positive and negative terms that will nearly cancel. However, the final result for a simple cubic lattice such as NaCl is

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$$E = \frac{MN_A|q|^2}{4\pi\varepsilon_0 r}\left(1 - \frac{1}{n}\right) \tag{1.2}$$

where N_A is the Avagadro constant (6.203×10^{23} mol^{-1}), and M is a number (which has the value 1.7476 for the NaCl structure) termed the Madelung constant. We note that the value of ε_r in eqn. (1.1) has been put equal to unity since the ions in the lattice are formally separated by vacuum.

If the NaCl crystal be now introduced into a solvent such as water, the attractive forces between the ions will be much reduced since the relative permittivity for water, ε_w, is 78.3 (at 25°C). The result is that ionic attraction between Na^+ and Cl^- ions dissolved in water is much weaker, sufficiently so that NaCl will readily dissolve in water to give freely moving Na^+ and Cl^- ions (a word derived from the Greek word for wanderer); the salt is said to dissociate into *ions*.

Actually, the reduction of attractive energy in the aqueous phase would not be sufficient by itself to dissolve NaCl. What is decisive is the fact that water has a strong dipole which preferentially orients itself around each ion in a process termed *solvation*, or, for water, *hydration*. Each positive or negative ion in aqueous solution is surrounded by a sheath of water molecules, and it is the energy gained by the ions from this solvation process that usually tips the balance in favour of dissolution, or at least reduces the dissolution enthalpy to the point where the *entropy* of dissolution (which is always positive) can tip the balance. The process is shown schematically in Fig. 1.1.

Chemical compounds that are dissociated into ions in solid, liquid or dissolved forms are termed electrolytes. The example of NaCl above is termed a 1—1 electrolyte, since two ions are formed for every formula unit of the material, and each carries one unit of elementary charge, e_0, of magnitude 1.602×10^{-19} C. From the dissolution

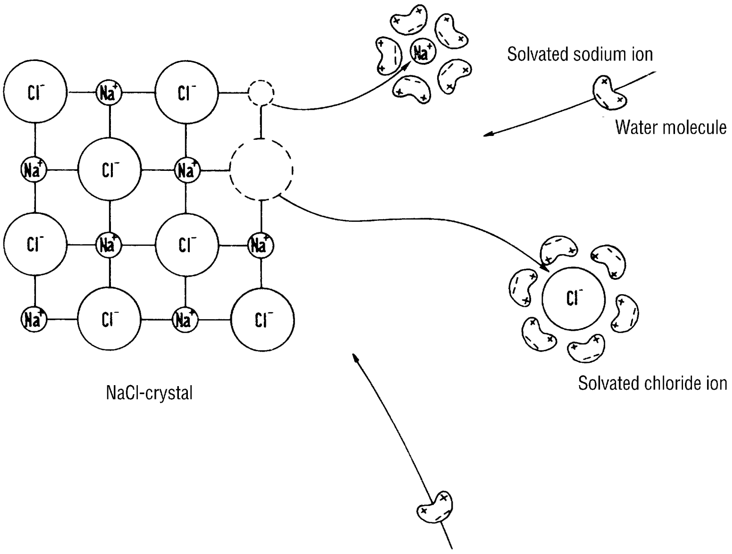

Fig. 1.1 Ionic solvation through dissolution of a NaCl crystal in water (two dimensional representation).

of multivalent electrolytes, more than two ions per formula unit may be obtained and such ions may carry a multiple of the elementary charge, $\pm ze_0$, where z is *the charge number of the ion*. As an example, the dissolution of Na_2SO_4 will give two Na^+ ions and one SO_4^{2-} ion.

It can be seen that for every electrolyte of the general form $A_{\nu_+}B_{\nu_-}$ which dissolves to yield A^{z+} and B^{z-} ions, then electroneutrality requires that $z_+\nu_+ = z_-\nu_- = z_\pm\nu_\pm$, where $z_\pm\nu_\pm$ is termed the equivalent number of the electrolyte. It is clear that for Na_2SO_4, $z_\pm\nu_\pm = 2$.

1.2

Transition from Electronic to Ionic Conductivity in an Electrochemical Cell

If the ions in an electrolyte solution are subjected to an electric field, $\boldsymbol{E}$, one has with the definition for the field $\boldsymbol{E} = \boldsymbol{F}/q$ as expression for the force on the ions

$$\boldsymbol{F} = ze_0\boldsymbol{E} \tag{1.3}$$

which will induce motion in or against the direction of the field depending on the sign of the charge on the ion, i.e. whether z is positive or negative. This ion motion leads to the transport of charge and hence to the flow of electrical current through the electrolyte solution.

