Chapter -
INTRODUCTION TO NANOMATERIALS

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1. Introduction

Nanomaterials are cornerstones of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

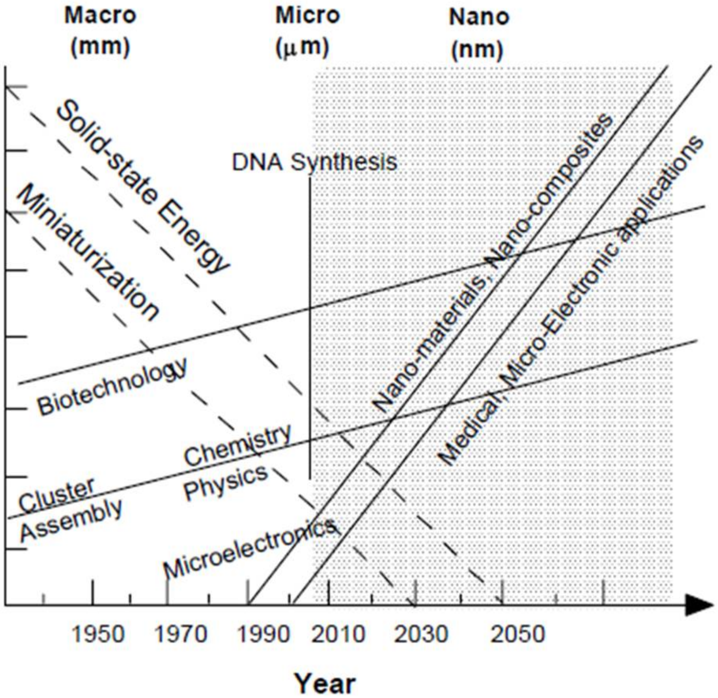


Fig. 1. Evolution of science and technology and the future

1.1. What are nanomaterials?

Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Fig. 2. Nanomaterial (For example: Carbon nanotube)

1.2. Where are nanomaterials found?

Some nanomaterials occur naturally, but of particular interest are engineered nanomaterials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery.

Engineered nanomaterials are resources designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours.

Nanomaterials are already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes. Nanocoatings and nanocomposites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight, and longer-lasting tennis balls using butyl-rubber/nano-clay composites. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows, and nanoscale silica is being used as filler in a range of products, including cosmetics and dental fillings.

2. Advances in Nanomaterials

The history of nanomaterials began immediately after the big bang when Nanostructures were formed in the early meteorites. Nature later evolved many other Nanostructures like seashells, skeletons etc. Nanoscaled smoke particles were formed during the use of fire by early humans. The scientific story of nanomaterials however began much later. One of the first scientific report is the colloidal gold particles synthesised by Michael Faraday as early as 1857. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940's, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements.

Nanosized amorphous silica particles have found large-scale applications in many every-day consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibers and catalyst supports. In the 1960s and 1970's metallic nanopowders for magnetic recording tapes were developed. In 1976, for the first time, nanocrystals produced by the now popular inert- gas evaporation technique was published by Granqvist and Buhrman. Recently it has been found that the Maya blue paint is a nanostructured hybrid material. The origin of its color and its resistance to acids and biocorrosion are still not understood but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (clay) crystals that form a superlattice with a period of 1.4 nm, with intercalates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue color is obtained only when both these nanoparticles and the superlattice are present, as has been shown by the fabrication of synthetic samples.

Today nanophase engineering expands in a rapidly growing number of structural and functional materials, both inorganic and organic, allowing to manipulate mechanical, catalytic, electric, magnetic, optical and electronic functions. The production of nanophase or cluster-assembled materials is usually based upon the creation of separated small clusters which then are fused into a bulk-like material or on their embedding into compact liquid or solid matrix materials. e.g. nanophase silicon, which differs from normal silicon in physical and electronic properties, could be applied to macroscopic semiconductor processes to create new devices. For instance, when ordinary glass is doped with quantized semiconductor "colloids," it becomes a high performance optical medium with potential applications in optical computing.

3. Classification of Nanomaterials

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica).

According to Siegel, Nanostructured materials are classified as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

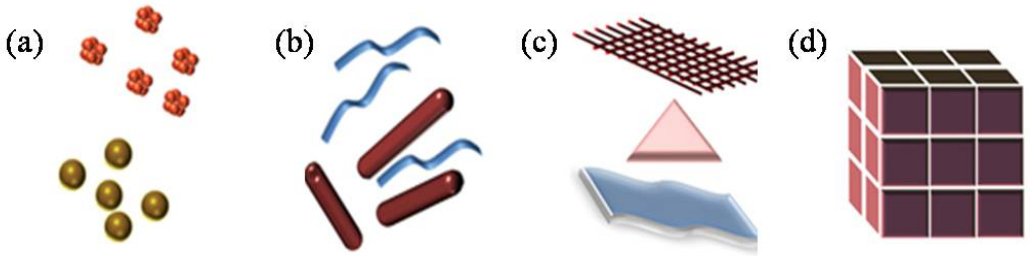


Fig. 3. Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

Nanomaterials are materials which are characterized by an ultra fine grain size (< 50 nm) or by a dimensionality limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multilayers), two (ultrafine-grained overlayers or buried layers), and three (nanophase materials consisting of equiaxed nanometer sized grains) as shown in the above figure 3.

4. Why are nanomaterials important?

These materials have created a high interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. Some examples are given below:

(i) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics.

(ii) Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells.

(iii) Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry.

(iv) Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains, while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states, which give rise to special properties in addition to the super-paramagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration.

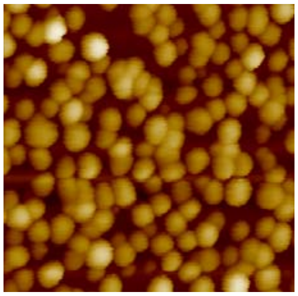
(v) Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages concerning activity, selectivity and lifetime in chemical transformations and electrocatalysis (fuel cells). Enantioselective catalysis was also achieved using chiral modifiers on the surface of nanoscale metal particles.

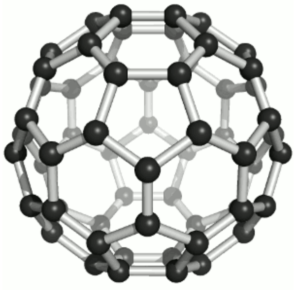
(vi) Nanostructured metal-oxide thin films are receiving a growing attention for the realization of gas sensors (NOx, CO, CO2, CH4 and aromatic hydrocarbons) with enhanced sensitivity and selectivity. Nanostructured metal-oxide (MnO2) finds application for rechargeable batteries for cars or consumer goods. Nanocrystalline silicon films for highly transparent contacts in thin film solar cell and nano-structured titanium oxide porous films for its high transmission and significant surface area enhancement leading to strong absorption in dye sensitized solar cells.

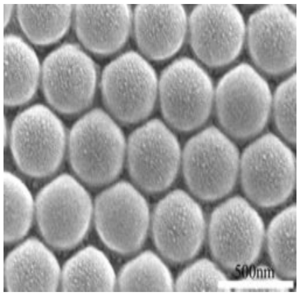
(vii) Polymer based composites with a high content of inorganic particles leading to a high dielectric constant are interesting materials for photonic band gap structure.

5. Examples of Nanomaterials

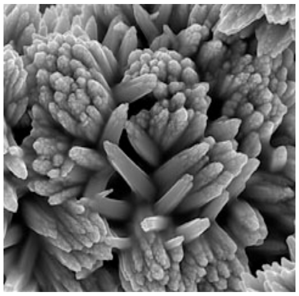
Nanomaterials (gold, carbon, metals, meta oxides and alloys) with variety of morphologies (shapes) are depicted in Fig. 4.

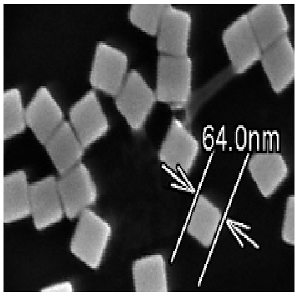

Au nanoparticle


Buckminsterfullerene



FePt nanosphere


Titanium nanoflower



Silver nanocubes

SnO2 nanoflower

Fig. 4. Nanomaterials with a variety of morphologies

6. Nanomaterial - synthesis and processing

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. This indeed allows us to think in both the 'bottom up' or the 'top down' approaches (Fig. 5) to synthesize nanomaterials, i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms. This domain is a pure example of interdisciplinary work encompassing physics, chemistry, and engineering upto medicine.

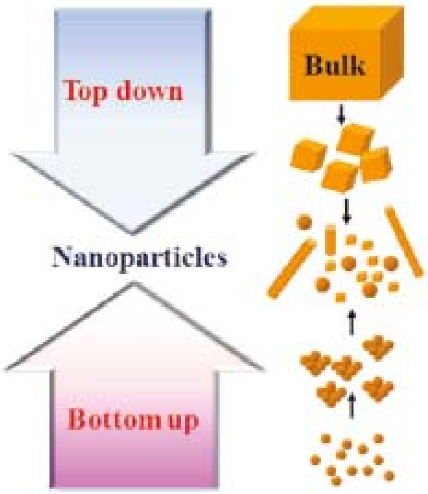


Fig. 5. Schematic illustration of the preparative methods of nanoparticles.

6.1. Methods for creating nanostructures

There are many different ways of creating nanostructures: of course, macromolecules or nanoparticles or buckyballs or nanotubes and so on can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly (sometimes also called bio-mimetic processes). Using these methods, synthesized materials can be arranged into useful shapes so that finally the material can be applied to a certain application.

6.1.2. Mechanical grinding

Mechanical attrition is a typical example of 'top down' method of synthesis of nanomaterials, where the material is prepared not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to essentially the synthesis of all classes of materials. The major advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for various applications. Similarly, the serious problems that are usually cited are;

1. contamination from milling media and/or atmosphere, and
2. to consolidate the powder product without coarsening the nanocrystalline microstructure.

In fact, the contamination problem is often given as a reason to dismiss the method, at least for some materials. Here we will review the mechanisms presently believed responsible for formation of nanocrystalline structures by mechanical attrition of single phase powders, mechanical alloying of dissimilar powders, and mechanical crystallisation of amorphous materials. The two important problems of contamination and powder consolidation will be briefly considered.

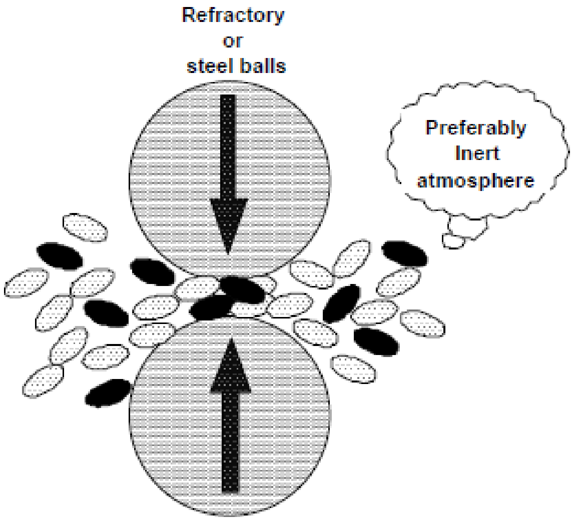


Fig. 6. Schematic representation of the principle of mechanical milling

Mechanical milling is typically achieved using high energy shaker, planetary ball, or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere. Nanoparticles are produced by the shear action during grinding.

Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process. As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere and that the powder particles be handled in an appropriate vacuum system or glove box. This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed. Based on the energy of the milling process and thermodynamic properties of the constituents the alloy can be rendered amorphous by this processing.

6.1.3. Wet Chemical Synthesis of Nanomaterials

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups:

1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching.
2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

6.1.3.1. Sol-gel process

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as $Si(OEt)_4$ (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR)**z** can be described as follows:

$$MOR + H_2O \rightarrow MOH + ROH \text{ (hydrolysis)}$$

$$MOH + ROM \rightarrow M\text{-}O\text{-}M + ROH \text{ (condensation)}$$

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

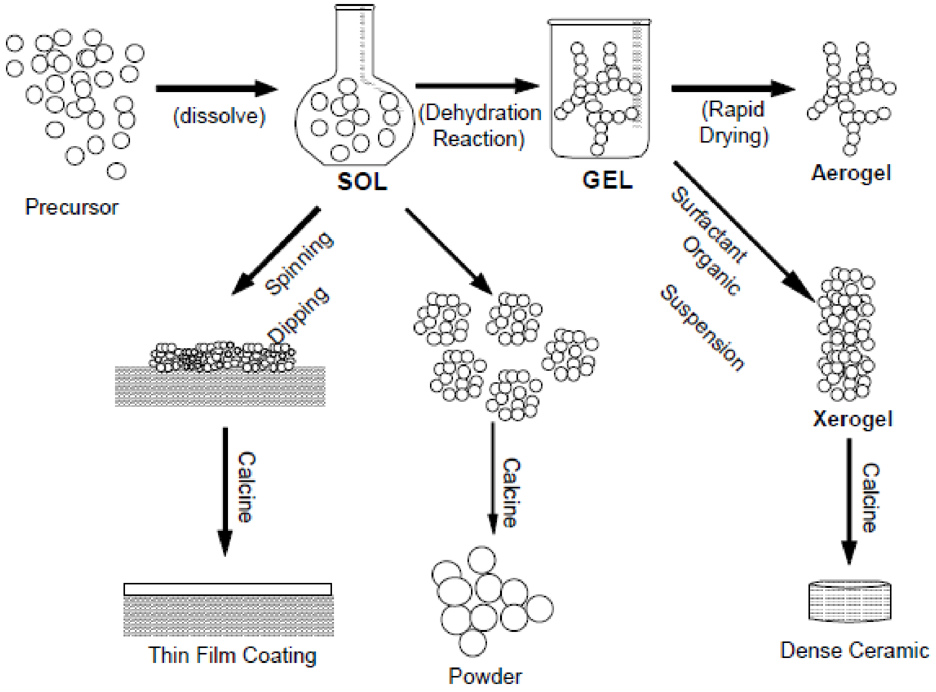


Fig. 7. Schematic representation of sol-gel process of synthesis of nanomaterials.

1. Formation of different stable solutions of the alkoxide or solvated metal precursor.
2. Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation reaction that results in a dramatic increase in the viscocity of the solution.

3. Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores. Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.
4. Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps: (i) the constant rate period, (ii) the critical point, (iii) the falling rate period, (iv) the second falling rate period. If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.
5. Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800^0C.
6. Densification and decomposition of the gels at high temperatures ($T>800^0$C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.

The interest in this synthesis method arises due to the possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to the high temperature process required by melting glass or firing ceramics.

The major difficulties to overcome in developing a successful bottom-up approach is controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwanted reactant is left on the product and completely removing any growth aids that may have been used in the process. Also production rates of nano powders are very low by this process. The main advantage is one can get monosized nano particles by any bottom up approach.

6.1.4. Gas Phase synthesis of nanomaterials

The gas-phase synthesis methods are of increasing interest because they allow elegant way to control process parameters in order to be able to produce size, shape and chemical composition controlled nanostructures. Before we discuss a few selected pathways for gas-phase formation of nanomaterials, some general aspects of gas-phase synthesis needs to be discussed. In conventional chemical vapour deposition (CVD) synthesis, gaseous products either are allowed to react homogeneously or heterogeneously depending on a particular application.

1. In homogeneous CVD, particles form in the gas phase and diffuse towards a cold surface due to thermophoretic forces, and can either be scrapped of from the cold surface to give nano-powders, or deposited onto a substrate to yield what is called ***'particulate films'***.
2. In heterogeneous CVD, the solid is formed on the substrate surface, which catalyses the reaction and a dense film is formed.

In order to form nanomaterials several modified CVD methods have been developed. Gas phase processes have inherent advantages, some of which are noted here:

- An excellent control of size, shape, crystallinity and chemical composition
- Highly pure materials can be obtained
- Multicomonent systems are relatively easy to form
- Easy control of the reaction mechanisms

Most of the synthesis routes are based on the production of small clusters that can aggregate to form nano particles (condensation). Condensation occurs only when the vapour is supersaturated and in these processes homogeneous nucleation in the gas phase is utilised to form particles. This can be achieved both by physical and chemical methods.

