Nickel Chemistry

An excellent site for finding the properties of the elements, including nickel is at WebElements periodic table

History

Nickel had been in use centuries before its actual discovery and isolation. As far back as 3500 BC Syrian bronzes contained a small amount of the element. In 235 BC, coins in China were minted from nickel. However there was no real documentation of the element until thousands of years later.

In the 17thcentury, German miners discovered a red coloured ore they believed to contain copper. They discovered upon analysis that there was no copper but that a useless, smelly material was actually present. Thinking the ore was evil they dubbed it "Kupfernickel" or Old Nick's Copper, which meant false or bad copper. Swedish scientist Baron Axel Frederich Cronstedt in 1751 finally isolated nickel from an ore closely resembling kupfernickel. Hence, he named this new element after the traditional mineral.

At the time of its discovery nickel was thought to be useless but as its valuable properties came to light the demand for the metal increased dramatically. The usefulness of nickel as a material in alloys was eventually discovered as the strength, corrosion resistance and hardness it adds to other metals came to be appreciated. In the 1800s, the technique of silver plating was developed with a nickel-copper-zinc alloy being utilised in the process. Today, stainless steel, another nickel containing alloy, is one of the most valuable materials of the 20th century.

Occurrence

Nickel is the earth's 22nd most abundant element and the 7th most abundant transition metal. It is a silver white crystalline metal that occurs in meteors or combined with other elements in ores. Two important groups of ores are:

1. Laterites: oxide or silicate ores such as garnierite, $(Ni, Mg)_6\ Si_4O_{10}\ OH)_8$ which are predominantly found in tropical areas such as New Caledonia, Cuba and Queensland.
2. Sulphides: these are ores such as pentlandite, which contain about 1.5%, nickel associated with copper, cobalt and other metals. They are predominant in more temperate regions such as Canada, Russia and South Africa.

Canada is the world's leading nickel producer and the Sudbury Basin of Ontario contains one of the largest nickel deposits in the world.

Extraction of Nickel

In 1899 Ludwig Mond developed a process for extracting and purifying nickel. The so-called "Mond Process" involves the conversion of nickel oxides to pure nickel metal. The oxide is obtained from nickel ores by a series of treatments including concentration, roasting and smelting of the minerals.

In the first step of the process, nickel oxide is reacted with water gas, a mixture of H_2 and CO, at atmospheric pressure and a temperature of 50 °C. The oxide is thus reduced to impure nickel. Reaction of this impure material with residual carbon monoxide gives the toxic and volatile compound, nickel tetracarbonyl, $Ni(CO)_4$. This compound decomposes on heating to about 230 °C to give pure nickel metal and CO, which can then be recycled.

The actual temperatures and pressures used in this process may very slightly from one processing plant to the next. However the basic process as outlined is common to all.

The process can be summarised as follows:

$$\mathrm{Ni} + 4\mathrm{CO} \xrightarrow{50^{\circ}\mathrm{C}} \underset{\text{(impure)}}{\mathrm{Ni(CO)_4}} \xrightarrow{230^{\circ}\mathrm{C}} \underset{\text{(pure)}}{\mathrm{Ni}} + 4\mathrm{CO}.$$

Properties

Nickel is a hard silver white metal, which occurs as cubic crystals. It is malleable, ductile and has superior strength and corrosion resistance. The metal is a fair conductor of heat and electricity and exhibits magnetic properties below 345°C. Five isotopes of nickel are known.

In its metallic form nickel is chemically unreactive. It is insoluble in cold and hot water and ammonia and is unaffected by concentrated nitric acid and alkalis. It is however soluble in dilute nitric acid and sparingly soluble in dilute hydrochloric and sulphuric acids.

Nickel Compounds

Nickel is known primarily for its divalent compounds since the most important oxidation state of the element is +2. There do exist however certain compounds in which the oxidation state of the metal is between -1 to +4. Blue and green are the characteristic colours of nickel compounds and they are often hydrated.

Nickel hydroxide usually occurs as green crystals that can be precipitated when aqueous alkali is added to a solution of a nickel (II) salt. It is insoluble in water but dissolves readily in acids and ammonium hydroxide.

Nickel oxide is a powdery green solid that becomes yellow on heating.
It is difficult to prepare this compound by simply heating nickel in oxygen and it is more conveniently obtained by heating nickel hydroxide, carbonate or nitrate. Nickel oxide is readily soluble in acids but insoluble in hot and cold water.

Nickel oxides

Formula	Colour	Oxidation State	MP	Structure / comments
NiO	green powder	Ni^{2+}	1955	NaCl

Thermal decomposition of $Ni(OH)_2$, $NiCO_3$, or $NiNO_3$ gives NiO.

Nickel sulfides consist of NiS_2, which has a pyrite structure, and Ni_3S_4, which has a spinel structure.