An electric field can be applied across an electrolyte solution quite straightforwardly by introducing two electronic conductors (solids or liquids containing free electrons, such as metals, carbon, semiconductors etc), and applying a *dc* potential difference. These electronic conductors are termed *electrodes.*

The actual arrangement of the electrodes is shown in Fig. 1.2. The electrical circuit between the electrodes is completed by a resistor, an ammeter and a *dc* voltage source connected by external wiring from one electrode to the other. The electrolyte solution in Fig. 1.2 is formed from the dissolution of $CuCl_2$ in water, which leads to one Cu^{2+} and two Cl^- ions per formula unit. The electrodes themselves are formed from a suitable inert metal such as platinum.

When current flows in the cell, the negatively charged chloride ions migrate to the positive electrode and the positively charged ions to the negative electrode. At the

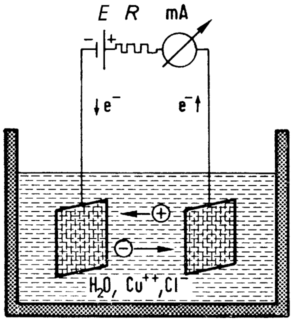

Fig. 1.2 Electrochemical cell for the electrolysis of aqueous $CuCl_2$ solution - *E*: *dc* voltage; *R*: resistance; mA: galvanometer for current measurement.

phase boundary between ionic and electronic conductors, the ions arriving are transformed by capture or release of electrons. At the negative electrode, the Cu^{2+} ions are plated out as copper metal:

$$Cu^{2+} + 2e^- \rightarrow Cu^0 \tag{1.4}$$

and at the positive electrode the chloride ions release electrons to form chlorine gas:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1.5}$$

It can be seen that the fundamental difference between charge transport through electrolyte solution by ion migration and through electronic conductors by electron migration is that the latter leaves the conductor essentially unaltered whereas the former leads to changes in the electrolyte. In the case above, the flow of current leads to the appearance of concentration differences, since the Cu^{2+} ions move from right to left and the chloride ions from left to right, and it also leads to changes in the total electrolyte concentration as both copper and chlorine are lost from the solution. From the addition of the two electrode reactions, (1.4) and (1.5) above, the overall cell reaction follows

$$\begin{array}{ll} \text{Electrode Reactions} & \left\{ \begin{array}{l} Cu^{++} + 2e^- \rightarrow Cu^0 \\ 2Cl^- \rightarrow Cl_2 + 2e^- \end{array} \right. \\ \text{Cell Reactions} & Cu^{++} + 2Cl^- \rightarrow Cu^0 + Cl_2 \end{array} \tag{1.6}$$

It should be emphasised at this point that a constant *direct current* through an ionic conductor is only possible if electrode reactions take place at the phase boundaries between the electronic and ionic components of the circuit. These reactions must permit electrons to be exchanged between the two phases, in the manner indicated in the fundamental considerations given above. However, a constant *alternating* current can flow through an ionic conductor without *any* electrode reaction taking place, as will be seen in section 2.1.2.

1.3
Electrolysis Cells and Galvanic Cells: The Decomposition Potential and the Concept of emf.

If the aqueous $CuCl_2$ solution in the electrochemical cell of Fig. 1.2 is replaced by an aqueous solution of HCl, which dissociates into aquated hydrogen ions (protons) of approximate formula H_3O^+ and chloride ions, a *dc* current flow will again lead to the loss of Cl^- at the positive electrode. However, at the negative electrode, the H_3O^+ ions are reduced to hydrogen. Thus, the flow of charge is accompanied by the electrochemical decomposition of HCl to its component parts

$$\begin{array}{ll} 2Cl^- & \rightarrow Cl_2 + 2e^- \\ \underline{2H_3O^+ + 2e^-} & \underline{\rightarrow H_2 + 2H_2O} \\ \quad 2HCl & \rightarrow H_2 + Cl_2 \end{array} \tag{1.7}$$

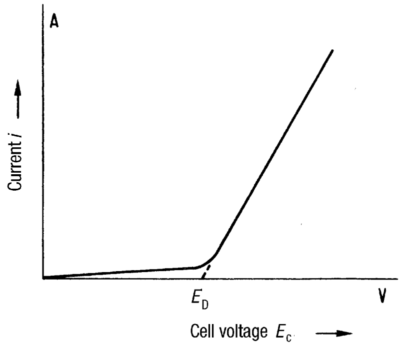

Fig. 1.3 Electrolysis current as a function of the cell voltage E. E_D is the decomposition voltage.