6.1.4.1. Furnace

The simplest fashion to produce nanoparticles is by heating the desired material in a heat-resistant crucible containing the desired material. This method is appropriate only for materials that have a high vapour pressure at the heated temperatures that can be as high as 2000°C. Energy is normally introduced into the precursor by arc heating, electron-beam heating or Joule heating. The atoms are evaporated into an atmosphere, which is either inert (e.g. He) or reactive (so as to form a compound). To carry out reactive synthesis, materials with very low vapour pressure have to be fed into the furnace in the form of a suitable precursor such as organometallics, which decompose in the furnace to produce a condensable material. The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas and undergo condensation into small clusters via homogeneous nucleation. In case a compound is being synthesized, these precursors react in the gas phase and form a compound with the material that is separately injected in the reaction chamber. The clusters would continue to grow if they remain in the supersaturated region. To control their size, they need to be rapidly removed from the supersaturated environment by a carrier gas. The cluster size and its distribution are controlled by only three parameters:

1) the rate of evaporation (energy input),
2) the rate of condensation (energy removal), and
3) the rate of gas flow (cluster removal).

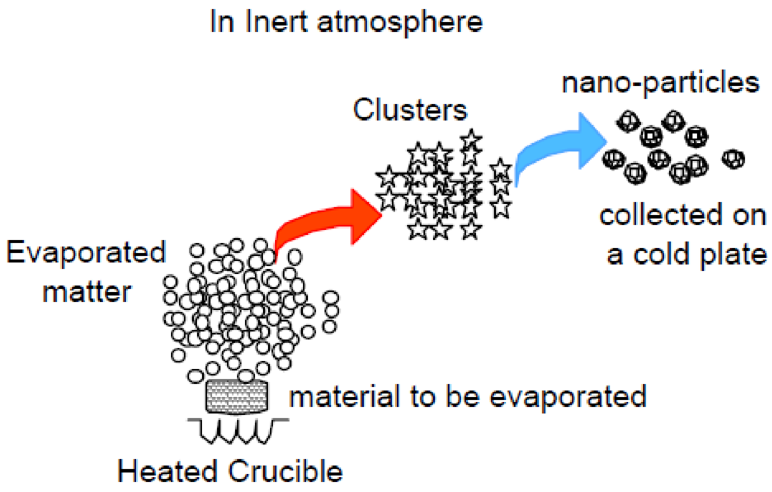


Fig. 8. Schematic representation of gas phase process of synthesis of single phase nanomaterials from a heated crucible

Because of its inherent simplicity, it is possible to scale up this process from laboratory (mg/day) to industrial scales (tons/day).

6.1.4.2. Flame assisted ultrasonic spray pyrolysis

In this process, precusrsors are nebulized and then unwanted components are burnt in a flame to get the required material, eg. ZrO_2 has been obtained by this method from a precursor of $Zr(CH_3\ CH_2\ CH_2O)_4$. Flame hydrolysis that is a variant of this process is used for the manufacture of fused silica. In the process, silicon tetrachloride is heated in an oxy-hydrogen flame to give a highly dispersed silica. The resulting white amorphous powder consists of spherical particles with sizes in the range 7-40 nm. The combustion flame synthesis, in which the burning of a gas mixture, e.g. acetylene and oxygen or hydrogen and oxygen, supplies the energy to initiate the pyrolysis of precursor compounds, is widely used for the industrial production of powders in large quantities, such as carbon black, fumed silica and titanium dioxide. However, since the gas pressure during the reaction is high, highly agglomerated powders are produced which is disadvantageous for subsequent processing. The basic idea of low pressure combustion flame synthesis is to extend the pressure range to the pressures used in gas phase synthesis and thus to reduce or avoid the agglomeration. Low pressure flames have been extensively used by aerosol scientists to study particle formation in the flame.

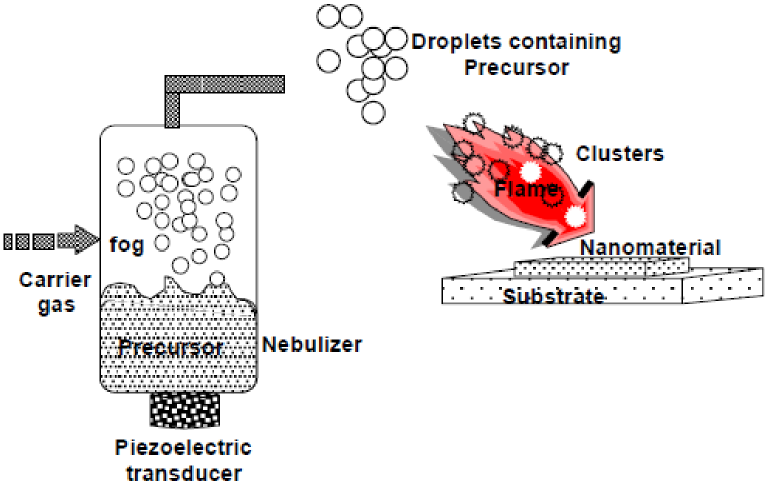


Fig. 9. Flame assisted ultrasonic spray pyrolysis

A key for the formation of nanoparticles with narrow size distributions is the exact control of the flame in order to obtain a flat flame front. Under these conditions the thermal history, i.e. time and temperature, of each particle formed is identical and narrow distributions result. However, due to the oxidative atmosphere in the flame, this synthesis process is limited to the formation of oxides in the reactor zone.

6.1.4.3. Gas Condensation Processing (GPC)

In this technique, a metallic or inorganic material, e.g. a suboxide, is vaporised using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr). Cluster form in the vicinity of the source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase.

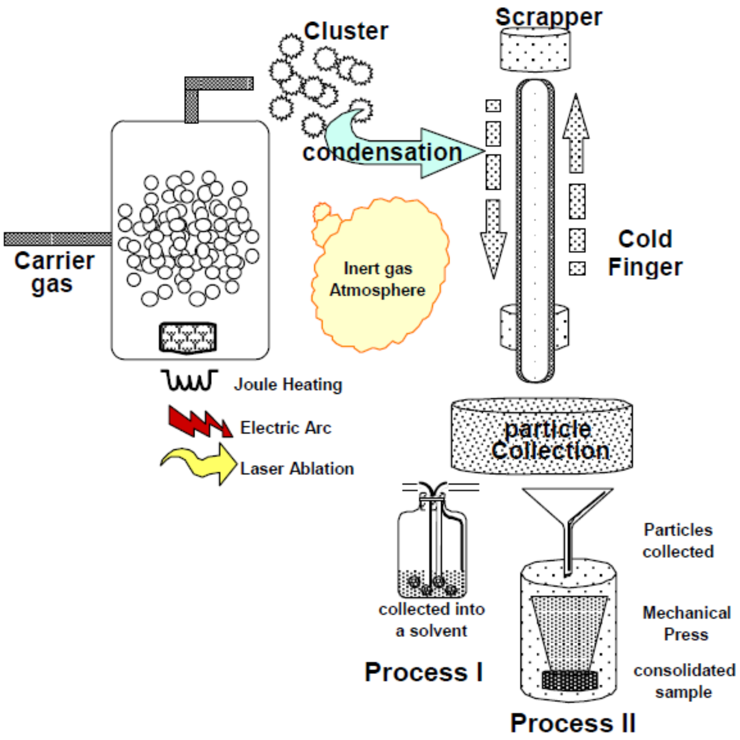


Fig. 10. Schematic representation of typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.

The cluster or particle size depends critically on the residence time of the particles in the growth system and can be influenced by the gas pressure, the kind of inert gas, i.e. He, Ar or Kr, and on the evaporation rate/vapour pressure of the evaporating material. With increasing gas pressure, vapour pressure and mass of the inert gas used the average particle size of the nanoparticles increases. Lognormal size distributions have been found experimentally and have been explained theoretically by the growth mechanisms of the particles. Even in more complex processes such as the low pressure combustion flame synthesis where a number of chemical reactions are involved the size distributions are determined to be lognormal.

Originally, a rotating cylindrical device cooled with liquid nitrogen was employed for the particle collection: the nanoparticles in the size range from 2-50 nm are extracted from the gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density and no agglomeration. Subsequenly, the nanoparticles are removed from the surface of the cylinder by means of a scraper in the form of a metallic plate. In addition to this cold finger device several techniques known from aerosol science have now been implemented for the use in gas condensation systems such as corona discharge, etc. These methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nanopowders. However, these methods can only be used in a system designed for gas flow, i.e. a dynamic vacuum is generated by means of both continuous pumping and gas inlet via mass flow controller. A major advantage over convectional gas flow is the improved control of the particle sizes. It has been found that the particle size distributions in gas flow systems, which are also lognormal, are shifted towards smaller average values with an appreciable reduction of the standard deviation of the distribution. Depending on the flow rate of the He-gas, particle sizes are reduced by 80% and standard deviations by 18%.

The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta or Mo). If metals with high melting points or metals which react with the crucibles, are to be prepared, sputtering, i.e. for W and Zr, or laser or electron beam evaporation has to be used. Synthesis of alloys or intermetallic compounds by thermal evaporation can only be done in the exceptional cases that the vapour pressures of the elements are similar. As an alternative, sputtering from an alloy or mixed target can be employed. Composite materials such as Cu/Bi or W/Ga have been synthesised by simultaneous evaporation from two separate crucibles onto a rotating collection device. It has been found that excellent intermixing on the scale of the particle size can be obtained.

However, control of the composition of the elements has been difficult and reproducibility is poor. Nanocrystalline oxide powders are formed by controlled postoxidation of primary nanoparticles of a pure metal (e.g. Ti to TiO2) or a suboxide (e.g. ZrO to ZrO2). Although the gas condensation method including the variations have been widely employed to prepared a variety of metallic and ceramic materials, quantities have so far been limited to a laboratory scale. The quantities of metals are below 1 g/day, while quantities of oxides can be as high as 20 g/day for simple oxides such as CeO2 or ZrO2. These quantities are sufficient for materials testing but not for industrial production. However, it should be mentioned that the scale-up of the gas condensation method for industrial production of nanocrystalline oxides by a company called nanophase technologies has been successful.

6.1.4.4. Chemical Vapour Condensation (CVC)

As shown schematically in Figure, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapour Condensation or the CVC process. Depending on the processing parameters nucleation of nanoparticles is observed during chemical vapour deposition (CVC) of thin films and poses a major problem in obtaining good film qualities. The original idea of the novel CVC process which is schematically shown below where, it was intended to adjust the parameter field during the synthesis in order to suppress film formation and enhance homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time both particle and film formation can be obtained.

Adjusting the residence time of the precursor molecules by changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber occurs. Then the temperature of the hot wall reactor results in the fertile production of nanosized particles of metals and ceramics instead of thin films as in CVD processing. In the simplest form a metal organic precursor is introduced into the hot zone of the reactor using mass flow controller. Besides the increased quantities in this continuous process compared to GPC has been demonstrated that a wider range of ceramics including nitrides and carbides can be synthesised. Additionally, more complex oxides such as $BaTiO_3$ or composite structures can be formed as well. Appropriate precursor compounds can be readily found in the CVD literature. The extension to production of nanoparticles requires the determination of a modified parameter field in order to promote particle formation instead of film formation. In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of

1. mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and
2. coated nanoparticles, i.e., n-ZrO_2 coated with n-Al_2O_3 or vice versa, by supplying a second precursor at a second stage of the reactor. In this case nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in a second stage of the reactor.

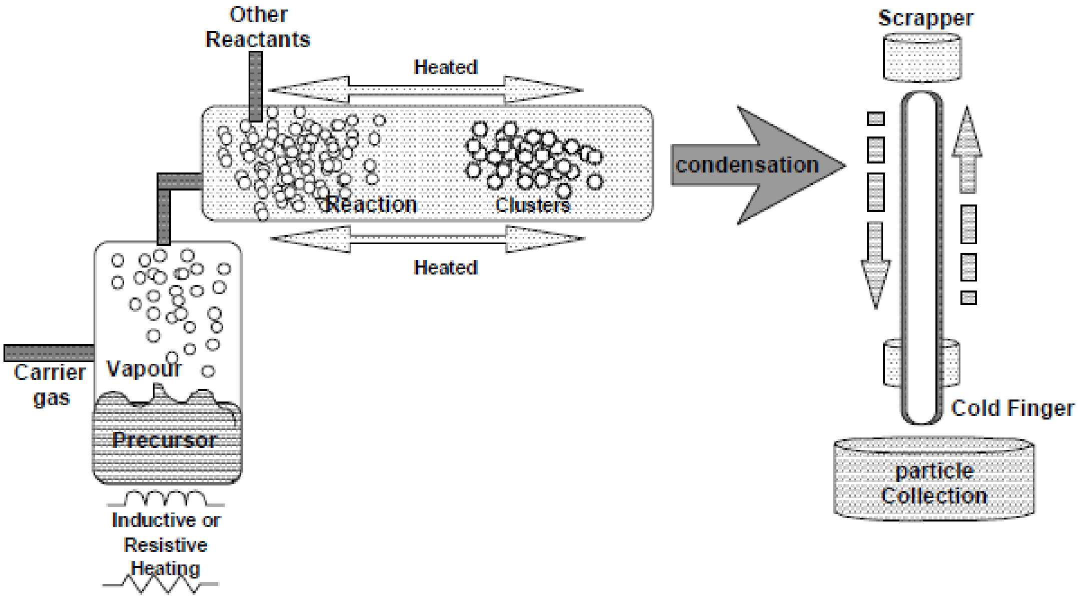


Fig. 11. A schematic of a typical CVC reactor

Because CVC processing is continuous, the production capabilities are much larger than in GPC processing. Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

6.1.5. Sputtered Plasma Processing:

In this method is yet again a variation of the gas-condensation method excepting the fact that the source material is a sputtering target and this target is sputtered using rare gases and the constituents are allowed to agglomerate to produce nanomaterial. Both dc (direct current) and rf (radio-frequency) sputtering has been used to synthesize nanoparticles. Again reactive sputtering or multitarget sputtering has been used to make alloys and/or oxides, carbides, nitrides of materials. This method is specifically suitable for the preparation of ultrapure and non-agglomerated nanoparticles of metal.

6.1.5.1. Microwave Plasma Processing

This technique is similar to the previously discussed CVC method but employs plasma instead of high temperature for decomposition of the metal organic precursors. The method uses microwave plasma in a 50 mm diameter reaction vessel made of quartz placed in a cavity connected to a microwave generator. A precursor such as a chloride compound is introduced into the front end of the reactor. Generally, the microwave cavity is designed as a single mode cavity using the TE10 mode in a WR975 waveguide with a frequency of 0.915 GHz. The major advantage of the plasma assisted pyrolysis in contrast to the thermal activation is the low temperature reaction which reduces the tendency for agglomeration of the primary particles. This is also true in the case of plasma-CVD processes. Additionally, it has been shown that by introducing another precursor into a second reaction zone of the tubular reactor, e.g. by splitting the microwave guide tubes, the primary particles can be coated with a second phase. For example, it has been demonstrated that ZrO_2 nanoparticles can be coated by Al_2O_3. In this case the inner ZrO_2 core is crystalline, while the Al_2O_3 coating is amorphous. The reaction sequence can be reversed with the result that an amorphous Al_2O_3 core is coated with crystalline ZrO_2. While the formation of the primary particles occurs by homogeneous nucleation, it can be easily estimated using gas reaction kinetics that the coating on the primary particles grows heterogeneously and that homogeneous nucleation of nanoparticles originating from the second compound has a very low probability. A schematic representation of the particle growth in plasma's is given below:

6.1.6. Particle precipitation aided CVD:

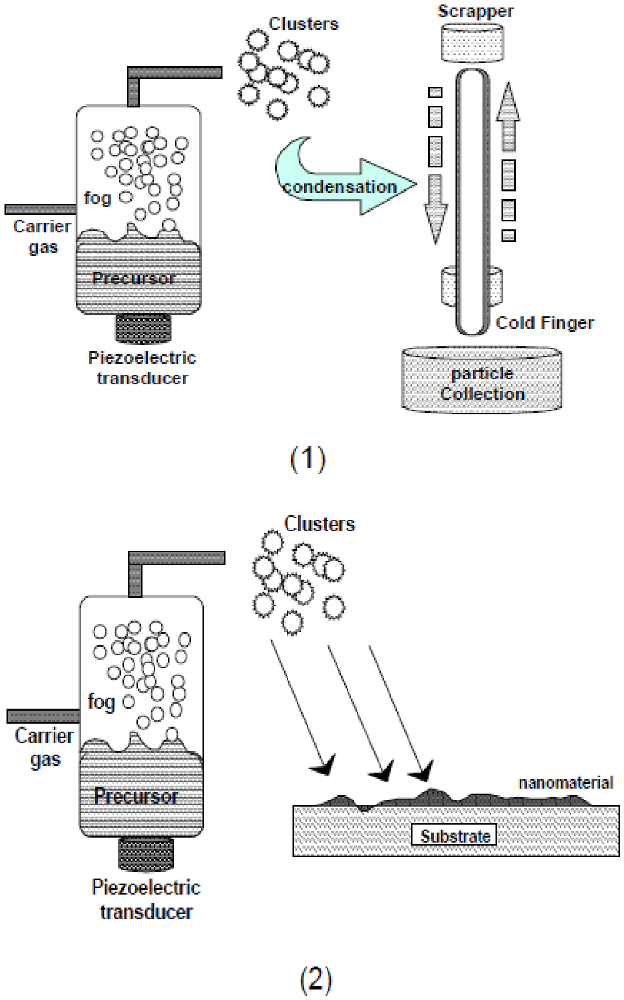


Fig. 12. Schematic representation of (1) nanoparticle, and (2) particulate film formation

In another variation of this process, colloidal clusters of materials are used to prepare nanoparticles. The CVD reaction conditions are so set that particles form by condensation in the gas phase and collect onto a substrate, which is kept under a different condition that allows heterogeneous nucleation. By this method both nanoparticles and particulate films can be prepared. An example of this method has been used to form nanomaterials eg. SnO2, by a method called pyrosol deposition process, where clusters of tin hydroxide are transformed into small aerosol droplets, following which they are reacted onto a heated glass substrate.

