Fundamental Definitions

GENERAL TERMS

Metal (Surface) Finishing
is a general term used to describe processes which result in the deliberate modification of the surface of a material in order to improve its qualities and/or properties.

An Atom
is the smallest component of an element which has the same properties as the bulk element.

Atomic Mass, (units: g)
is the mass of one atom of a substance based upon the mass of carbon-12 being 12.000g. For example, hydrogen has an atomic mass of 1.008 g and copper has a value of 63.54 g.

Relative Atomic Mass, RAM, (dimensionless)
is the mass of one atom of the substance relative to the mass of one atom of ^{12}C being 12.000. For example, hydrogen and copper have values of 1.008 and 63.54.

A Molecule
is the smallest group of atoms which has the same properties as the bulk compound. For example, Cu, H_2 and H_2O.

Molecular Mass, (units: g)
is the mass of one molecule of the substance.

Relative Molecular Mass, RMM (dimensionless)
is the mass of one molecule of the sub- stance relative to that of 12c. For example, Cu: 63.54, H_2: 2.016, HP: 18.015.
(An obsolete term for this is the "molecular weight").

An Electron
is a fundamental subatomic particle having a negative charge of 1.60219 x 10^{-19} C (coulomb). This value is known as the fundamental electronic charge, q_e

An Ion
is an atom or molecule which has a deficit or surplus of unit electronic charges.
Cations are positively charged ions (e.g. H^+, Cu^{2+}, Fe^{2+}) whereas anions are negatively charged ions (e.g. F^-, SO_4^{2-}, Cr_2O_7).

Molar Mass, M, (units: g mol - 1)
is the mass per unit amount of substance
i.e. the mass per mole of specified objects . For example, H_2: 2.016 g mol^{-1}, Cu: 63.54 g mol^{-1}, H_20 : 18.015 g mol^{-1}.

Note : in practice, the relative molecular mass is the numerical value of molar mass expressed in g mol - 1.

pH
The notional definition is:

$$pH = -\log_{10}(cH^+ / mol\ dm^{-3})$$

i.e. pH is the negative logarithm to the base ten of the aqueous hydrogen ion concentration expressed in molar terms - see "Acids and Bases" later.

ELECTRICAL TERMS

Current, I, (units: A (ampere))
is the rate of change of electrical charge with respect to time:

$$I = dq/dt$$

1 ampere is the current flowing in two parallel and infinitely long linear conductors 1 metre apart which produces a force between them of 2 x 10^7 Nm^{-2}
Current may be measured directly by using an ammeter connected in series with the electrical circuit. Sensitive ammeters are sometimes called " galvanometers" . In practice, it is common to measure the current as the potential difference ($\triangle E$) across a known resistance (R_e) or "shunt" via Ohm's Law:

$$I = \triangle E / R_e$$

Current Density, j, (units: A m^{-2})
is the current (I) divided by the electrode area **(A):**

$$j = I/ A$$

Potential Difference or Voltage, (units: V)
1 volt is the potential difference across the two ends of a resistance of 1 ohm when a current of 1 A flows through it. At constant temperature, the potential difference across a resistance is equal to the product of current and resistance according to Ohm's Law. Potential difference and voltage are often measured by a digital voltmeter or "dvm".

Charge, q, (units: C = A s)
1 coulomb is the quantity of electricity which corresponds to a current of 1 ampere flowing for 1 second. Charge is the integral of current (I) with respect to time (t):

$$q = \int I\ dt$$

Electrical charge is usually measured by a digital coulometer (although electro- chemical cells involving deposition of copper or silver and the application of Faraday's Laws of Electrolysis are still occasionally used).

Resistance, R., (units: ohm or Ω)
1 Ohm is the resistance of a filament of mercury 106.3 cm in length which has a mass of 14.452 g and a constant diameter at 0^oC.

Resistivity, ***e.,*** **(units: ohm m or nm)**
I ohm m is the resistance (Re) of a conductor of 1 m length (I) and I m^2 cross sectional area **(A):**

$$e = ReA/I$$

(An obsolete and incorrect term is "specific resistance").

Conductance, C, (units: S (siemens) =ohm^{-l} = Ω^{-1})
is the reciprocal of resistance (Re):

$$C = I/R_e$$

The Transformer
is a device for increasing or decreasing the amplitude of an alternating current (a.c.) or an a.c. voltage at constant power.
A variable transformer is often termed an 'auto transformer' or ' variac'.

The Rectifier
is a device for converting alternating current (a.c .) to direct current (d.c.) .

ELECTROCHEMICAL SERIES

An Electrochemical Reaction

Is a chemical reaction which involves electron transfer to or from the electrode surface. Typically, charge transfer takes place across an electrode/electrolyte interface.

An Electrochemical Cell

contains the following essential components: an anode, a cathode, an electrolyte and a container.

The Electrodes

are electronic conductors in which the net current flow is unidirectional and in the same direction as electron flow.

The Electrolyte

is an ionic conductor in which the current is carried by cations and anions moving in opposite directions.

The Anode

is the electrode at which oxidation (i.e. electron loss) occurs. Examples of anodic processes include the following:

dissolution of copper

$Cu - 2e^- - Cu^{2+}$

oxygen evolution

$H_2O - 2e^- = 2H^+ + ½ O^2$

The Cathode

is the electrode at which reduction (i.e. electron gain) occur s. Examples of cathodic processes include the following:

deposition of copper

$Cu^{2+} + 2e^- = Cu$

(11)

hydrogen evolution

$2H^+ + 2e^- = H_2$

A Galvanic Cell

is an electrochemical cell which spontaneously produces electrical energy via chemical changes at the electrode surfaces. The potential difference between the electrodes acts as a driving force for current flow. Examples are batteries and corrosion cells.