The electrochemical decomposition of a substance through the passage of an electrical current is termed *electrolysis*, and corresponds to the conversion of electrical to chemical energy.

For a significant rise in the current through an electrolysis cell, the potential difference between the electrodes, or *cell voltage, E*, must exceed a certain value, the *decomposition potential difference*, E_D as shown schematically in Fig. 1.3. The decomposition potential difference for HCl at a concentration of 1.2M has the value 1.37V at 25°C, and the value usually lies between one and four volts for other electrolytes.

If the electrolysis process is suddenly brought to a halt by removing the voltage source in the external circuit of Fig. 1.2, and swiftly reconnecting the electrodes through a voltmeter, a voltage of about 1V is observed. If the electrodes are reconnected by a resistor and ammeter, a current can also be observed. This current has its origin in the reversal of the two electrode reactions of equation 1.7; hydrogen is oxidised to hydrated protons, the electrons released travel round the external circuit and reduce chlorine gas to chloride ions. Actually, the current in this case would decay rapidly since the gases hydrogen and chlorine are only slightly soluble in water, and will, for the most part, have escaped from solution. However, if their concentrations can be maintained by bubbling the two gases over the electrodes, as shown in Fig. 1.4, then the current will remain fairly constant with time; the cell can continually provide electrical energy from chemical energy.

Electrochemical cells in which the electrode reactions take place spontaneously, giving rise to an electrical current, are termed *galvanic* cells, and are capable of the

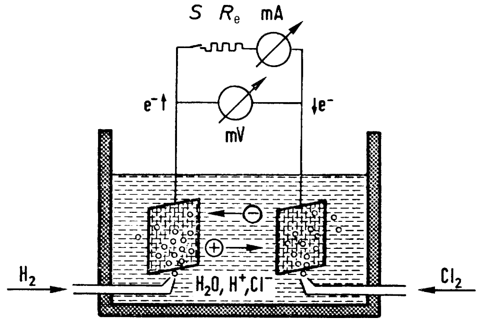

Fig. 1.4 Galvanic cell based on the H_2/Cl_2 reaction - mV: voltage measurement; mA: current measurement; R_e: external resistance; S: switch.

direct conversion of chemical to electrical energy. If the external resistance between the electrodes is made very high, so that very little current flows, the observed potential difference of the galvanic cell becomes the rest potential, E_r, which, under equilibrium conditions, is equal to the *electro-motive force or EMF* of the cell, E_0, related, in turn, to the free energy of the overall cell reaction (for a thermodynamic treatment, see chapter 3).

Irrespective of whether electrolysis is taking place or the cell is behaving in a galvanic mode, the electrode at which negative charge *enters* the electrolyte solution is termed the ***cathode***. Equivalently, it is at this electrode that positive charge may be said to leave the solution. Thus, typical cathode reactions are:

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

$$Cu^{2+} + 2e^- \rightarrow Cu^0$$

In these cases, the reactant, Cl_2 or Cu^{2+} is said to be *reduced*. In a similar fashion, at the ***anode*** negative charge leaves the electrolyte solution, or, equivalently, positive charge enters the solution, and typical anode reactions include:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$2H_2O + H_2 \rightarrow 2H_3O^+ + 2e^-$$

In these cases, the reactant is said to be *oxidised*.

It should now be clear that for the electrolysis cell above, the cathode is that electrode at which hydrogen is evolved, whereas in the case of the galvanic cell, the cathode is that electrode at which chlorine gas is reduced to chloride. Since, in electrolysis, the positively charged ions migrate towards the cathode, they are termed *cations*, and the negative ions are termed *anions*. That part of the solution near the cathode is termed the *catholyte*, and that part near the anode is termed the *anolyte*.