6.1.7. Laser ablation

Laser ablation has been extensively used for the preparation of nanoparticles and particulate films. In this process a laser beam is used as the primary excitation source of ablation for generating clusters directly from a solid sample in a wide variety of applications. The small dimensions of the particles and the possibility to form thick films make this method quite an efficient tool for the production of ceramic particles and coatings and also an ablation source for analytical applications such as the coupling to induced coupled plasma emission spectrometry, ICP, the formation of the nanoparticles has been explained following a liquefaction process which generates an aerosol, followed by the cooling/solidification of the droplets which results in the formation of fog. The general dynamics of both the aerosol and the fog favours the aggregation process and micrometer-sized fractal-like particles are formed. The laser spark atomizer can be used to produce highly mesoporous thick films and the porosity can be modified by the carrier gas flow rate. ZrO_2 and SnO_2 nanoparticulate thick films were also synthesized successfully using this process with quite identical microstructure. Synthesis of other materials such as lithium manganate, silicon and carbon has also been carried out by this technique.

7. Properties of Nanomaterials

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most microstructured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them: (i) large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials.

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to length, the entire material will be affected by the surface properties of nanomaterials. This in turn may enhance or modify the properties of the bulk materials. For example, metallic nanoparticles can be used as very active catalysts. Chemical sensors from nanoparticles and nanowires enhanced the sensitivity and sensor selectivity. The nanometer feature sizes of nanomaterials also have spatial confinement effect on the materials, which bring the quantum effects.

The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic and optical properties of the materials. For example, lasers and light emitting diodes (LED) from both of the quantum dots and quantum wires are very promising in the future optoelections. High density information storage using quantum dot devices is also a fast developing area. Reduced imperfections are also an important factor in determination of the properties of the nanomaterials. Nanosturctures and Nanomaterials favors of a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing. This increased materials perfection affects the properties of nanomaterials. For example, the chemical stability for certain nanomaterials may be enhanced, the mechanical properties of nanomaterials will be better than the bulk materials. The superior mechanical properties of carbon nanotubes are well known. Due to their nanometer size, nanomaterials are already known to have many novel properties. Many novel applications of the nanomaterials rose from these novel properties have also been proposed.

7.1. Optical properties

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine.

The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have dramatic influence on optical properties of metal nanostructures. Fig. () exemplifies the difference in the optical properties of metal and semiconductor nanoparticles. With the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles. When metal nanoparticles are enlarged, their optical properties change only slightly as observed for the different samples of gold nanospheres in fig. (). However, when an anisotropy is added to the nanoparticle, such as growth of nanorods, the optical properties of the nanoparticles change dramatically.

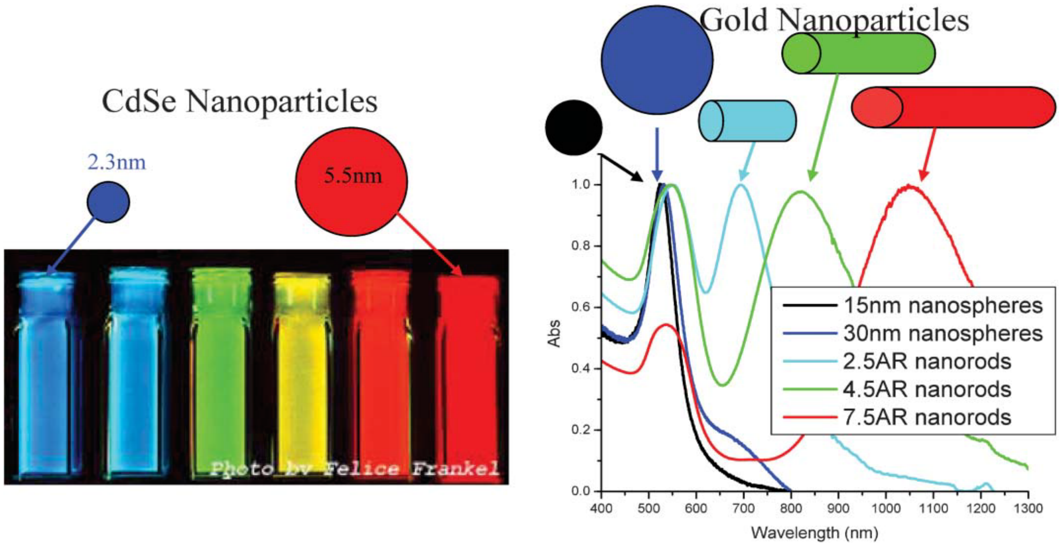


Fig. 13. Fluorescence emission of (CdSe) ZnS quantum dots of various sizes and absorption spectra of various sizes and shapes of gold nanoparticles (Chem. Soc. Rev., 2006, 35, 209–217).

7.2. Electrical properties

Electrical Properties of Nanoparticles" discuss about fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, electrical conductivity of nanocomposites. One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.

In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information: (i) the influence of carbon nanotube length on the resistance; and (ii) the resistances of the different nanotubes. As the nanotubes have different lengths, then with increasing protrusion of the fiber bundle an increasing number of carbon nanotubes will touch the surface of the mercury droplet and contribute to the electrical current transport.

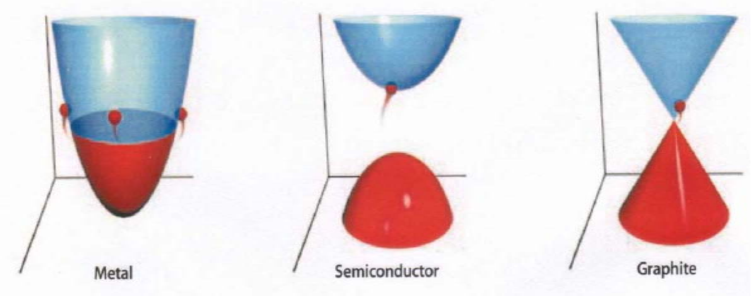


Fig. 14. Electrical behavior of naotubes (P. G. Collins and Ph. Avouris, *Scientific American*, 62, 2000, 283).

7.3. Mechanical properties

"Mechanical Properties of Nanoparticles" deals with bulk metallic and ceramic materials, influence of porosity, influence of grain size, superplasticity, filled polymer composites, particle-filled polymers, polymer-based nanocomposites filled with platelets, carbon nanotube-based composites. The discussion of mechanical properties of nanomaterials is, in to some extent, only of quite basic interest, the reason being that it is problematic to produce macroscopic bodies with a high density and a grain size in the range of less than 100 nm. However, two materials, neither of which is produced by pressing and sintering, have attracted much greater interest as they will undoubtedly achieve industrial importance.

These materials are polymers which contain nanoparticles or nanotubes to improve their mechanical behaviors, and severely plastic-deformed metals, which exhibit astonishing properties. However, because of their larger grain size, the latter are generally not accepted as nanomaterials. Experimental studies on the mechanical properties of bulk nanomaterials are generally impaired by major experimental problems in producing specimens with exactly defined grain sizes and porosities. Therefore, model calculations and molecular dynamic studies are of major importance for an understanding of the mechanical properties of these materials.

Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is conducted. The latter point is of special importance, as any specific advantages of a nanoparticulate filler may be lost if the filler forms aggregates, thereby mimicking the large particles. Particulate-filled polymer-based nanocomposites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles or platelets, and on the degree of agglomeration. In this class of material, polymers filled with silicate platelets exhibit the best mechanical properties and are of the greatest economic relevance. The larger the particles of the filler or agglomerates, the poorer are the properties obtained. Although, potentially, the best composites are those filled with nanofibers or nanotubes, experience teaches that sometimes such composites have the least ductility. On the other hand, by using carbon nanotubes it is possible to produce composite fibers with extremely high strength and strain at rupture. Among the most exciting nanocomposites are the polymer-ceramic nanocomposites, where the ceramic phase is platelet-shaped. This type of composite is preferred in nature, and is found in the structure of bones, where it consists of crystallized mineral platelets of a few nanometers thickness that are bound together with collagen as the matrix. Composites consisting of a polymer matrix and defoliated phyllosilicates exhibit excellent mechanical and thermal properties.

7.4. Magnetic properties

Bulk gold and Pt are non-magnetic, but at the nano size they are magnetic. Surface atoms are not only different to bulk atoms, but they can also be modified by interaction with other chemical species, that is, by capping the nanoparticles. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, it should be possible that non-ferromagnetic bulk materials exhibit ferromagnetic-like behavior when prepared in nano range. One can obtain magnetic nanoparticles of Pd, Pt and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, the ferromagnetism arises from the structural changes associated with size effects.

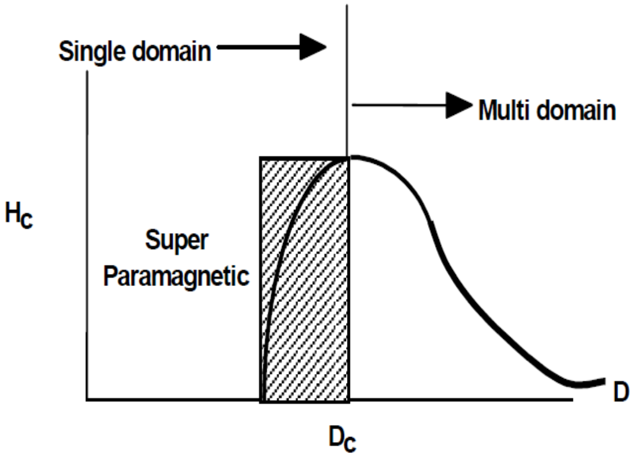


Fig. 15. Magnetic properties of nanostrucutred materials

However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules: the charge localized at the particle surface gives rise to ferromagnetic-like behavior.

Surface and the core of Au nanoparticles with 2 nm in diameter show ferromagnetic and paramagnetic character, respectively. The large spin-orbit coupling of these noble metals can yield to a large anisotropy and therefore exhibit high ordering temperatures. More surprisingly, permanent magnetism was observed up to room temperature for thiol-capped Au nanoparticles. For nanoparticles with sizes below 2 nm the localized carriers are in the 5d band. Bulk Au has an extremely low density of states and becomes diamagnetic, as is also the case for bare Au nanoparticles. This observation suggested that modification of the d band structure by chemical bonding can induce ferromagnetic like character in metallic clusters.

8. Selected Application of nanomaterials

Nanomaterials having wide range of applications in the field of electronics, fuel cells, batteries, agriculture, food industry, and medicines, etc... It is evident that nanomaterials split their conventional counterparts because of their superior chemical, physical, and mechanical properties and of their exceptional formability.

8.1. Fuel cells

A fuel cell is an electrochemical energy conversion device that converts the chemical energy from fuel (on the anode side) and oxidant (on the cathode side) directly into electricity. The heart of fuel cell is the electrodes. The performance of a fuel cell electrode can be optimized in two ways; by improving the physical structure and by using more active electro catalyst. A good structure of electrode must provide ample surface area, provide maximum contact of catalyst, reactant gas and electrolyte, facilitate gas transport and provide good electronic conductance. In this fashion the structure should be able to minimize losses.

8.1.1. Carbon nanotubes - Microbial fuel cell

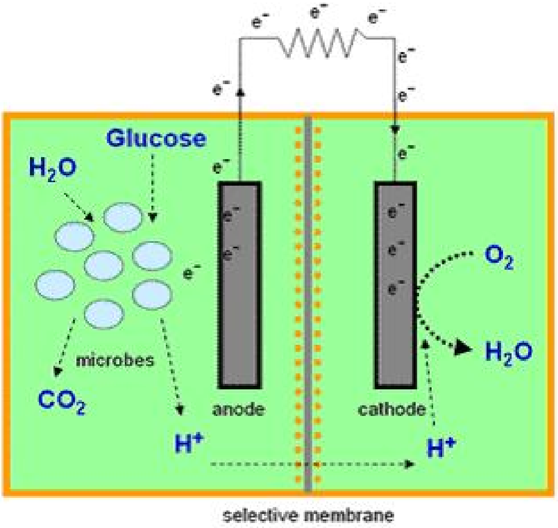


Fig. 16. Schematic representation of microbial fuel cell

Microbial fuel cell is a device in which bacteria consume water-soluble waste such as sugar, starch and alcohols and produces electricity plus clean water. This technology will make it possible to generate electricity while treating domestic or industrial wastewater. Microbial fuel cell can turn different carbohydrates and complex substrates present in wastewaters into a source of electricity. The efficient electron transfer between the microorganism and the anode of the microbial fuel cell plays a major role in the performance of the fuel cell. The organic molecules present in the wastewater posses a certain amount of chemical energy, which is released when converting them to simpler molecules like CO_2. The microbial fuel cell is thus a device that converts the chemical energy present in water-soluble waste into electrical energy by the catalytic reaction of microorganisms.

Carbon nanotubes (CNTs) have chemical stability, good mechanical properties and high surface area, making them ideal for the design of sensors and provide very high surface area due to its structural network. Since carbon nanotubes are also suitable supports for cell growth, electrodes of microbial fuel cells can be built using of CNT. Due to three-dimensional architectures and enlarged electrode surface area for the entry of growth medium, bacteria can grow and proliferate and get immobilized. Multi walled CNT scaffolds could offer self-supported structure with large surface area through which hydrogen producing bacteria (e.g., E. coli) can eventually grow and proliferate. Also CNTs and MWCNTs have been reported to be biocompatible for different eukaryotic cells. The efficient proliferation of hydrogen producing bacteria throughout an electron conducting scaffold of CNT can form the basis for the potential application as electrodes in MFCs leading to efficient performance.

8.2. Catalysis

Higher surface area available with the nanomaterial counterparts, nano-catalysts tend to have exceptional surface activity. For example, reaction rate at nano-aluminum can go so high, that it is utilized as a solid-fuel in rocket propulsion, whereas the bulk aluminum is widely used in utensils. Nano-aluminum becomes highly reactive and supplies the required thrust to send off pay loads in space. Similarly, catalysts assisting or retarding the reaction rates are dependent on the surface activity, and can very well be utilized in manipulating the rate-controlling step.

8.3. Phosphors for High-Definition TV

The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel techniques are candidates for improving the resolution of monitors. The use of nanophosphors is envisioned to reduce the cost of these displays so as to render high-definition televisions (HDTVs) and personal computers affordable to be purchase.

8.4. Next-Generation Computer Chips

The microelectronics industry has been emphasizing miniaturization, whereby the circuits, such as transistors, resistors, and capacitors, are reduced in size. By achieving a significant reduction in their size, the microprocessors, which contain these components, can run much faster, thereby enabling computations at far greater speeds. However, there are several technological impediments to these advancements, including lack of the ultrafine precursors to manufacture these components; poor dissipation of tremendous amount of heat generated by these microprocessors due to faster speeds; short mean time to failures (poor reliability), etc. Nanomaterials help the industry break these barriers down by providing the manufacturers with nanocrystalline starting materials, ultra-high purity materials, materials with better thermal conductivity, and longer-lasting, durable interconnections (connections between various components in the microprocessors).

Example: Nanowires for junctionless transistors

Transistors are made so tiny to reduce the size of sub assemblies of electronic systems and make smaller and smaller devices, but it is difficult to create high-quality junctions. In particular, it is very difficult to change the doping concentration of a material over distances shorter than about 10 nm. Researchers have succeeded in making the junctionless transistor having nearly ideal electrical properties. It could potentially operate faster and use less power than any conventional transistor on the market today. The device consists of a silicon nanowire in which current flow is perfectly controlled by a silicon gate that is separated from the nanowire by a thin insulating layer. The entire silicon nanowire is heavily n-doped, making it an excellent conductor. However, the gate is p-doped and its presence has the effect of depleting the number of electrons in the region of the nanowire under the gate. The device also has near-ideal electrical properties and behaves like the most perfect of transistors without suffering from current leakage like conventional devices and operates faster and using less energy.