An Electrolytic Cell

is an electrochemical cell which utilises electrical energy to produce chemical changes at the electrode sur faces. Examples include electroplating cells, anodising cells and electrolysis cells.

Electrochemical Corrosion Cells

are effectively "short-circuited" galvanic cells in which degradation of a metal surface occurs via electrochemical reactions.

Faraday's Laws of Electrolysis

For a single electrode reaction which involves z electrons per molecule of a species, the amount of species undergoing electrochemical reaction (m) may be related to the electrical charge (qM) by the equation:

$$m = q_m / zF. \quad (a)$$

where F is a universal constant known as the Faraday Constant.

The amount of a species is equal to its mass divided by the molar mass:

$$m = w / M$$

which allows the equation (a) to be written as:

$$w / M = q_m / zF. \quad (b)$$

If the current is constant, charge is the product of current and time:

$$q_m = It$$

and substitution for q_m in equation (b) followed by a rearrangement gives an expression for the mass of material undergoing an electrochemical change:

$$w = MIt / zF$$

where M is the molar mass, I is the current, t is the time, z is the number of electrons involved and F is the Faraday Constant. In this case the percentage current efficiency may be defined as:

0-/0=

100 <u>mass of species actually transformed</u>
mass of species transformed according to Faradays Law

Electrodeposition

is the production of species on a surface via an electrochemical reaction. The surface species may be a metal (plate or powder), an alloy (e.g. Sn-Pb), a polymer (e.g. polypyrrole), or a composite (e.g. Ni - PTFE). Cathodic or anodic reactions may be involved in electrodeposition, although the majority of practical processes e.g. metal plating involve cathodic reactions.

Electroplating

is the production of an adherent and compact film on an electrode; the term is most frequently used to refer to the cathodic electrodeposition of a metal or an alloy in compact form.

Anodising

is the production of an adherent surface oxide film on a metal (often an aluminium alloy) by an anodic treatment.

Chemical Reactions are usually written in shorthand form which describes the chemical transformation of reactants (on the left hand side) to products (on the right hand side).
For example, the electrolysis of an acidic solution containing high levels of dissolved copper sulphate, using an inert anode, results in the following overall reaction:

$CuSO_4$ (l) + H_2O (l) $\rightarrow$ Cu (s) + ½ O_2 (g) + H_2SO_4 (l)

The terms in brackets are sometimes included to show the phase of the species i.e. (l) liquid (s) solid (g) gas. If water based (aq) often replaces (l).
The number placed before a species is known as the "stoichiometric coefficient"
In the case of the above reaction as written all the species except O_2 have a value of 1. The $CuSO_4$ and H_2SO_4 are largely present in ionic form as Cu2+, $2H^+$ and SO_4^{2-}
The reaction can therefore be written as:

Cu^{2+}(aq) + H_2O(l) $\rightarrow$ Cu(s) + ½ O^2(g) + $2H^+$ (aq)

The unidirectional arrow indicates the reaction takes place left to right.

A bidirectional arrow is used to indicate that the reaction can take place in either direction.
For example, the cathodic deposition of copper from acid copper sulphate solution may be considered a reversible reaction:

$$Cu_c + 2e^- \leftrightarrows Cu_A$$

as the copper may be dissolved by using as a soluble anode.

Electrochemical Reactions.
These are chemical reactions in which electrons participate (as reactants or products). The above two reactions do not usually occur via direct chemical reaction but rather by an electrochemical route as follows:

Anode reaction
$H_2O - 2e^- \rightarrow ½ O_2 + 2H^{+.}$ (a)

Cathode reaction
$Cu^{2+} + 2e^- \rightarrow Cu.$ (b)

overall cell reaction

$Cu^{2+} + H_2O \rightarrow Cu + ½ O_2 + 2 H^{+.}$ (c)

Reactions (a) and (b) have been written with the same number of electrons and are own as "balanced half-cell reactions". Reaction (c) may be obtained by addition the cathodic (reduction) reaction and the anodic (oxidation) reaction.

Acids and Bases
The proton is a hydrogen cation, H^+ according to the Brønsted-Lowry classification, acids (pH<7) are proton donors and bases (pH>7) are proton acceptors. For example, sulphuric acid dissociates readily in aqueous solution i.e. the following equilibria lie strongly to the right:

$H_2SO_4 \leftrightarrows H^+ + HSO_4^-$

$H_2SO_4 \leftrightarrows 2H^+ + SO_4^{2-}$

On the other hand, sodium hydroxide is a strong base as it produces a high level of hydroxyl ions (OH^-), according to the equilibrium:

$NaOH. \leftrightarrows Na^+ + OH^-$

These equilibria may be rewritten in terms of reactions involving the hydroxonium ion, H_3O + , as follows:

$H_2SO_4 + H2O \leftrightarrows H3O^+ + HSO_4^-$ (d)

$H_2SO_4 + 2H_2O \leftrightarrows 2H_2O + SO^2_{4.}$ (e)

The hydroxonium ion better represents the hydrogen ion in aqueous solution as, in reality each H^+ ion has a water molecule firmly attached to it.

In reactions (d,e) H_2SO_4 is the acid and H_2O is the "conjugate base"
In the case of sodium hydroxide:

$NaOH + H_3O^+ \leftrightarrows Na^+ + 2H_2O$

And the NaOH base reacts with H_3O^+ as a "conjugate acid"
Water is only weakly dissociated into ions and is amphoteric (i.e. it shows both acid and base behavior) due to its self ionisation:

$$H_2O \leftrightarrows H^+ + OH^-$$

Which is better represented by the equilibrium:

$H_2O + H_2O \leftrightarrows H_3O^+ + OH^-$