If a galvanic cell is set up as shown in Fig. 1.4, and both current and potential difference are monitored simultaneously, it is found that as the current increases, the measured external potential difference between the electrodes, E, decreases, as shown schematically in Fig. 1.5. In fact, the potential drop is partitioned between internal (R_i) and external (R_e) resistances as:

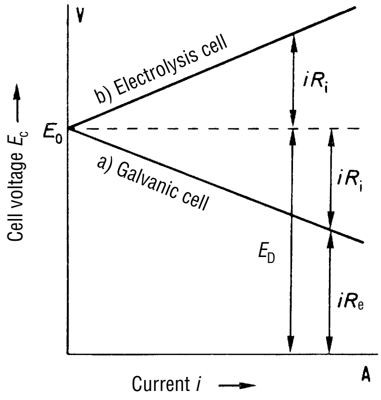

Fig. 1.5 Schematic variation of cell voltage, E_C, against load current i for (a) a galvanic cell; (b) an electrolysis cell. E_0 is the voltage without current passing, also termed the *electro-motive force* or EMF. E_D is the decomposition voltage, R_i the internal resistance of the cell and R_e the external resistance.

$$\begin{aligned} E_0 &= iR_i + iR_e \\ E &= E_0 - iR_i \end{aligned} \tag{1.8}$$

The power output, P, of the cell is clearly the product of potential and current:

$$P = iE = i(E_0 - iR_i) \tag{1.9}$$

and this is a maximum for $i = E_0/2R_i$, and $E = E_0/2$.

In the case of an electrolysis cell, when the current is forced through the cell, the potential drop across the inner resistance of the cell must be added to the decomposition potential, E_D, so we have

$$E = E_D + iR_i \tag{1.10}$$

1.4
Faraday's Laws

If each ion is assigned a charge of $\pm ze_0$, and the electron current in the external circuit has the value i_e (which will evidently be equal to the current flow associated with the ion flux of both positive and negative ions, i_I), then, at either electrode, the mass of material converted by the total charge passing between ionic and electronic conductors must be proportional to this charge. The charge, Q, itself will just be the product of current and time, i.e. $Q = i_e \cdot t$, so the mass, m, of material that reacts is given by:

$$m = \text{const.}Q = \text{const.}i_e \cdot t \tag{1.11}$$

For an ion with unit elementary charge, e_0, the total charge passed in oxidising or reducing one mole, Q_M, is evidently equal to $N_A e_0$, where N_A is the Avagadro constant, and for the conversion of one mole of z-valent ion a charge of $zN_A e_0$ will be necessary. The value of the product $N_A e_0$ is numerically equal to 96485 Coulomb mol^{-1}, and this quantity is termed the Faraday, and denoted by the symbol F. It follows that the passage of one Coulomb of charge will lead to the conversion of $M/(96485z)$ g of material, where M is the molar mass. As an example, silver metal can be deposited at the cathode from solutions of $AgNO_3$; the passage of one Coulomb will lead to the deposition of $107.88/96485 \equiv 1.118$ mg of silver metal.

It follows from this that the ratio of the masses of material converted at the two electrodes will have the form

$$m_1/m_2 = (M_1/z_1)/(M_2/z_2) \tag{1.12}$$

The ratio M/z is termed the molar mass of an ion-equivalent, and equation (1.12) tells us that for the passage of equal amounts of charge, the ratio of the masses of material converted at the two electrodes is equal to the ratio of the molar masses of the ion equivalents.

The relationships (1.11) and (1.12) were first expressed as laws by Faraday in 1833 and are known as Faraday's first and second laws. Faraday established his laws purely experimentally and Helmholtz went on to deduce from this that there must be an

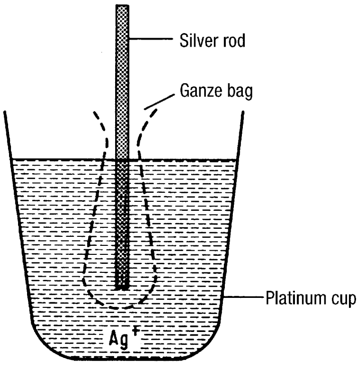

Fig. 1.6 Schematic construction of a silver coulometer for determination of the total quantity of electricity passed.

elementary unit of charge, a fact we have used effectively to derive his laws from a theoretical standpoint.