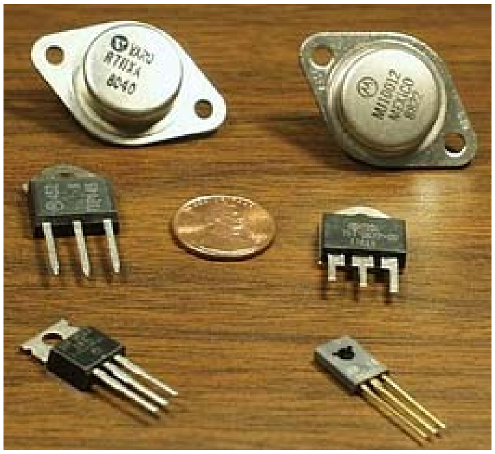


Fig. 17. Silicon nanowires in junctionless transistors

8.5. Elimination of Pollutants

Nanomaterials possess extremely large grain boundaries relative to their grain size. Hence, they are very active in terms of their chemical, physical, and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal.

8.6. Sun-screen lotion

Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nano-TiO2 provide enhanced sun protection factor (SPF) while eliminating stickiness. The added advantage of nano skin blocks (ZnO and TiO2) arises as they protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin color while working better than conventional skin-lotions.

8.7. Sensors

Sensors rely on the highly active surface to initiate a response with minute change in the concentration of the species to be detected. Engineered monolayers (few Angstroms thick) on the sensor surface are exposed to the environment and the peculiar functionality (such as change in potential as the CO/anthrax level is detected) is utilized in sensing.

9. Disadvantages of Nanomaterials

(i) Instability of the particles - Retaining the active metal nanoparticles is highly challenging, as the kinetics associated with nanomaterials is rapid. In order to retain nanosize of particles, they are encapsulated in some other matrix. Nanomaterials are thermodynamically metastable and lie in the region of high-energy local-minima. Hence they are prone to attack and undergo transformation. These include poor corrosion resistance, high solubility, and phase change of nanomaterials. This leads to deterioration in properties and retaining the structure becomes challenging.

(ii) Fine metal particles act as strong explosives owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.

(iii) Impurity - Because nanoparticles are highly reactive, they inherently interact with impurities as well. In addition, encapsulation of nanoparticles becomes necessary when they are synthesized in a solution (chemical route). The stabilization of nanoparticles occurs because of a non-reactive species engulfing the reactive nano-entities. Thereby, these secondary impurities become a part of the synthesized nanoparticles, and synthesis of pure nanoparticles becomes highly difficult. Formation of oxides, nitrides, etc can also get aggravated from the impure environment/ surrounding while synthesizing nanoparticles. Hence retaining high purity in nanoparticles can become a challenge hard to overcome.

(iv) Biologically harmful - Nanomaterials are usually considered harmful as they become transparent to the cell-dermis. Toxicity of nanomaterials also appears predominant owing to their high surface area and enhanced surface activity. Nanomaterials have shown to cause irritation, and have indicated to be carcinogenic. If inhaled, their low mass entraps them inside lungs, and in no way they can be expelled out of body. Their interaction with liver/blood could also prove to be harmful (though this aspect is still being debated on).

(v) Difficulty in synthesis, isolation and application - It is extremely hard to retain the size of nanoparticles once they are synthesized in a solution. Hence, the nanomaterials have to be encapsulated in a bigger and stable molecule/material. Hence free nanoparticles are hard to be utilized in isolation, and they have to be interacted for intended use via secondary means of exposure. Grain growth is inherently present in nanomateirals during their processing. The finer grains tend to merge and become bigger and stable grains at high temperatures and times of processing.

(vi) Recycling and disposal - There are no hard-and-fast safe disposal policies evolved for nanomaterials. Issues of their toxicity are still under question, and results of exposure experiments are not available. Hence the uncertainty associated with affects of nanomaterials is yet to be assessed in order to develop their disposal policies.

Chapter
THERMODYNAMICS

1. Objectives

(i) To predict the possibility of the process.

(ii) To differentiate system and surroundings from universe.

(iii) To define various process, properties; state and path functions; spontaneous and non-spontaneous; exo-and endo-thermic process.

(iv) Interrelate work, heat, and energy.

(v) Laws of thermodynamics.

(vi) To measure changes in internal energy and enthalpy.

(vii) To relate E and H

(viii) To determine enthalpy changes of various physical process.

(ix) To determine enthalpy changes in formation, formation, combustion, neutralization.

(x) To understand non-conventional energy resources and to identify different renewable energy resources.

2. Introduction

The term thermodynamics is derived from Greek word, ‘Thermos’ meaning heat and ‘dynamics’ meaning flow. Thermodynamics deals with the inter-relationship between heat and work. It is concerned with the interconversions of one kind of energy into another without actually crating or destroying the energy. Energy is understood to be the capacity to do the work. It can exist in many forms like electrical, chemical, thermal, mechanical, gravitational, etc. Transformations from one to another energy from and prediction of the feasibility of the process are the important aspects of thermodynamics.

As an illustration, from our common experience steam engines are seen to transform heat energy to mechanical energy, by burning of coal which is a fossil fuel. Actually, the engines use the energy stored in the fuel to perform mechanical work. In chemistry, many reactions are encountered that can be utilized to provide heat and work along with required products. At present thermodynamics is widely used in physical, chemical and biological sciences focusing mainly on the aspect of predicting the possibility of the process connected with each science. On the other hand, it fails to provide insight into two aspects: firstly, the factor of time involved during the initial to final energy transformation and secondly, on the quantitative microscopic properties of matter like atoms and molecules.

3. Terminology used in thermodynamics

It is useful to understand few terms that are used to define and explain the basic concepts and law of thermodynamics.

3.1. System

Thermodynamically a system is defined as any portion of matter under consideration which is separated from the rest of the universe by real or imaginary boundaries.

3.2. Surroundings

Everything in the universe that is not the part of system and can interact with it is called as surroundings.

3.3. Boundary

Anything (fixed or moving) which separates the system from its surroundings is called boundary.

For example, if the reaction between A and B substances are studied, the mixture A and B, from the system. All the rest, which includes beaker, its wall, air room etc. From the surroundings. The boundaries may be considered as part of the system or surroundings depending upon convenience. The surroundings can affect the system by the exchange of matter or energy across the boundaries.

3.1.1. Types of systems

In thermodynamics different types of systems are considered, which depends on the different kinds of interactions between the system and surroundings.

3.1.1.1. Isolated system

A system which can exchange neither energy nor matter with its surroundings is called isolated system. For example, a sample in a sealed thermos flask with walls made of insulating materials represents an isolated system (fig. 1).

3.1.1.2. Closed system

A system which permits the exchange of energy but not mass, across the boundary with its surroundings is called a closed system.

For example, A liquid in equilibrium with its vapours in a sealed tube represents a closed system since the sealed container may be heated or cooled to add or remove energy from its contents while no mater (liquid or vapour) can be added or removed.

3.1.1.3. Open system

A system is said to be open if it can exchange both energy and matter with its surroundings.

For example, a open beaker containing an aqueous salt solution represents open system. Here, mater and heat can be added or removed simultaneously or separately from the system to its surroundings.

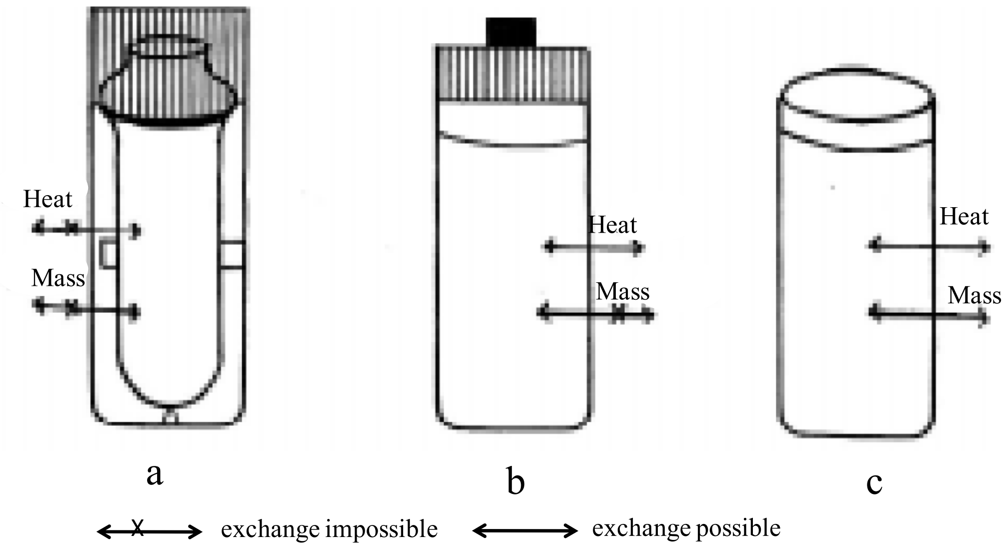


Fig. 1. Pictorial representation of (a) Isolated (thermos flask), (b) Closed (closed beaker) and (c) Open (open beaker) systems

3.1.2. Homogeneous and Heterogeneous systems

A system is said to be homogeneous if the physical states of all its matter are uniform. For example, mixture of gases, completely miscible mixture of liquid etc.

A system is said to be heterogeneous, if its contents does not possess the same physical state. For example, immiscible liquids, solid in contact with a gas, etc.

3.1.3. Macroscopic properties of system

The properties which are associated with bulk or macroscopic state of the system such as pressure, volume, temperature, concentration, density, viscosity, surface tension, refractive index, colour etc. are called as macroscopic properties.

3.1.3.1. Types of macroscopic properties of system

Measurable properties of a system can be divided into two types.

3.1.3.1.1. Extensive properties

The properties that depend on the mass or size of the system are called as extensive properties. Examples, volume, number of moles, mass, energy, internal energy, etc. the value of the extensive property is equal to the sum of extensive properties of smaller parts into which the system is divided. Suppose x1 ml, x2 ml, x3 ml of 1,2,3 gases are mixed in a system, the total volume of the system equals to (x1 + x2 + x3) ml. Thus volume is an extensive property.

3.1.3.1.2. Intensive property

The properties that are independent of the mass or size of the system are known as intensive properties. For example, refractive index, surface tension, density, temperature, boiling point, freezing point, etc., of the system. These properties do not depend on the number of moles substance in the system.

If any extensive property is expressed per mole or per gram or per ml, it becomes an intensive property. For example, mass, volume, heat capacity are extensive properties while density, specific volume, specific heat, are intensive properties.

4. State functions

4.1. State of a system

A system is said to be in a particular physical state when specific values of the macroscopic properties of the system are known. For example, the gaseous state of matter can be described by parameters like Pressure (P), Volume (V), and Temperature (T) etc. The values of these parameters change when the matter is in liquid state. Thus, the state of the system defined by specific measurable macroscopic properties of the system.

The initial state of the system refers to the starting state of the system before any kind of interaction with surroundings.

The final state of the system refers to the state after the interaction of system with its surroundings. A system can interact with its surroundings by means of exchange of matter or heat or energy.

The variables like P, V, T, composition (no. of moles) ‘n’ that are used to describe the state of the system are called as state variables or state functions. When the state of the system changes, the values of the state functions of the system also change. Thus, the state functions depend only on the initial and final states of the system and not on how the changes occur. Also, if the values of state functions of a system are known, all other properties like mass, viscosity, density, etc., of the system become specified.

For specifying a state of the system, it is not necessary to know all the state functions, since they are independent and only a few of them are sufficient. A system which satisfies the conditions of thermal, mechanical and chemical equilibria and contains the macroscopic properties which are independent of time is said to be in thermodynamic equilibrium.

4.1.1. Thermodynamic equilibrium sets the condition that there should be no flow of heat from one portion or part of the system to another portion or part of the system. ie. Temperature of the system remaining constant at every point of the system.

4.1.2. Mechanical equilibrium implies that there is no work done by one portion or part of the system over another portion or part of the same system. ie. pressure of the system being constant at all its points.

4.1.3. Chemical equilibrium is demands that the composition of one or more phase of chemicals present in the system should remain constant.

5. Thermodynamic process

A thermodynamic (physical or chemical) process may be defined as the pathway of series of intermediate changes that occur when a system is changed from initial to final state. Processes starting with the same initial state and ending at different final states corresponds to different thermodynamic processes.

Different types of processes are commonly used in the study of thermodynamics.

5.1. Isothermal process is defined as one in which the temperature of the system remains constant during the change from its initial to final states. During the isothermal process, the system exchanges heat with its surroundings and the temperature of the system remains constant.

5.2. Adiabatic process is defined as one in which the temperature of the system remains constant during the change from initial to final states. During, the isothermal process, the system exchanges heat with its surroundings and temperature of the system remains constant.

A thermally and completely insulated system with its surroundings can have changes in temperature during transformation from initial to final states in adiabatic process. This is because; the system cannot exchange heat with its surroundings.

5.3. Isobaric process is that process in which the pressure of the system remains constant during its change from the initial to final state of the process.

5.4. Cyclic process: The process which brings back the system to its original or initial state after a serious of changes is called as cyclic process.

5.5. Spontaneous process is those that occur on their own accord. For example heat flowing from a hotter end of the metal rod to a colder end. In these processes, the transformation of the system from initial, to the final state is favourable in a particular direction only. Many of these spontaneous processes are natural processes and are also, irreversible process.

5.6. Non-spontaneous processes are those that do not occur on their own accord. For example, although carbon burns in air evolving heat to from carbon dioxide, on its own carbon does not catch fire and an initial supply is required. Since many of the non-spontaneous processes are slow processes, they also exist as equilibrium processes.

5.7. Reversible process. In a reversible process the serious of changes carried out on the system during its transformation from initial state may be possibly reversed in an exact manner.

This is possible when the changes are carried out very slowly in many smaller steps on the system during its change from initial to final state. By doing so, each of its intermediate state will be in equilibrium with its surroundings. Under such conditions the initial and final states of the system become reversible completely.

For example, when ice melts a certain amount of heat is absorbed. The water formed can be converted back to ice if the same amount of heat is removed from it. This indicates that many reversible processes are non-spontaneous processes also.

5.8. Irreversible processes

An irreversible process is one which cannot be retraced to the initial state without making a permanent change in the surroundings. Many of the spontaneous processes are irreversible in nature.

For example, biological ageing is an irreversible process. Water flowing down a hill on its own accord is an irreversible process.

Some of the characteristics of thermodynamically reversible and irreversible processes are compared as below:

Reversible processes	**Irreversible processes**
It is a slow process going through a serious of smaller stages with each stage maintaining equilibrium between the system and surroundings.	In this process the system attains final state from the initial state with a measurable speed. During the transformation, there is no equilibrium maintained between the system and surroundings.
A reversible process can be made to proceed in forward or backward direction.	Irreversible process can take place in one direction only.
The driving force for the reversible process is small since the process proceeds in small steps.	There is a definite driving force required for the progress of the irreversible process.
Work done in reversible process is greater than the corresponding work done in irreversible process.	Work done in a irreversible process is always lower than the same kind of work done in a reversible process.
A reversible process can be brought back to the initial state without making a change in the adjacent surroundings.	An irreversible process cannot be brought back to its initial state without making a change in the surroundings.

5.9. Exothermic and endothermic processes

When the thermodynamic process is a chemical reaction or a physical transformation, process is classified as either exothermic or endothermic depending on the nature of the heat involved in the overall process. These two processes are differentiated as follows:

Endothermic process	Exothermic process
A process when transformed from initial to final states by adsorption of heat is called as an endothermic process.	A process when transformed from initial to final states by evolution of heat is called as exothermic process.
The final state of the system possesses higher energy than the initial state. The excess energy needed is adsorbed as heat by the system from the surroundings.	The final state of the system possesses lower energy than the initial state. The excess energy is evolved as heat. Example: All combustion processes are exothermic.
Generally in a physical transformation which is endothermic heat is supplied to bring about the initial to final state. Example: melting of solid by supplying heat is an endothermic process.	If the physical transformation is exothermic heat is removed to bring about the initial to final state. Example: freezing of liquid at its freezing point is an exothermic process.

6. Nature of thermodynamic functions

The properties of thermodynamic system depend on variables which are measurable and change in values when the state of the system changes. These variables are classified as state variables or state functions and path variables (or) path functions.

The state function considered in gaseous systems like, P, V, and Tare called state functions. A state function is thermodynamic property of a system which as specific values for each state of the system and does not depend on the path in which a particular state is reached. Other than P, V, T there are other important thermodynamic properties existing as state functions like internal energy (U), enthalpy (H), free energy (G) etc.