All the nickel dihalides are known to exist. These compounds are usually yellow to dark brown in colour. Preparation directly from the elements is possible for all except NiF_2, which is best prepared from reaction of F_2 on $NiCl_2$ at 350°C. Most are soluble in water and crystallisation of the hexahydrate containing the $[Ni(H_2O)_6]^{2+}$ ion can be achieved. NiF_2 however is only slightly soluble in water from which the trihydrate crystallizes. The only nickel trihalide known to exist is an impure specimen of NiF_3.

Nickel(II) halides

Formula	Colour	MP	µ (BM)	Structure
NiF_2	yellow	1450	2.85	tetragonal rutile
$NiCl_2$	yellow	1001	3.32	$CdCl_2$
$NiBr_2$	yellow	965	3.0	$CdCl_2$
NiI_2	Black	780	3.25	$CdCl_2$

Preparations:

$Ni + F_2$ 55°C /slow → NiF_2
$Ni + Cl_2$ EtOH/ 20°C → $NiCl_2$
$Ni + Br_2$ red heat → $NiBr_2$
$NiCl_2 + 2NaI \rightarrow NiI_2 + 2NaCl$

Nickel carbonate usually occurs as a light green crystalline solid or a brown powder. It dissolves in ammonia and dilute acids but is insoluble in hot water. It exhibits vigorous reaction with iodine, hydrogen sulphide or a mixture of barium oxide and air. It decomposes on heating before melting occurs.

Nickel carbonyl is a colourless, volatile, liquid. It is soluble in alcohol, benzene, and nitric acid but only slightly soluble in water, and insoluble in dilute acids and alkalis. Upon heating or in contact with acid or acid fumes, nickel carbonyl emits toxic carbon monoxide gas, a property exploited in preparation of nickel metal. When exposed to heat or flame the compound explodes and it can react violently with air, oxygen and bromine.

Identification of nickel compounds can be achieved by employing the use of an organic reagent dimethylglyoxine. This compound forms a red flocculent precipitate on addition to a solution of a nickel compound.

Nickel complexes

The Nickel (II) ion forms many stable complexes as predicted by the Irving Williams series. Whilst there are no other important oxidation states to consider, the Ni(II) ion can exist in a wide variety of CN's which complicates its coordination chemistry.
For example, for CN=4 both tetrahedral and square planar complexes can be found.
For CN=5 both square pyramid and trigonal bipyramid complexes are formed.
The phrase ***"anomalous nickel"*** has been used to describe this behaviour and the fact that equilibria often exist between these forms.

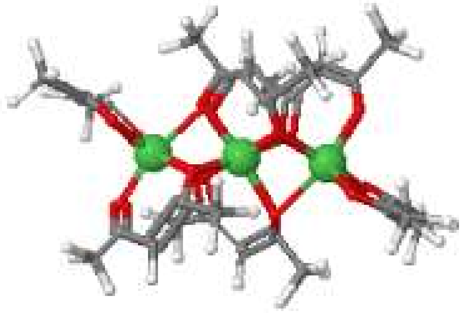
Some examples include:

(a) addition of ligands to square planar complexes to give 5 or 6 coordinate species
(b) monomer/polymer equilibria
(c) square-planar/ tetrahedron equilibria
(d) trigonal-bipyramid/ square pyramid equilibria.

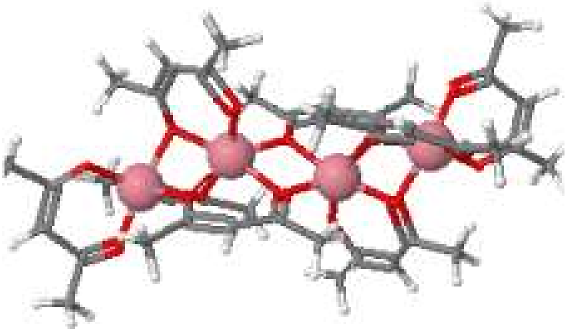
(a) substituted acacs react with Ni^{2+} to give green dihydrates (6 coordinate). On heating, the two coordinated water groups are generally removed to give tetrahedral species. The unsubstituted acac complex, $Ni(acac)_2$ normally exists as a trimer, see below.

Lifschitz salts containing substituted 1,2-diaminoethanes can be isolated as either 4 or 6 coordinate species depending on the presence of coordinated solvent.

(b) $Ni(acac)_2$ is only found to be monomeric at temperatures around 200°C in non-coordinating solvents such as n-decane. 6-coordinate monomeric species are formed at room temperature in solvents such as pyridine, but in the solid state $Ni(acac)_2$ is a trimer, where each Ni atom is 6-coordinate. Note that $Co(acac)_2$ actually exists as a tetramer.



$[Ni(acac)_2]_3$



$[Co(acac)_2]_4$

(c) Complexes of the type NiL_2X_2, where L are phosphines, can give rise to either tetrahedral or square planar complexes. It has been found that:
L=P(aryl)3 are tetrahedral
L=P(alkyl)3 are square planar
for L= mixed aryl and alkyl phosphines, both stereochemistries can occur in the same crystalline substance. The energy of activation for conversion of one form to the other has been found to be around 50kJ mol^{-1}.