The quantitative laws found by Faraday can be used in order to determine the total amount of charge passed in a circuit if we insert a suitable electrolysis cell in the circuit and measure the amount of material formed or deposited at one of the electrodes. Commonly the measurement is carried out by measuring the amount of metal deposited as a coating on an inert electrode, such as platinum, or in the form of an amalgam on a mercury cathode. From this mass, m, and from the electrochemical ion-equivalent of the material deposited, the total charge passed is given by

$$Q = \frac{m}{M/zF} \tag{1.13}$$

In practice, the so-called silver coulometer is normally used for the measurement of charge. A silver coulometer consists, in principle, of a platinum crucible which is filled with ca 30% $AgNO_3$ solution and into which is inserted a silver rod, as shown in Fig. 1.6. The crucible is connected to the negative pole of the circuit and the silver rod to the positive pole, so that passage of charge results in a build up of a silver coating on the inside of the platinum crucible whilst at the same time, silver dissolves as Ag^+ from the rod. The electrode reactions are:

$$\begin{array}{ll} \text{Platinum Crucible:} & Ag^+ + e^- \rightarrow Ag^0 \\ \text{Silver Rod:} & Ag^0 \rightarrow Ag^+ + e^- \end{array} \tag{1.14}$$

Around the silver rod is arranged a porous bag, whose main purpose is to prevent any particles that may fall off the silver rod due to mechanical damage from collecting in the crucible and being weighed as well. By carefully weighing the mass of the crucible before and after passage of charge, the total amount of charge passed can be determined by the expression $Q(/\text{Coulomb}) = m(/\text{mg})/1.118$.

Another type of coulometer, used particularly for the measurement of small amounts of charge, is the so-call *combustion-gas coulometer*. In this device, water is made ionically conducting by addition of Na_2CO_3, and electrolysed between two platinum electrodes. The electrode reactions are:

$$\begin{array}{ll} \text{Cathode:} & 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \\ \text{Anode:} & 2OH^- \rightarrow H_2O + {}^1/_2O_2 + 2e^- \\ \text{Overall cell reaction:} & H_2O \rightarrow {}^1/_2O_2 + H_2 \end{array} \qquad (1.15)$$

The mixture of O_2 and H_2 produced is termed ‘combustion gas’, and is determined volumetrically.

It is evident that the current passed during the measurement need not be constant with time, since the amount of material deposited or converted at the electrode depends solely on the integral of the current with respect to time. In measurements using modern electronic equipment, the charge $Q = \int idt$ is determined by integration of the accurately measured current and displayed directly.

Accurate measurement of charge is necessary above all in the analytical technique of *coulometry*, in which either the material to be analysed is converted completely into a form suitable for weighing, or is converted into a species that can be determined volumetrically. Further information can be found in Chapter 10 and in the references cited there on analytical chemistry.

1.5
Systems of Units

The fundamental quantities measured in electrochemical studies are current, charge and voltage, the latter being the potential difference between two defined points in a circuit. The current itself is often replaced by the *current density*, defined as the current per unit area of electrode surface.

From the discussion above, it is obviously possible to use Faraday’s laws to relate current and charge to mass and time. This gives rise to the ‘practical international electromagnetic’ system of measurement, in which the ampère is *defined* as that current which, flowing for one second, deposits 1.118 mg of silver in a silver coulometer. In this system, the unit of potential difference, the volt, is fixed by reference to the potential difference of the ‘Weston’ cell, an easily prepared galvanic cell which is described in detail in section 4.11. The potential difference of the Weston cell is defined to be 1.01830V at 20°C. The unit of electric field strength is the volt per centimetre, and is defined as the *gradient* of the potential at any given point. It is clearly a *vector* quantity, in contrast to potential, which is a *scalar*.

The connection between the electrical current, I flowing through a simple electronic conductor, and the potential difference, V, applied between its ends is given by Ohm’s law:

$$V = IR \qquad (1.16)$$

where R is termed the resistance and is strongly dependent on the material from which the conductor is made. Its unit is the ohm (Ω) $\equiv$ V A^{-1}, and the value is defined by the resistance of mercury. In fact, a column of mercury of 1mm^2 cross-section and length 106.300 cm at 0°C and 1 atm pressure ($\equiv$ 101325 Pa) is defined as having a resistance of one ohm. The necessity of specifying cross-section and length arises because the resistance of any material can be factored into two components, one dependent on the intrinsic properties of that material and one dependent on the geometry of the particular sample. For samples of uniform cross-sectional area A, and length l, it is easily shown that

$$R = \rho(l/A) \tag{1.17}$$

where ρ is termed the resistivity of the material and has the units ohm-cm.

Although this system of units is quite internally consistent, there was considerable pressure from professional organisations and learned journals for the universal use of a system based on the ampère as the basic electrical unit, with mass, length and time being in units of kg, metre and second. The basic units of this internationally agreed system, the 'Système International d'Unités' or SI system, are defined in Table 1.1. This set of units is the preferred set for scientific publishing, but the reality is that the older units, particularly those based on the unit of length one centimetre and unit of weight one gram are exceedingly well established, especially in the secondary literature of compilations of physical quantities; both sets will be used throughout this book, and the inter-relationships described where appropriate.