A path function is a thermodynamic property of the system whose value depends on the path or manner by which by the system goes from its initial to final states. It is also depends on the previous history of the system. for example, work (w) and heat (q) are some of the thermodynamic properties of the system that are path functions. There values change when there is change in manner in which the system goes from initial to final states.

7. Zeroth law of thermodynamics

Consider any two objects each maintained at different temperature, when brought in thermal contact with each other such that heat is exchanged until a thermal equilibrium is reached, then the two objects are consider to have equal temperatures. For example, if a beaker containing water and a thermometer are the two objects, while reading the temperature of the water in the beaker using the thermometer, a thermal equilibrium is reached between the two objects having a contact with each other. Also, when the temperatures of the thermometer bulb and that of water in the beaker are same, thermal equilibrium has said to be occurred.

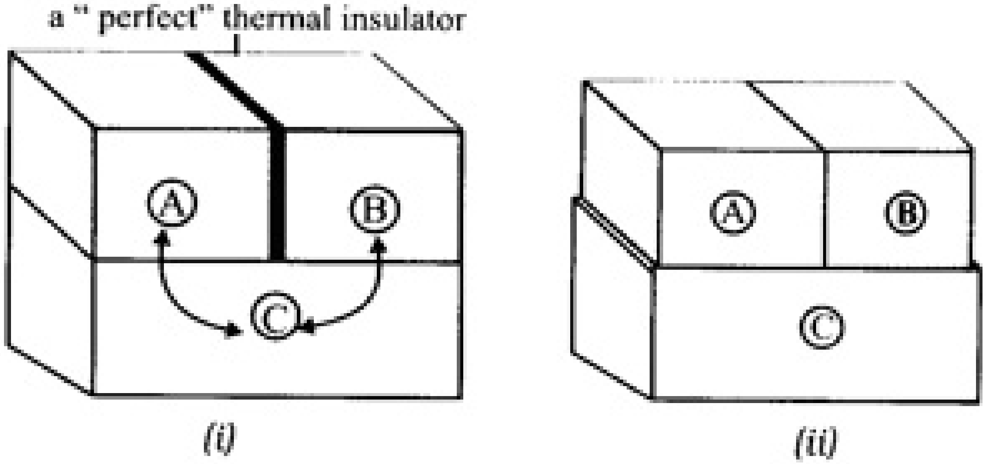


Fig. 2. (i) A and B are thermal equilibrium with C, (ii) A, B, and C are in thermal equilibrium with each other.

Zeorth law of thermodynamics is also known as the law of thermal equilibrium. It provides a logical basis for the concept of temperature of a system. it can be stated as follows.

‘If two systems at different temperature are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves’.Conversely, the zeroth law can be stated in another manner as,

‘When two objects are in thermal equilibrium with the third object, then there is thermal equilibrium between the two objects itself’.

7.1. Work, heat, and energy

In order to formulate the laws of thermodynamics it becomes necessary to know the properties and nature of work (w), heat (q), and energy (U).

$$1 \text{ Torr} = 1 \text{ mm of Hg}$$

7.1.1. Work (w)

In thermodynamics work is generally defined as the force (F) multiplied by the distance of displacement (s). That is,

$$W = F.s.$$

Several aspects should be considered in the definition of work which are listed below:

(i) work appears only at the boundary of the system.

(ii) work appears during the change in the state of the system.

(iii) work brings in a permanent effect in the surroundings.

(iv) work is an algebraic quantity.

(v) work is a path function and it is not a state function.

Types of work

Many types of work are known. Some of the types of work are as follows:

7.1.1.1. Gravitational work

This work is said to be done when a body is raised to a certain height against the gravitational field. If a body of mass `m' is raised through a height `h' against acceleration due to gravity `g', then the gravitational work carried out is `mgh'. In this expression, force is `mg' and the distance is `h'.

7.1.1.2. Electrical work

This type of work is said to be done when a charged body moves from one potential region to another. The electrical work is Q .V. if V is the potential difference causing the quantity of electricity 'Q' during its movement

7.1.1.3. Mechanical work

This type of work is associated with changes in volume of a system when an external pressure is applied or lowered. This pressure-volume work is also referred to as the mechanical work.

7.1.2. Heat

Like work, heat (q) is regarded in thermodynamics as energy in transit across the boundary separating a system from its surroundings. Heat changes result in temperature differences between system and surroundings. Heat cannot be converted into work completely without

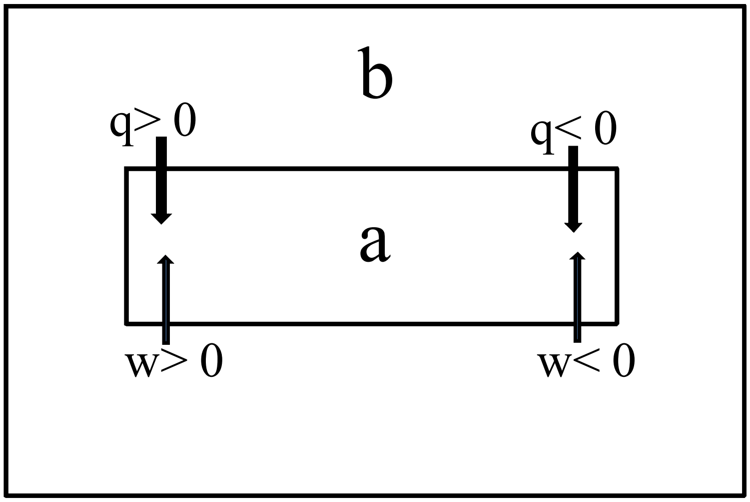
Producing permanent change either in the system or in the surroundings. Some of the characteristics of heat (q) are:

(i) heat is an algebraic quantity.

(ii) heat is a path function and is not a state function.

(iii) heat changes are generally considered as temperature changes of the system.

Sign convention for heat (q) and work (w)



a = system; b = surroundings
q = heat; w = work

when,

(i) heat is absorbed by the system (or) heat is lost by surroundings to the system: +q

(ii) heat is evolved by the system (or) heat is gained by surroundings: -q.

(iii) work is done by the system : -w

(iv) work is done on the system : +w

If heat (q) is supplied to the system, the energy of the system increases and `q' is written as a positive quantity. If work is done on the system, the energy of the system increases and `w' is written as a positive quantity. When w or q is positive, it means that energy has been supplied to the system as work or as heat. In such cases internal energy (U) of the system increases. When w or q is negative, it means that energy is lost by the system as work or as heat. In such cases, the internal energy (U) of the system decreases.

7.1.3. Energy `U'

Energy is easily, defined as the capacity to do work. Whenever there is a change in the state of matter of a system, then there is a change in energy (ΔU) of the system. For example energy changes are involved in processes like melting, fusion, sublimation, vapourisation etc. of the matter in a system. Energy (U) exists in many forms. Kinetic energy (K.E.) arises due to motion of a body and potential energy (P.E.) arises due to its position in space.

In chemical systems, there are two types of energy available. The energies acquired by the system like electrical, magnetic, gravitational etc. and termed as external energies of the system. The internal energy is generally referred to as the energy (U) of a thermodynamic system which is considered to be made up of mainly by P.E. and K.E.

Characteristics of energy (U) are:

(i) U is a state function. Its value depend on the initial and final states of the system.

(ii) U is an extensive property. Its magnitude depend on the quantity of material in the system.

(iii) U is not a path function. Its value remains constant for fixed initial and final states and does not vary even though the initial and final states are connected by different paths.

(iv) In S.I. system the unit of energy is Joules `J' or kJ.

8. First law of thermodynamics

First law of thermodynamics is also known as the law of conservation of energy which may be stated as follows:

"Energy may be converted from one form to another, but cannot be created or be destroyed".

There are many ways of enunciating the first law of thermodynamics. Some of the selected statements are given below:

(i) "Energy of an isolated system must remain constant although it may be changed from one form to another".

(ii) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".

(iii) "Heat and work are equivalent ways of changing a system's internal energy".

(iv) "Whenever other forms of energies are converted into heat or vice versa there is a fixed ratio between the quantities of energy and heat thus converted".

Significance of first law of thermodynamics is that, the law ascertains an exact relation between heat and work. It establishes that ascertain quantity of heat will produce a definite amount of work or vice versa. Also, when a system apparently shows no mechanical energy but still capable of doing work, it is said to possess internal energy or intrinsic energy.

8.1. Enthalpy

In chemistry most of the chemical reactions are carried out at constant pressure. To measure heat changes of the system at constant pressure, it is useful to define a new thermodynamic state function called enthalpy ‘H’.

H is defined as sum of the internal energy ‘U’ of a system and the product of pressure and volume of the system.

That is,

$H = U + PV$

8.1.1. Characteristic of H

Enthalpy, H depends on the three state functions U, P, V and hence it is also a state function. H is independent of the path by which it is reached. Enthalpy is also known by the term ‘heat content’.

Relationship between enthalpy ‘H’ internal energy ‘U’

When the system at constant pressure undergoes changes from an initial state with H_1, U_1, V_1, P parameters to a final state with H_2, U_2, V_2, P parameters the change in enthalpy ΔH, is given by,

$$\Delta H = (H_2 - H_1) = (U_2 - U_1) + P(V_2 - V_1)$$

i.e. $$\Delta H = \Delta U + P\Delta V$$

Considering $\Delta U = q - w$ or $q - P\Delta V$, $\Delta U + P\Delta V$ becomes equals to ‘q_p’. ‘q_p’ is the heat adsorbed by the system at constant pressure for increasing the volume from V1 to V2. This is so because, -w indicates that the work is done by the system. Therefore volume increase against constant pressure is considered.

□ eqn. becomes $q_p = \Delta U + P\Delta V$

$= \Delta H$. or $\Delta H = q_p$

`qp' is the heat absorbed by the system at constant pressure and is considered as the heat content of the system.

Heat effects measured at constant pressure indicate changes in enthalpy of a system and not in changes of internal energy of the system. Using calorimeters operating at constant pressure, the enthalpy change of a process can be measured directly.

Considering a system of gases which are chemically reacting to produce product gases with Vr and Vp as the total volumes of the reactant and product gases respectively, and nr and np as the number of moles of gaseous reactants and products, then using ideal gas law we can write that, at constant temperature and constant pressure,

$$PV_r = n_rRT \text{ and } PV_p = n_pRT.$$

Then considering reactants as initial state and products as final state of the system,

$$P(V_p - V_r) = RT\,(n_p - n_r)$$

$$P\Delta V = \Delta n_g RT \text{ where,}$$

Δng refers to the difference in the number of moles of product and reactant gases. But, already known that $\Delta H = \Delta U + P\Delta V$

□ $\Delta H = \Delta U + \Delta n_g RT$

Incertain processes internal energy change $\Delta U = \Delta E$ also.

8.1.2. Standard enthalpy changes

The standard enthalpy of a reaction is the enthalpy change for a reaction when all the participating substances are present in their standard states.

The standard state of substance at any specified temperature is its pure from at 1 atm pressure. For example standard state of solid iron at 500 K is pure iron 500 K and 1 atm. Standard conditions are denoted by adding the superscript 0 to the symbol ΔH.

For reaction, the standard enthalpy change is denoted by $\Delta_r H^0$. Similarly, the standard enthalpy changes for combustion, formation, etc., are denoted by $\Delta_c H^0$ and $\Delta_f H^0$ etc., respectively. Generally the reactants are presented in their standard states during the enthalpy change.

Thermochemical equations

A balanced chemical equation together with standard conventions adopted and including the value of ΔH of the reaction is called a thermochemical equation.

The following conventions are necessarily adopted in thermochemical equation:

(i) The coefficients in a balanced thermocahmical equation refers to number of moles of reactants and products involved in the reactions

(ii) The enthalpy change of reaction $\Delta_r H$ has unit KJ mol^{-1} and will remain as it is, even if more than one mole of the reactant or product are involved but with only the magnitude changing.

(iii) When a chemical equation is reversed the value of ΔH is reversed in sign with the magnitude remaining the same.

(iv) Physical states of all species are important and must be specified in a thermochemical equation since ΔH depends on the phases of the reactants and products.

(v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also be multiplied by the same number value.

(vi) The negative sign of $\Delta_r H^0$ indicates the reaction to be exothermic reaction and positive sign of $\Delta_r H^0$ indicates an endothermic type of reaction

For example, consider the following reaction,

$2H_{2(g)} + O_{2(g)} + 2H_2O_{(g)}\ \Delta H^0 = -483.7$ KJ.mol^{-1}

$2H_{2(g)} + O_{2(g)} + 2H_2O_{(l)}\ \Delta H^0 = -571.1$ KJ.mol^{-1}

The above thermochemical equations can be interpreted in several ways.

483.7 KJ given off per mole of the reaction =

483.7 KJ given off per 2 moles of $H_{2(g)}$ consumed =

483.7KJ given off per mole of $O_{2(g)}$ consumed =

483.7 KJ given off per 2 moles of water vapour formed

The above equation describes the combustion of H_2 gas to water in a general sense. The first reaction can be considered as the formation reaction of water vapour and the second reaction as the formation of liquid water. Both the reaction refer to constant temperature and pressure.

The negative sign of ΔH indicates that it is an exothermic reaction. The reaction which is exothermic in the forward direction is endothermic in the reverse direction and vice-versa. This rule applies to both physical and chemical process.

For example,

$2H_2O(l)\square 2H_2(g) + O2(g) \qquad \Delta_r H^0 = +571.1$ KJ mol^{-1}

$2H_2O(g)\square 2H_2(g) + O2(g) \qquad \Delta H_r^0 = +483.7$ KJ mol^{-1}

8.1.3. Enthalpy of combustion

Generally combustion reactions occur in oxygen atmosphere with evolution of heat. These reactions are exothermic in nature. Enthalpy changes of combustion reactions are used in industrial heating and in rocket fuels and in domestic fuels.

Enthalpy change of combustion $\Delta_c H$, of substance at a given temperature is defined as the enthalpy change of reaction accompanying the complete combustion of one mole of substance in presence of excess oxygen at that temperature. The enthalpy changes of combustion of substance in their standard states are known as standard enthalpy change of combustion $\Delta_c H^0$. These values are useful to experimentally determine the standard enthalpy change of formation of organic compounds.

8.1.4. Bomb calorimeter

Enthalpy changes of combustion of chemical substances are experimentally determined using a bomb calorimeter.

The inner vessel or the bomb and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws. A weighed amount of substance is taken in a platinum cup or boat connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressured with excess oxygen. The bomb is lowered in water which is placed inside the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started in the bomb by heating the substance through electrical heating. During burning, the exothermic heat generated inside the bomb raises the temperature of the surrounding water bath. The enthalpy measurements in this case correspond to the heat of reaction at constant volume. Although the temperature raise is small, the temperature change can be measured accurately using Beckman thermometer.

In a typical bomb calorimeter experiment, a weighed sample of benzoic acid (w) is placed in the bomb which is then filled with excess oxygen and sealed. Ignition is brought about electrically. The raise in temperature (ΔT) is noted. Water equivalent (w_c) of the calorimeter is known from the standard value of enthalpy of combustion of benzoic acid.

$$\Delta H_c^0\ C_6H_5COOH_{(s)} = -3227\ \mathrm{KJ\ mol^{-1}}$$

$$\Delta H_c^0\ C_6H_5COOH \text{ X } w/M_2 = wc.\Delta T$$

(where M_2 = mol.wt of benzoic acid).

Knowing w_c value, the enthalpy of combustion of any other substance is determined adopting the similar procedure and using the substance in place of benzoic acid. By this experiment, the enthalpy of combustion at constant volume (ΔH_c^0 vol) is known

$$\Delta H_c^0(\text{vol}) = wc.\Delta T$$

Enthalpy of combustion at constant pressure of the substance is calculated from the equation,

$$\Delta H_c^0(pr) = \Delta H_c^0(vol) + \Delta n_g RT$$

and Δn_g is known from the difference in the number of moles of the products and reactants in the completely balanced equation of combustion of the substance with excess oxygen.

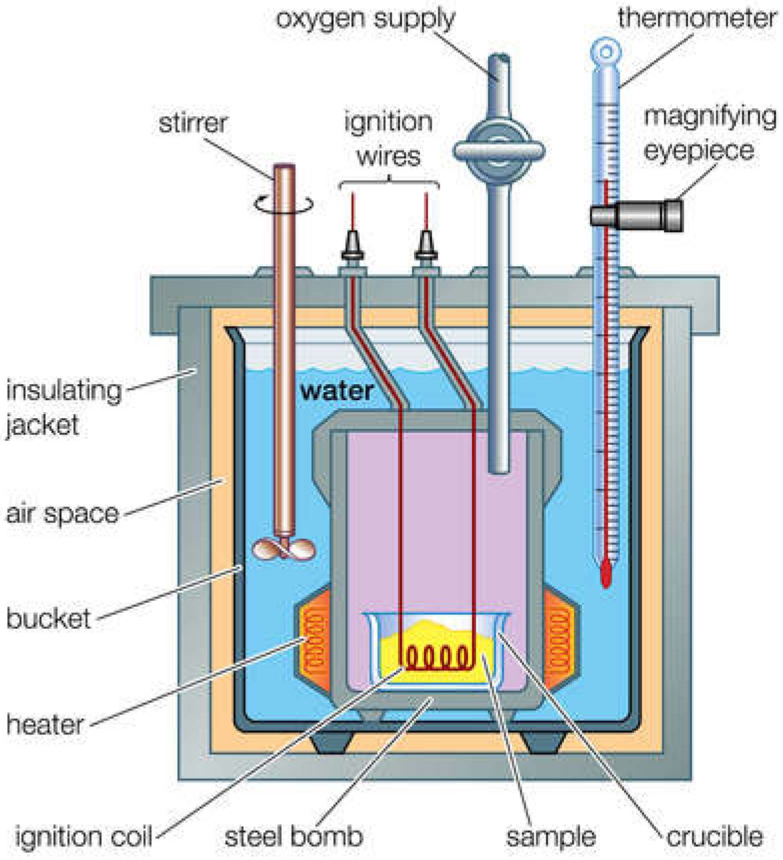


Fig. 3. Bomb calorimeter

Enthalpy of neutralization

The enthalpy change of neutralization is defined as the enthalpy change accompanied by the complete neutralization of one gram-equivalent amount of strong acid by a gram-equivalent amount of a strong base under fully ionised state in dilute conditions. It is found that the enthalpy of neutralization of strong acid and a strong base is a constant value equal to -57.32 KJ. This value is independent of the nature of the strong acid and strong base. Strong acids and strong bases exist in the fully ionised form in aqueous solutions as below:

$$H_3O^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + 2H_2O$$

(or)

$$H_3O^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow 2H_2O_{(l)} \quad \Delta_{neu}H^o = -57.32 \text{ KJ.}$$

The H^+ ions produced in water by the acid molecules exist as H_3O^+. During the neutralization reaction, water and salt are produced in solution. Thus, enthalpy change of neutralization is essential due to enthalpy change per mole of water formed from $H3O^+$ and OH^- ions. Therefore, irrespective of the chemical nature, the enthalpy of neutralisation of strong acid by strong base is a constant value. At infinite dilutions, complete ionisation of acids and bases are ensured and also the inter ionic interactions exist in the lowest extents.

In the case of neutralisation of a weak acid like acetic acid (CH_3COOH) by a strong base (NaOH) or neutralisation of weak base (NH_4OH) by a strong acid, two steps are involved. The first step is the ionisation of weak acid or weak base since these molecules are only partially ionised. The second step being the neutralisation step of $H3O^+$ and OH^- ions. Since ionisation of weak acids and weak bases in water are endothermic and some energy will be used up in dissociating weak acid and weak base molecules. Thus, acetic acid with NaOH and ammonium hydroxide with HCl neutralisation reactions can be written as,

$$CH_3COOH_{aq} + H_2O \rightarrow CH3COO^-{}_{aq} + H3O^+{}_{aq}$$

$$Na^+{}_{aq} + H_3O^+{}_{aq} + OH^-{}_{aq} \rightarrow 2H_2O_{(l)} + Na^+{}_{aq}$$

and

$$NH_4OH \rightarrow NH_4{}^+ + OH^-$$

$$H_3O^+ + Cl^- + OH^- \rightarrow 2H_2O + Cl^-.$$

Enthalpy of neutralisation of a weak acid or a weak base is equal to -57.32 kJ + enthalpy of ionisation of weak acid (or) base. Since enthalpy of ionisation of weak acid or base is endothermic it is a positive value, hence enthalpy of neutralisation of a weak acid or base will be lower than the neutralisation of strong acid and strong base.

9. Exercises

1. From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.

$$C_6H_{6(l)} + 7\tfrac{1}{2}O_{2(g)} \rightarrow 6CO_{2(g)} + 13H_2O_{(l)} \quad \Delta E_{25°C} = -781.1 \text{ kcal}$$

2. Calculate the enthalpy of combustion of ethylene at 300K at constant pressure if its enthalpy of combustion at constant volume is -1406 kJ mol^{-1}.
3. The measured heats of neutralization of acetic acid, formic acid, hydrocyanic acid, and hydrogen sulphide are 13.20, 13.40, 2.90 and 3.80 KCal per g.equiv. respectively. Arrange these acids in a decreasing order of strength.
4. Heat of neutralization of formic acid by NH_4OH is 11.9 KCal per g.equiv. What is the heat of ionization of NH_4OH?
5. Calculate the enthalpy of combustion of acetic acid (l) when burnt in excess of O_2 in a bomb calorimeter. Given that ΔH_f^0, $H_2O_{(l)}$ = -285.84 kJ mol^{-1}, and for $CO_{2(g)}$ = -393.52 kJmol-1 and $CH_3COOH_{(l)}$ = -463 kJ mol^{-1}.
6. Heat of neutralisation of a weak acid HA by NaOH is -12.13 kJ mol^{-1}. Calculate the enthalpy of ionization of HA.
7. ΔH for the reaction qt 298 K $CO_{(g)}$ + ½ $O_{2(g)}$ □CO2(g) is 282.85 $kJmol^{-1}$. Calculate ΔU reaction.

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Chapter -
ELECTRO CHEMISTRY

G Keerthiga

1. Objectives

(i) To learn to differentiate conductors, insulators and semiconductors by their properties (with examples)
(ii) Statements of Faraday's laws of electrolysis and their significance
(iii) To learn the quantitative calculations on Faraday's laws
(iv) To apply Nernst equation for calculating the emf of galvanic cell and define standard potential of the cell
(v) Understanding quantitative aspects of electrolysis
(vi) To describe the construction of some primary, secondary batteries and fuel cells
(vii) Explaining corrosion as an electrochemical process

2. Introduction

Electrochemistry is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution.

A chemical reaction is driven by an external applied voltage, as in electrolysis, or if a voltage is created by a chemical reaction as in a battery, it is then an electrochemical reaction. In general, electrochemistry deals with situations where oxidation and reduction reactions are separated in space or time, connected by an external electric circuit to understand each process.

3. Advances in electrochemistry

1663- Otto von Guericke	First electric generator
Mid 18th century	Two forms of static electricity - like charges repel each other whilst unlike charges attract.

Late 18th century - Luigi Galvani	Birth of electrochemistry – bridge between muscular contractions and electricity established
1800 - William Nicholson and Johann Wilhelm Ritter	Electrolysis
1827 - Georg Ohm	Theory of electricity
1832 - Michael Faraday	Laws of electrochemistry
1839 - William Grove	First fuel cell
1886 - Charles M. Hall	The Hall–Héroult process for Aluminium extraction
1888 - Walther Hermann Nernst	Electromotive force of the voltaic cell
1898 - Fritz Haber	Work on electrolytic oxidation and reduction
1902	The Electrochemical Society (ECS) was founded
1909 - Millikan	Experiments to determine the electric charge carried by a single electron
1949	The International Society of Electrochemistry (ISE) was founded

The subject is of importance both for theoretical and practical considerations. A large number of metals, sodium hydroxide, chlorine, fluorine and many other chemicals are produced by electrochemical methods. Batteries and fuel cells convert chemical energy into electrical energy and are used on a large scale in various instruments and devices. The reactions carried out electrochemically can be energy efficient and less polluting. Therefore, study of electrochemistry is important for creating new technologies that are eco-friendly. The transmission of sensory signals through cells to brain and vice versa and communication between the cells are known to have electrochemical origin. Electrochemistry is therefore, a very vast and interdisciplinary subject.

4. Terminology in electrochemistry

4.1. Conductors

Those substances which allow electrical current to pass through them completely are known as conductors. Examples are metals, alloys and fused electrovalent compounds.

Silver is the best conductor, followed by copper, gold, and aluminum. Copper is used more often than silver because of cost.

4.2. Insulators

Those substances which do not allow electrical current to pass through them are known as insulators. Examples of insulators are wood, silk, cotton, glass, rubber, organic compounds like benzene and carbon tetra chloride.

4.3. Semiconductors

Those substances that allow the electrical current to pass through them partially (or) possess very low electrical conductivity are known as semiconductors. Examples of semiconductors are Silicon, Germanium, oxides of Manganese, Cobalt oxide, Titanium dioxide etc.

Conductors of electricity are further classified into two types depending on their mode of transport of electrical charges inside them. These are electronic conductors and electrolytic conductors. They are descried and compared below.

4.4. Metallic conductors

Metals and alloys conduct electricity due to the movement (mobility) of de-localised outer shell electrons present inside them and are known as electronic conductors (or) metallic conductor. Electrical conductors in general transport electrical charges from one point in a circuit to another. Electrical conduction through metals do not bring about any chemical transformations. Conductivity of metallic conductor decreases with increase in temperature due to the enhanced thermal vibration of metal atoms disrupting the movement of electrons passing through them.

4.5. Electrolytic conductors

Electrolytic conductors differ from metal conductors or semi-conductors in that the electric charges are transported by free moving ions through a fluid. Electrolytes can conduct electricity either in the fused state or in an aqueous solution. Solutions of acids, bases and salts in water, molten salts, etc. are common examples. The conductivity of electrolytes increases with increase in temperature. This is due to increase of ionic mobility.

4.6. Electrodes

The medium through which an electric current enters or leaves the electrolyte is called an electrode. An electrode may be a rod, a plate or even a foil. There are two types of electrodes-the Positive Electrode called the Anode and the Negative Electrode called the Cathode. The anode, or the positive electrode, is connected to the positive terminal of the battery and allows the current to leave the electrolyte. The cathode, or the negative electrode, is the electrode that is connected to the negative terminal of the battery and allows the current to enter the electrolyte.

4.7. Ions

Molecules of electrolytes consist of two oppositely charged particles called Radicals or ions. In the solid state, the oppositely charged ions are bound together tightly by electrostatic forces of attraction. On the other hand, when these electrolytes are dissolved in water or melted to a liquid state, the forces of attraction between them are decreased, which results in the formation of positively and negatively charged particles. Such particles are known as ions and they lead an independent existence.

Example: When sodium chloride is dissolved in water, it splits up into sodium and chloride ions, each having an independent existence.

$$\underset{\substack{\text{Sodium}\\ \text{chloride}}}{Na^+\,Cl^-} \rightleftharpoons \underset{\substack{\text{Sodium}\\ \text{ion}}}{Na^+} + \underset{\substack{\text{Chloride}\\ \text{ion}}}{Cl^-}$$

5. Electrolysis – Principle and application

When electric current is passed through an electrolyte solution, the ions of an electrolyte undergo chemical changes at the respective electrodes. The chemical reaction carried out by passing electricity is called as electrolysis. This principally works by *Preferential discharge theory*. According to this theory, “If more than one type of ion is attracted towards a particular electrode, then the ion which is discharged is the one which requires least energy or ions with lower discharge potential or which occur low in the electrochemical series”.

The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge or deposition potential, (D.P.). The values of discharge potential are different for different ions.

For cations: Li^+, K^+, Na^+, Ca^{2+}, Mg^{2+}

For anions: SO_4^{2-}, NO_3^-, OH^-

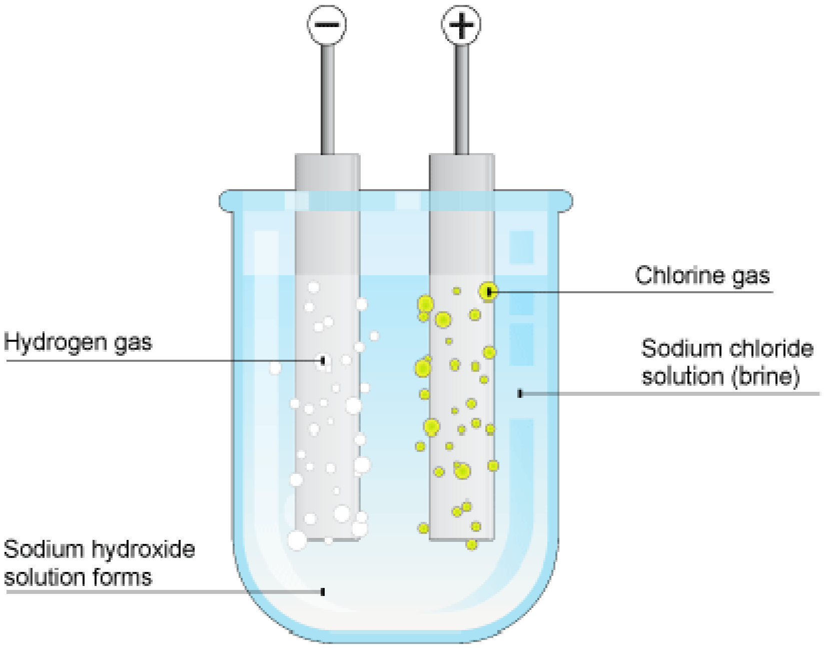
5.1. Electrolysis of sodium chloride solution using platinum electrodes

In aqueous solution, sodium chloride dissociates completely while water dissociates to a small extent. There are four different ions present in the solution. The positive ions (cations), Na^+ and H^+, move toward the cathode. The negative ions (anions), Cl^- and OH^- in turn move to the anode. At cathode H^+ ions are discharged in preference to Na^+ ions as the discharge potential of H^+ ions is lower than Na^+ ions. Similarly at anode, Cl^- ions are discharged in preference to OH^- ions.

$$NaCl \longrightarrow Na^+ Cl^- \text{ (completely dissociated)}$$

$$H_2O \longrightarrow H^+ OH \text{ (dissociated to a small extent)}$$

The following reactions take place at the two electrodes.



At cathode	*At Anode*
$H^+ + e^- \rightarrow H$	$Cl^- \rightarrow Cl + e^-$
$2H \rightarrow H_2$	$2Cl \rightarrow Cl_2$

Thus, Na^+ and OH^- ions remain in solution and the solution when evaporated yields crystals of sodium hydroxide.

5.2. Industrial uses of electrolysis

The process of electrolysis is used in a number of industries.

(i) Production of aluminum by electrolysis of fused alumina, called the Hall and Heroult process

(ii) Refining of aluminum by Hoope's process

(iii) Production of sodium by Castner's process or Down's process

(iv) Preparation of sodium hydroxide by using Nelson's cell

(v) Preparation of Bleach

(vi) Refining of Copper

(vii) Electroplating of gold on silver in making ornaments and electroplating of silver and gold on iron for decorative purposes

6. Faraday's laws of electrolysis

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis.

After his extensive investigations on electrolysis of solutions and melts of electrolytes, Faraday published his results during 1833-34 in the form of the following well known Faraday's two laws of electrolysis.

6.1. Faraday's first law

The amount of chemical reaction (w) which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity (Q) passed through the electrolyte (solution or melt).

$W \propto Q$

Q = quantity of electricity (in coulombs) that flows through

But we know that,

$$Q = \text{current C in amperes x time T in seconds}$$

$$Q = c * t$$

$$w = Z\ ct$$

Where, Z is proportionality constant and is known as Electro Chemical Equivalent (ECE) of the substance. Its value depends on the nature of the ion liberated.

The electrochemical equivalent (ECE) of a substance may be defined as the amount of the substance deposited by passing a current of one ampere for one second (that is by passing one coulomb of electricity, one gram-equivalent of an ion is liberated by 96,500 coulombs of electricity)

Therefore, ECE(Z) = $\frac{\text{Equivalent weight}}{96{,}500}$

6.2. Faraday's second law

The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal/Number of electrons required to reduce the cation).

Chemical equivalent = atomic mass / valence

$m_1/m_2 = E_1/E_2$

where m_1 and m_2 are the respective masses liberated or deposited on the electrodes and E_1 and E_2 are the chemical equivalents of the substances liberated or deposited.

6.3. Quantitative aspects of electrolysis

It has been found experimentally that the quantity of electricity required to liberate one gram equivalent of a substance is 96,495 coulombs. This quantity of electricity is known as Faraday and is denoted by the symbol F.

1 Faraday = 1F = Electrical charge carried by one mole of electrons

1F = Charge on an electron x Avogadro's number

$1F = e^- \times N_A = (1.602 \times l0^{-19}\ C) \times (6.02 \times 10^{-23}\ rnol^{-1})$

$1F = 96488\ C\ mol^{-1}$

6.4. Limitations

The Faraday's laws of electrolysis are applicable only

(i) When the whole electrical conduction is electrolytic in nature, i.e., the current is carried only by the ions

(ii) No other side-reaction takes place after the electrode reaction has taken place

7. Electrochemical cell

Electrochemical cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge. Electrochemical cells are of two types:

(a) Electrolytic cell

(b) Galvanic or voltaic cell

An electrochemical cell can be created by placing metallic electrodes into an electrolyte where a chemical reaction either uses or generates an electric current.