In the S.I. system of units, the unit of potential difference is still the volt, but it is now defined in terms of the units of energy, the joule or kg m^2 s^{-2} and current: in fact, 1V $\equiv$ 1 joule/(1 ampere second). The unit of resistance is similarly defined as 1 ohm $\equiv$ 1 volt/1 ampere. In this system, the unit of resistivity should now be the ohm-metre. However, it should be again emphasised that the overwhelming number of values quoted in the older literature are in the units of ohm-cm, and caution should be used in importing literature values into the formulae quoted.

Table 1.1 The International System of Units.

Quantity	Unit	Symbol	Definition (abridged)
Length	metre	m	The length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second
Mass	kilogram	kg	The mass of a piece of platinum-iridium kept in Sèvres.
Time	second	s	9 192 631 770 periods of the radiation corresponding to the transition between the hyper-fine levels of the ground state of the ^{133}Cs atom.
Electrical Current	ampere	A	The current that produces a force of 2.10^{-7} newton per metre of length between two infinitely long negligibly thick parallel conductors 1 metre apart in vacuo.
Thermo-dynamic temperature	kelvin	K	The fraction 1/273.16 of the thermodynamic temperature of the triple point of water.
Amount of substance	mole	mol	The amount of substance of a system containing as many specified elementary entities (atoms, molecules, ions etc) as there are atoms in 12g of ^{12}C.

Two units of concentration are used in the rigorous SI system. The concentration per unit volume has units mol m^{-3} (mole per cubic metre), and denoted by *c*. However, the subsidiary unit of dm^3 (known familiarly as the litre) is permitted, and concentrations of solutions are often quoted in units of mol dm^{-3}, and denoted by the symbol M the molarity of the solution. Whilst it is correct to refer to a solution as having concentration *x*M, the concentration units used in rational S.I. formulae must be the (rational) mol m^{-3}.

The second unit of concentration has units of mol kg^{-1}, i.e. moles per kg of *solvent*. This is the more useful measure of concentration when considering the thermodynamics of solutions, as will become apparent below, and it has the further advantage of being independent of temperature, but it is less useful from the practical point of view. For dilute solutions in water at 25°C, to a high degree of accuracy, a solution of x mol kg^{-1} is very close to *x*M or to $1000x$ mol m^{-3}. For dilute solutions in other solvents, a molality of x mol kg^{-1} will correspond to a concentration of $\rho_s x$ mol m^{-3}, provided the density of the solvent, ρ_s, is expressed in kg m^{-3}.

In order to ensure that equilibrium constants involving concentrations of reactant and product do not possess units themselves, all concentration terms in such formulae are expressed as ratios of the molarity or molality to a standard value, usually written c^0 or m^0. The choice of m^0 is straightforward, and is invariably taken as one mol kg^{-1}. The choice of c^0 is less obvious, since values of one mol m^{-3} or one mol dm^{-3} might be chosen. Conventionally, the latter has been used, leading to some confusion in formulae. To avoid this, we shall use *molality* as the main unit of concentration in this book, save in those areas, such as electrolyte conductivity, where volume-based units are normally used.

Although this discussion of units may seem quite dry, it actually has considerable practical importance. It should become second-nature to check any formula for consistency of units, a process that is immeasurably helped by having a rational system of units in the first place. Unfortunately, the unit of concentration remains a problem; the unit of molarity is deeply ingrained in chemical practice, and cannot be erased easily. This is a particular problem in the development of solution thermodynamics, and the choice of standard states remains a real difficulty, for which the only remedy is constant caution. Let the reader be warned!

References for Chapter One

The most useful background reading is in elementary physics and physical chemistry, and the textbooks listed below are intended to provide some further material on electricity and electrical measurements.

A good background text in physics is:

R. Muncaster: "'A'-level Physics", 3rd. Edition, Stanley Thornes (Publishers) Ltd, 1989.

More advanced but with a wealth of illustrative material is:

D. Halliday, R. Resnick and K.S. Krane: "Physics", Volume 2, 4th Edition, John Wiley and Sons Inc., 1992.

The best introductory text in physical chemistry at this level is

P.W. Atkins: "Introduction to Physical Chemistry", Oxford University Press, 1998.