7.1. Electrolytic cell

It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

7.2. Galvanic or voltaic cell

It is a device, in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The redox reaction in a galvanic cell is a spontaneous reaction. For this reason, galvanic cells are commonly used as batteries. Galvanic cell reactions supply energy which is used to perform work. The energy is harnessed by situating the oxidation and reduction reactions in separate containers, joined by an apparatus that allows electrons to flow.

7.3. Differences in electrolytic cell and galvanic cell

Electrolytic cell	Galvanic cell
Electrical energy is converted into chemical energy.	Chemical energy is converted into electrical energy.
Anode positive electrode. Cathode negative electrode.	Anode negative electrode. Cathode positive electrode.
Ions are discharged on both the electrodes.	Ions are discharged only on the cathode.
If the electrodes are inert, concentration of the electrolyte decreases when the electric current is circulated.	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are

Both the electrodes can be fitted in the same compartment.	joined by a wire. The electrodes are fitted in different compartments.

7.4. **Terminology used in electrochemical cell**

7.4.1. Anode is the electrode at which oxidation occurs.

7.4.2. Cathode is the electrode at which electrons are received from the outer circuit. It has a positive charge and is known as (+) in the cell diagrams.

7.4.3. Oxidation is the *loss* of electrons or an *increase* in oxidation state by a molecule, atom, or ion.

7.4.4. Reduction is the *gain* of electrons or a *decrease* in oxidation state by a molecule, atom, or ion.

Oxidation occurs at the anode and reduction occurs at the cathode. There is a very easy way for remembrance is by OIL and RIG, where Oxidation is loss and reduction in gain.

7.4.5. Electrolyte is the salt solution in a cell.

7.4.6. Half-cell is half of an electrolytic or voltaic cell, where either oxidation or reduction occurs. The half-cell reaction at the anode is oxidation, while the half-cell reaction at the cathode is reduction.

7.5. Salt bridge and its significance

Salt bridge is usually an inverted U-tube filled with concentrated solution of inert electrolytes. The functions of the salt bridge are

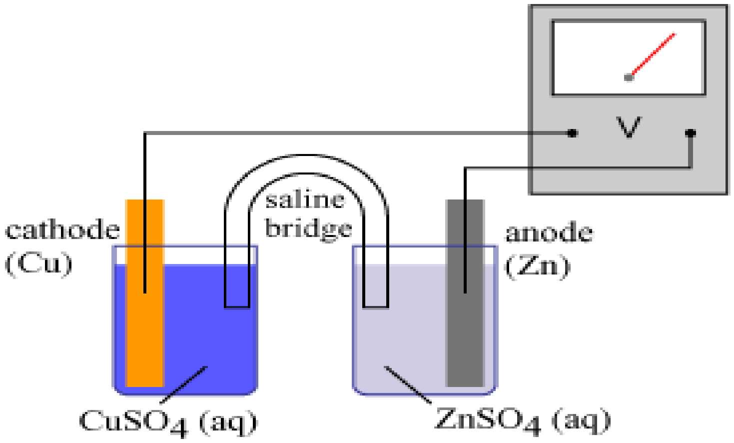
(i) It connects the solutions of two half-cells and completes the cell circuit

(ii) It prevents transference or diffusion of the solutions from one half-cell to the other

(iii) It keeps the solutions in two half-cells electrically neutral

(iv) It prevents liquid-liquid junction-potential

A common galvanic cell is the Daniell cell is a kind of copper-zinc battery which employs a porous barrier between the two metals, shown below



Daniell cell discussed earlier is one such cell in which the following redox reaction occurs.

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

This reaction is a combination of two half reactions whose addition gives the overall cell reaction:

(i) $Cu^{2+} + 2e^- \longrightarrow Cu(s)$ (reduction half reaction)

(ii) $Zn(s) \longrightarrow Zn^{2+} + 2e^-$ (oxidation half reaction)

These reactions occur in two different portions of the Daniell cell. The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode. These two portions of the cell are also called half-cells or redox couples. The copper electrode may be called the reduction half cell and the zinc electrode, the oxidation half-cell.

7.6. Representation of an Electrochemical Cell

7.6.1. IUPAC conventions

In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell. The following universally accepted conventions are followed in representing an electrochemical cell called a cell diagram.

(i) The anode (negative electrode) is written on the left hand side and cathode (positive electrode) on the right hand side.

(ii) A vertical line or semicolon (;) indicates a contact between two phases (separation of phases). The anode of the cell is represented by writing metal first and then the metal ion present in the electrolytic solution. Both are separated by a vertical line or a semicolon. For example,

$$Zn|Zn^{2+} \quad \text{or } Zn; Zn^{2+}$$

The molar concentration or activity of the solution is written in brackets after the formula of the ion. For example:

$$Zn|Zn^{2+} \text{ (1 M)} \quad \text{or } Zn \mid Zn^{2+} \text{ (0.1 M)}$$

(i) The cathode of the cell is represented by writing the cation of the electrolyte first and then the metal. Both are separated by a vertical line or semicolon. For example,

$$Cu^{2+}|Cu \quad \text{or} \quad Cu^{2+}; Cu \quad \text{or } Cu2^{+} \text{ (1 M)}|Cu$$

(ii) The salt bridge which separates the two half-cells is indicated by two parallel vertical lines.

The Daniell cell can be represented as:

$$Zn|ZnSO_4\,(aq)||CuSO_4(aq)|Cu^{+}$$

Anode Salt bridge Cathode

Oxidation half-cell Reduction half-cell

$$\text{or} \quad Zn|Zn^{2+}||Cu^{2+}|Cu$$

$$\text{or} \quad Zn|Zn^{2+}(1\text{ M})||Cu^{2+}(1\text{ M})|Cu$$

8. Standard electrode potential

In electrochemistry, the standard electrode potential, abbreviated (E° or E), is the measure of individual potential of a reversible electrode at standard state, which is with solutes at an effective concentration of 1 mol dm^{-3}, and gases at a pressure of 1 bar. The potential of a single electrode in a half-cell is called the Single electrode potential. The single electrode potential of a half-cell depends on

(a) Concentration of ions in solution

(b) Tendency to form ions

(c) Temperature.

8.1. Standard emf of a cell

The potential difference between the two electrodes of a galvanic cell is called the cell potential and is measured in volts. The cell potential is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the cell electromotive force (emf) of the cell when no current is drawn through the cell. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing the galvanic cell. It can be measured with the help of a potentiometer. The emf of the cell or cell potential can be calculated from the values of electrode potentials of the two half-cells constituting the cell.

The following three methods are in use:

(i) When oxidation potential of anode and reduction potential of cathode are taken into account:

$$E_{Cell}^{o} = \text{Oxidation potential of anode} + \text{Reduction potential of cathode}$$

$$= E_{ox}^{o}\ (\text{anode}) + E_{red}^{o}\ (\text{cathode})$$

(ii) When reduction potentials of both electrodes are taken into account:

$$E_{Cell}^{o} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$

$$= E_{Cathode}^{o} - E_{Anode}^{o}$$

$$= E_{right}^{o} - E_{left}^{o}$$

(iii) When oxidation potentials of both electrodes are taken into account:

$$E_{Cell}^{o} = \text{Oxidation potential of anode} - \text{Oxidation potential of cathode}$$

$$= E_{ox}^{o}\ (\text{anode}) - E_{red}^{o}\ (\text{cathode})$$

The points of difference between emf and potential difference are given below.

Emf	**Potential difference**
It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the difference of the electrode potentials of the two electrons two electrodes when the cell is under operation.
It is the maximum voltage that the cell can deliver.	It is always less than the maximum the cell can deliver.
It is responsible for the steady flow of current in the cell.	It is not responsible for the steady flow of current in the cell.

Cell potential is illustrated by the following example:

8.2. Cell reaction

$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2\ Ag(s)$ -----(i)

8.2.1. Half-cell reactions

Cathode (reduction): $2Ag+(aq) + 2e^{-} \rightarrow 2Ag(s)$ ---(ii)

Anode (oxidation): $Cu(s) \rightarrow Cu^{2+}{}_{(}aq) + 2e^{-}$ -------(iii)

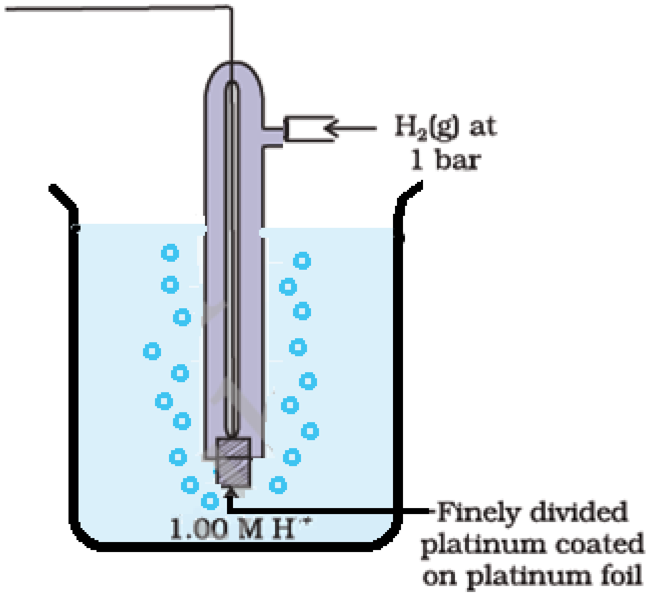
It can be seen that the sum of (ii) and (iii) leads to overall reaction (i) in the cell and that silver electrode acts as a cathode and copper electrode acts as an anode. The cell can be represented as

$$Cu(s)\ |Cu_2^{+}\ (aq)\ ||Ag^{-}(aq)\ |Ag(s)$$

and we have $E_{cell} = E_{right} - E_{left}$

$$= E_{Ag^{-}}/Ag - E_{Cu^{2+}}/Cu$$

8.3. Measurement of electrode potential



The potential of individual half-cell cannot be measured. We can measure only the difference between the two half-cell potentials that gives the emf of the cell. If we arbitrarily choose the potential of one electrode (half-cell) than that of the other can be determined with respect to this. According to convention, a half-cell called standard hydrogen electrode

Above represented by $Pt(s)/H_2(g) / H^{+}(aq)$, is assigned a zero potential at all temperatures corresponding to the reaction

$H^+ (aq) + e^- \rightarrow 0.5H2(g)$

The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced and oxidised forms of hydrogen is maintained at unity (in the above fig). This implies that the pressure of hydrogen gas is one bar and the concentration of hydrogen ion in the solution is one molar. The emf of the copper electrode, $Cu^{2+} \mid Cu$ can be determined by pairing it with the SHE when the electrochemical cell can be represented as:

$$Pt, H_2 \text{ (1 atm)} \mid H^+ \parallel Cu^{2+} \mid Cu$$

The emf of this cell has been determined to be 0.34 V which is the emf of the copper half-cell.

$$E_{ocell} = E_{oCu/Cu2+} - E_{o\ SHE}$$

$$= 0.34 - 0$$

$$= 0.34 \text{ V}$$

Similarly, the measured emf of the cell :

$$Pt(s)H_2(g, 1\ bar)H^+ (aq, 1\ M)//Zn^{2+} (aq, 1M)\ /Zn$$

is -0.76 V corresponding to the standard electrode potential of the half-cell reaction:

$$Zn^{2+} (aq, 1\ M) + 2e^- \longrightarrow Zn(s)$$

In view of this convention, the half reaction for the Daniell cell as shown before, it can be written as:

Left electrode: $Zn(s) \rightarrow Zn^{2+} (aq, 1\ M) + 2\ e^-$

Right electrode: $Cu^{2+} (aq, 1\ M) + 2\ e^- \rightarrow Cu(s)$

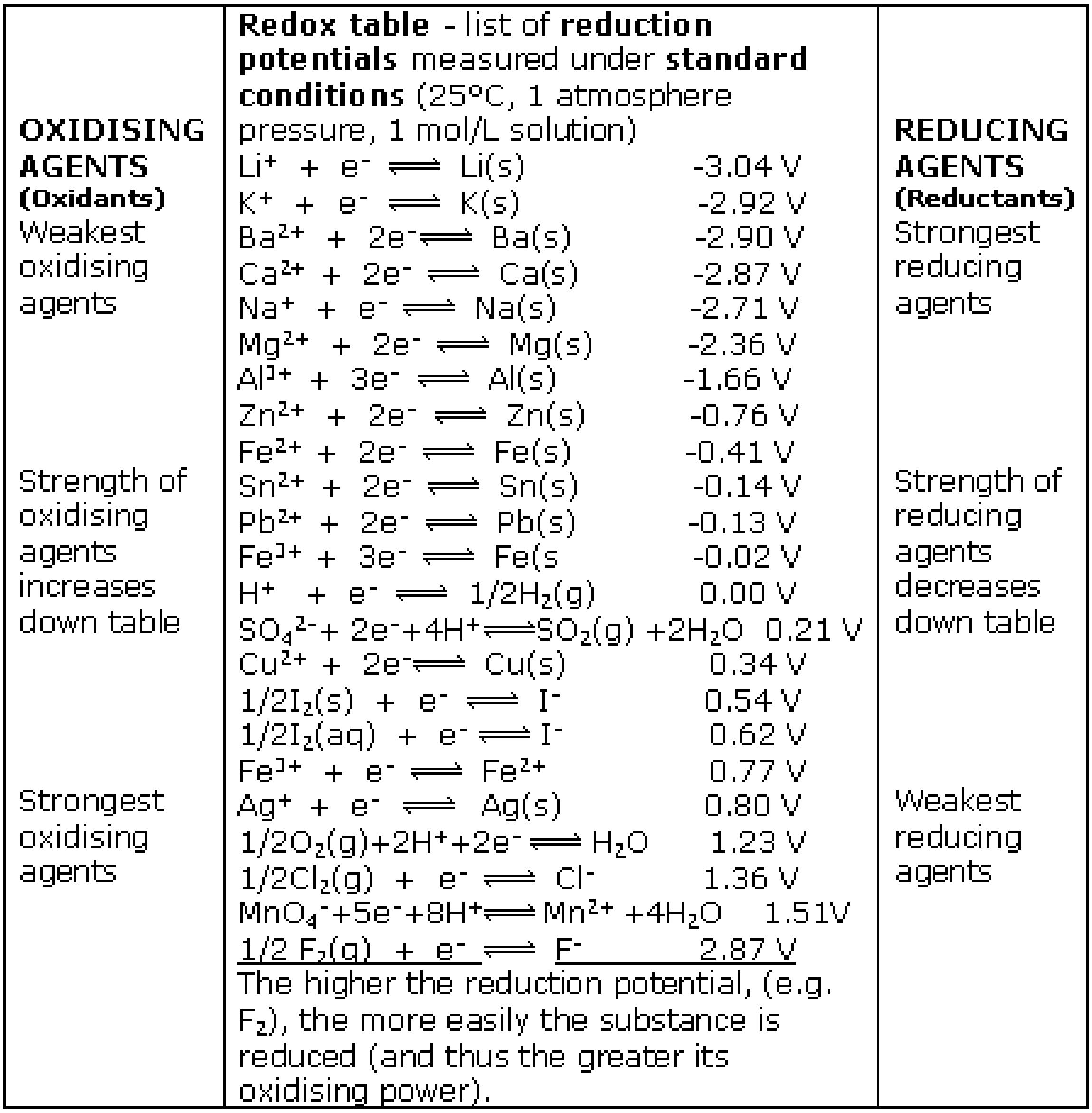
The overall reaction of the cell is the sum of above two reactions and we obtain the equation:

$Zn(s) + Cu^{2+} (aq) \rightarrow Zn^{2+} (aq) + Cu(s)$

Emf of the cell = $E_{0cell} = E_{0R} - E_{0L}$

$= 0.34V - (-0.76)\ V = 1.10\ V$

According to IUPAC convention, the standard reduction potentials alone are the standard potentials. The values of the standard potentials at 25 °C (298 K) for some common Reduction Half-reactions are listed in Table below



	Redox table - list of **reduction potentials** measured under **standard conditions** (25°C, 1 atmosphere pressure, 1 mol/L solution)	
OXIDISING AGENTS **(Oxidants)** Weakest oxidising agents	$Li^+ + e^- \rightleftharpoons Li(s)$ -3.04 V	**REDUCING AGENTS** **(Reductants)** Strongest reducing agents
	$K^+ + e^- \rightleftharpoons K(s)$ -2.92 V	
	$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$ -2.90 V	
	$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$ -2.87 V	
	$Na^+ + e^- \rightleftharpoons Na(s)$ -2.71 V	
	$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$ -2.36 V	
	$Al^{3+} + 3e^- \rightleftharpoons Al(s)$ -1.66 V	
	$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$ -0.76 V	
	$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$ -0.41 V	
Strength of oxidising agents increases down table	$Sn^{2+} + 2e^- \rightleftharpoons Sn(s)$ -0.14 V	Strength of reducing agents decreases down table
	$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$ -0.13 V	
	$Fe^{3+} + 3e^- \rightleftharpoons Fe(s$ -0.02 V	
	$H^+ + e^- \rightleftharpoons 1/2H_2(g)$ 0.00 V	
	$SO_4^{2-} + 2e^- + 4H^+ \rightleftharpoons SO_2(g) + 2H_2O$ 0.21 V	
	$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$ 0.34 V	
	$1/2I_2(s) + e^- \rightleftharpoons I^-$ 0.54 V	
	$1/2I_2(aq) + e^- \rightleftharpoons I^-$ 0.62 V	
	$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ 0.77 V	
Strongest oxidising agents	$Ag^+ + e^- \rightleftharpoons Ag(s)$ 0.80 V	Weakest reducing agents
	$1/2O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O$ 1.23 V	
	$1/2Cl_2(g) + e^- \rightleftharpoons Cl^-$ 1.36 V	
	$MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + 4H_2O$ 1.51V	
	$1/2\ F_2(g) + e^- \rightleftharpoons F^-$ 2.87 V	
	The higher the reduction potential, (e.g. F_2), the more easily the substance is reduced (and thus the greater its oxidising power).	

8.4. Predicting the feasibility of a reaction

The feasibility of a redox reaction can be predicted with the help of the electrochemical series. The net emf of the cell reaction, Ecell, can be calculated from the expression

$$E_{ocell} = E_{ocathode} - E_{oanode}$$

In general, if E_{ocell} = + ve, the reaction is feasible

Eocell = –ve, the reaction is not feasible.

8.4.1. Relation between EMF and free energy

The cell potential of a voltaic cell is a measure of the maximum amount of energy per unit charge which is available to do work when charge is transferred through an external circuit. This maximum work is equal to the change in Gibbs free energy, ΔG, in the reaction.

These relationships can be expressed as

Maximum work = $\Delta G = -nFE°_{cell}$

Where, n is the number of electrons transferred per mole and F is the Faraday constant.

If the standard cell potential is $E°_{cell} = 1.1$ volt and 2 electrons are transferred per mole of reactant. The change in free energy is then

$\Delta G = -nFE°_{cell} = -2 \text{ x } 96{,}485 \text{ coul/mole x } 1.10 \text{ joule/coul} = -212 \text{ kJ}$

This free energy change can also be related to the equilibrium constant K

$\Delta G = -RT \ln K$

8.4.2. Thermodynamics of a reversible cell

Suppose the reaction occurring in a reversible cell is represented by the equation

$A + B \longrightarrow C + D$, the decrease in free energy, – ΔG, accompanying the process is given by the well-known thermodynamic equation

$-\Delta G = -\Delta G_o - RT \ln J$

where $-\Delta G_o$ is the decrease in free energy accompanying the same process when all the reactants and products are in their standard states of unit activity and J stands for the reaction quotient of the activities of the products and reactants at any given stage of the reaction. Substituting the value of J, we have

$$-\Delta G = -\Delta G^o - RT \ln \frac{a_C \times a_D}{a_A \times a_B}$$

If E is the E.M.F. of the cell in volts and the cell reaction involves the passage of 'n' faradays (i.e.,) nF coulombs, the electrical work done by the cell is in nFE volt-coulombs or Joules. Hence free energy decrease of the system, –ΔG, is given by the expression

$$-\Delta G = n\text{FE}$$

$$n\text{FE} = -\Delta G^o - \text{RT}\ln\frac{a_C \times a_D}{a_A \times a_B}$$

$$= n\text{FE}^o - \text{RT}\ \ln\frac{a_C \times a_D}{a_A \times a_B}$$

$$\text{E} = \text{E}^o - \frac{\text{RT}}{n\text{F}}\ln\frac{a_C \times a_D}{a_A \times a_B}$$

Where, E_o is the E.M.F. of the cell in which the activity, or as an approximation, the concentration of each reactant and each product of the cell reaction is equal to unity. Eo is known as the standard E.M.F. of the cell. Replacing activities by concentrations, as an approximation, the Nernst equation may be written as

$$\text{E} = \text{E}^o - \frac{\text{RT}}{n\text{F}}\ln\frac{a_C \times a_D}{a_A \times a_B}$$

where the quantities in parentheses represent the concentration of the species involved. Replacing [C] [D]/ [A] [B] as equal to K, the equilibrium constant in the molar concentration units,

$$\text{E} = \text{E}^o - \frac{\text{RT}}{n\text{F}}\ln\frac{[\text{C}]\,[\text{D}]}{[\text{A}][\text{B}]}$$

This equation is known as Nernst equation.

$$\text{E} = \text{E}^o - \frac{\text{RT}}{n\text{F}}\ln \text{K}.$$

where Eo = standard electrode potential

R = gas constant

T = Kelvin temperature

n = number of electrons transferred in the half-reaction

F = Faraday of electricity

K = equilibrium constant for the half-cell reaction as in equilibrium law.

8.4.3. Calculation of Equilibrium constant for the cell reaction

The Nernst equation for a cell is

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log K$$

$$\log K = \frac{nE^{o}_{cell}}{0.0591}$$

9. Primary voltaic cell

9.1. Primary voltaic cell (the dry cell)

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy. The most common example of this type is dry cell.

The container of the dry cell is made of zinc which also serves as one of the electrodes. The other electrode is a carbon rod in the centre of the cell. The zinc container is lined with a porous paper. A moist mixture of ammonium chloride, manganese dioxide, zinc chloride and porous inert filler occupy the space between the paper lined zinc container and the carbon rod. The cell is sealed with a material like wax.

As the cell operates, the zinc is oxidised to Zn^{2+}

$$Zn \dashrightarrow Zn^{2+} + 2e^{-} \quad \text{(Anode reaction)}$$

The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.

$$2NH_4^{+} + 2e^{-} \dashrightarrow 2NH_3 + H_2 \quad \text{(Cathode reaction)}$$

The cell reaction is

$$Zn + 2\,NH_4^{+} \dashrightarrow Zn^{2+} + 2NH_3 + H_2$$

Hydrogen is oxidized by MnO_2 in the cell.

$$2MnO_2 + H_2 \dashrightarrow 2MnO(OH)$$

Ammonia produced at cathode combines with zinc ions to form complex ion.

$$Zn^{2+} + 4NH_3 \dashrightarrow [Zn(NH_3)_4]_{2+}$$

E_{cell} is 1.6 volt

9.2. Secodary voltaic cell (lead storage battery)

The cell in which original reactants are regenerated by passing direct current from external source, i.e., it is re-charged, is called secondary cell. Lead storage battery is the example of this type.

It consists of a group of lead plates bearing compressed spongy lead, alternating with a group of lead plates bearing leaf dioxide, PbO_2. These plates are immersed in a solution of about 30% H_2SO_4. When the cell discharges; it operates as a voltaic cell. The spongy lead is oxidized to Pb^{2+} ions and lead plates acquire a negative charge.

$$Pb \dashrightarrow Pb^{2+} + 2e^- \qquad \text{(Anode reaction)}$$

Pb^{2+} ions combine with sulphate ions to form insoluble lead sulphate, $PbSO_4$, which begins to coat lead electrode.

$$Pb^{2+} + SO_4^{2-} \dashrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

The electrons are utilized at PbO_2 electrode.

$$PbO_2 + 4H^+ + 2e^- \dashrightarrow Pb^{2+}\ 2H_2O \qquad \text{(Cathode reaction)}$$

$$Pb^{2+} + SO_4^{2-} \dashrightarrow PbSO_4 \qquad \text{(Precipitation)}$$

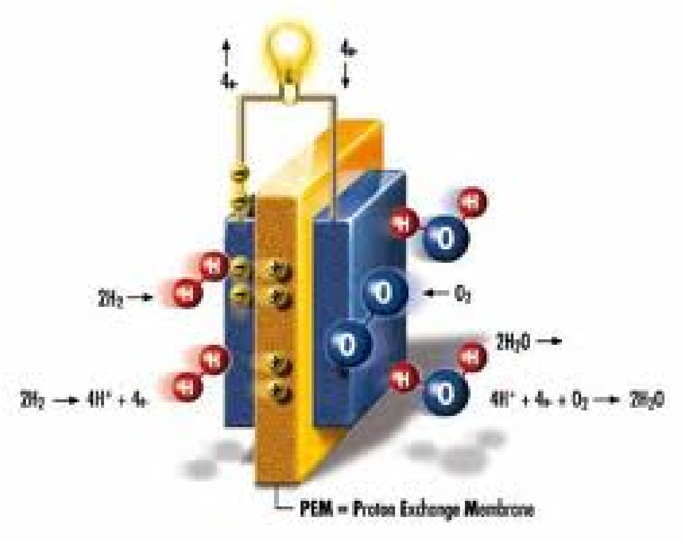
Overall cell reaction is:

$$Pb + PbO_2 + 4H^+ + 2\ SO_4^{2-} \dashrightarrow 2PbSO_4 + 2H_2O$$

Ecell is 2.041 volt

After many repeated charge-discharge cycles, some of the lead sulphate falls to the bottom of the container, the sulphuric acid concentration remains low and the battery cannot be recharged fully.

9.3. Fuel cell



Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water.The cell was used for providing electrical power in the Apollo space programmer. The water vapors produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $O_2\,(g) + 2\,H_2O\,(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode: $2H_2\,(g) + 4OH^-(aq) \longrightarrow 4\,H_2O\,(l) + 4e^-$

Overall reaction : $2\,H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. It has many types and it is the main topic of research in this era.

10. Commercial production of chemicals

A large number of chemicals are produced by electrolysis. A few of these are described below:

10.1. Manufacture of sodium

Sodium is obtained on large scale by two processes:

10.1.1. Castner's process

In this process, electrolysis of fused sodium hydroxide is carried out at 330°C using iron as cathode and nickel as anode.

$$2NaOH \Longleftrightarrow 2Na^+ + 2OH$$

At cathode $2Na^+ + 2e \longrightarrow 2Na$

At anode $4OH^- \longrightarrow 2H_2O + O_2 + 4e$

During electrolysis, oxygen and water are produced. Water formed at the anode gets partly evaporated and is partly broken down and hydrogen is discharged at cathode.

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

At cathode $2H^+ + 2e \longrightarrow 2\,H_2$

11. Corrosion

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion.

Corrosion of iron (commonly known as rusting) occurs in presence of water and air. Corrosion of steel on a seacoast is 400 to 500 times greater than in a desert. One researcher has shown that steel samples located eighty feet from a coastline corroded 12 times faster than those eight hundred feet from the coastline. Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmosphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.

Thus the theory of electrochemistry has been discussed with few applications in which it has been in use. Since the research on corrosion, fuel cell etc is the hot topic in his era, it is appropriate to learn about this topic in detail. Few problems on the basics discussed is illustrated.

12. Worked out examples based on Faraday's laws

12.1. Calculate the quantity of electricity obtained from 2 moles of electrons ?

Q = n x F

Q = ?

n = 2 mol

F = 96,500 C mol^{-1}

Q = 2 x 96,500 = 193,000 C

12.2. Calculate the time required to deposit 56g of silver from a silver nitrate solution using a current of 4.5A.

1. Calculate the moles of electrons required for the reaction:

$Ag^+ + e$ -----> Ag(s)

moles of Ag(s) deposited, n(Ag) = moles of electrons required, n(e)

moles of Ag = n(Ag) = mass ÷ MM

mass Ag deposited = 56g

MM = 107.9 g mol^{-1} (from Periodic Table)

n (Ag) 56 ÷ 107.9 = 0.519 mol = n(e)

2. Calculate the quantity of electricity required: Q = n(e) x F

   Q = ? C

   n(e) = 0.519 mol

   F = 96,500 C mol^{-1}

   Q = 0.519 x 96,500 = 50,083.5 C

3. Calculate the time required: t = Q ÷ I

   Q = 50,083.5 C

   I = 4.5 A

   t = 50,083.5 ÷ 4.5 = 11,129.67 seconds

   t = 11,129.67 ÷ 60 = 185.5 minutes

   t = 185.5 ÷ 60 = 3.1 hours

12.3. What mass of copper could be deposited from a copper (II) sulphate solution using a current of 0.50 A over 10 seconds?

1. Calculate the quantity of electricity: Q = I x t

   I = 0.50 A

   t = 10 seconds

   Q = 0.50 x 10 = 5.0 C

2. Calculate the moles of electrons: n(e) = Q ÷ F

   Q = 5.0 C

   F = 96,500 C mol^{-1}

   n(e) = 5.0 ÷ 96,500 = 5.18×10^{-5} mol

3. Calculate mass of copper: mass = n x MM

   $Cu^{2+} + 2e$ -----> Cu(s)

   1 mole of copper is deposited from 2 moles electrons

   n(Cu) = ½n(e) = ½ x $5.18 \times 10^{-5} = 2.59 \times 10^{-5}$ mol

MM = 63.55 g mol^{-1} (from Periodic Table)

mass (Cu) = $(2.59 \times 10^{-5}) \times 63.55 = 1.65 \times 10^{-3}$ g = 1.65 mg

12.4. 0.1978 g of copper is deposited by a current of 0.2 ampere in 50 minutes. What is the electrochemical equivalent of copper?

Here, *t* = 50 minutes = 50 *60 seconds; I = 0.2 ampere.

Quantity of electricity used is

Q = I *t = 0.2 *50 *60 = 600 coulombs

Amount of copper deposited by 600 coulombs = 0.1978 g

Amount of copper deposited by 1 coulomb =0. 1978/600g = 0.0003296

Electrochemical equivalent of copper = 0.0003296 = 3.296 *10^{-4}gc_{-1}

12.5. An electric current is passed through three cells in series containing respectively solutions of copper sulphate, silver nitrate and potassium iodide. What weights of silver and iodine will be liberated while 1.25 g of copper is being deposited?

(Wt.of copper/ Wt.of Iodine) = (Eqivalent.wt.copper / Eqivalent.wt.of Iodine)

or

1.25 /*x* =31. 7/127

x =1. 25 *127/31 7

Hence, Wt. of Iodine *x* = 5.0 g of iodine

Also,

Wt. of Copper/Wt .of Silver = 1.25/*y*

= Eqivalent.wt. of Cu (31.7)/ Eqivalent.wt. of Silver (108)

Wt. of silver (*y*) =108 *1. 25/31.7

= 4.26 g

12.6. Determine the feasibility of the reaction

$2Al_{(s)} + 3Sn^{4+}{}_{(aq)} \longrightarrow 2Al^{3+} + 3Sn^{2+}{}_{(aq)}$

The given reaction consists of the following half reactions

Anode : $2Al_{(g)} \longrightarrow 2Al^{3+} + 6e^{-}$ $E_o = +0.15$ V

Cathode : $3Sn^{4+} + 6e^{-} \longrightarrow 3Sn^{2+}$ $E_o = -1.66$ V

$E_{o\,cell} = 0.15 - (-1.66)$

= 1.81 V

Since E_{ocell} is positive, the reaction is feasible

12.7. Determine the standard emf of the cell and standard free energy change of the cell reaction.

$Zn, Zn^{2+} || Ni^{2+}, Ni$. The standard reduction potentials of Zn^{2+}, Zn and Ni^{2+}, Ni half cells are – 0.76 V and – 0.25 V respectively.

$E_{o\ cell} = E_{oR} - E_{oL} = -0.25 - (-0.76)$

$= +0.51$ V $E_{o\ cell}$ is + ve. $\Delta G_o = -$ ve

$\Delta G_o = -n FE_{ocell}$

$n = 2$ electrons

$\Delta G_o = -2 * 96495 * 0.51 = -97460$ Joules $= -97.46$ kJ.

12.8 What is the potential of a half-cell consisting of zinc electrode in 0.01 M $ZnSO_4$ solution 25 °C?

$E_o = 0.763$ V.

he half-cell reaction is

$Zn \longrightarrow Zn^{2+} + 2e^-$

The Nernst equation for the oxidation half-cell reaction is

$E = E_o - 0.059/n * log [Zn^{2+}]$

The number of electrons transferred n = 2 and $E_o = 0.763$ V.

Substituting these values in the Nernst equation we have

$E = 0.763 - (0\ 059/2* (-2))$

$= 0.763 + 0.0591 = 0.8221$ V