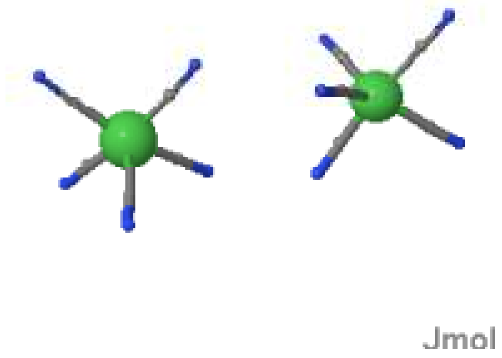
Similar changes have been observed with variation of the X group:

$Ni(P\varnothing_3)_2Cl_2$	green	tetrahedral	μ =2.83 BM
$Ni(P\varnothing_3)_2(SCN)_2$	red	sq. planar	μ =0 BM

where ∅ is shorthand for C_6H_5

Ni^{2+} reacts with CN- to give $Ni(CN)_2.nH_2O$ (blue-green) which on heating at 180-200°C is dehydrated to yield $Ni(CN)_2$. Reaction with excess KCN gives $K_2Ni(CN)_4.H_2O$ (orange crystals) which can be dehydrated at 100°C. Addition of strong concentrations of KCN produces red solutions of $Ni(CN)_5^{3-}$.

The crystal structure of the double salt prepared by addition of $Cr(en)_3^{3+}$ to $Ni(CN)_5^{3-}$ showed that two types of Ni stereochemistry were present in the crystals in approximately equal proportions.



50% as square pyramid and 50% as trigonal bipyramid.

Uses of Nickel and its Compounds

The primary use of nickel is in the preparation of alloys such as stainless steel, which accounts for approximately 67% of all nickel used in manufacture. The greatest application of stainless steel is in the manufacturing of kitchen sinks but it has numerous other uses as well.

Other nickel alloys also have important applications. An alloy of nickel and copper for example is a component of the tubing used in the desalination of sea water. Nickel steel is used in the manufacture of armour plates and burglar proof vaults. Nickel alloys are especially valued for their strength, resistance to corrosion and in the case of stainless steel for example, aesthetic value.

Electroplating is another major use of the metal. Nickel plating is used in protective coating of other metals. In wire form, nickel is used in pins, staples, jewellry and surgical wire. Finely divided nickel catalyses the hydrogenation of vegetable oils. Nickel is also used in the colouring of glass to which it gives a green hue.

Other applications of nickel include:

-Coinage
-Transportation and construction
-Petroleum industry
-Machinery and household appliances
-Chemical industry.

Nickel compounds also have useful applications. Ceramics, paints and dyes, electroplating and preparation of other nickel compounds are all applications of these compounds. Nickel oxide for example is used in porcelain painting and in electrodes for fuel cells. Nickel acetate is used as a mordant in the textiles industry. Nickel carbonate finds use in ceramic colours and glazes.

Nickel and Human Health

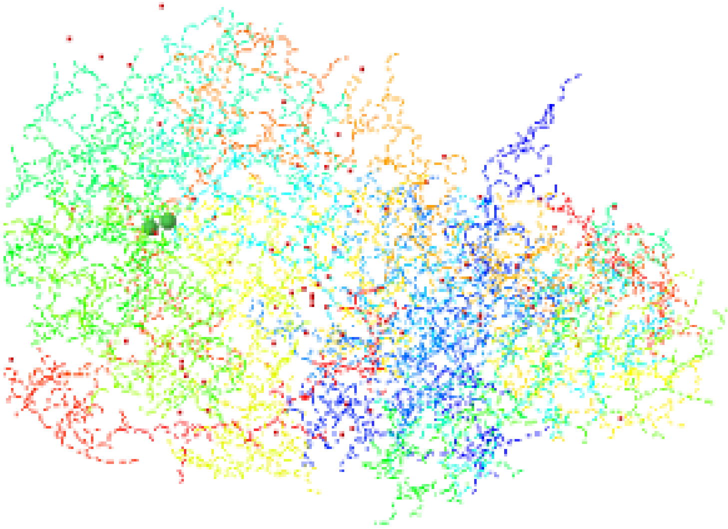
For an account of the limited information known about the role of nickel in human health see:

http://www.nutrition.org/nutinfo/
http://www.vitaminsplus.com/vplus/nickel.htm
http://www.findarticles.com/p/articles/mi_m0841/is_n1_v28/ai_13700591

The first crystallisation of an enzyme was reported in the 1920's. The enzyme was urease which converts urea to ammonia and bicarbonate. One source of the enzyme is the bacterium *Helicobacter Pylori*. The release of ammonia is beneficial to the bacterium since it partially neutralizes the very acidic environment of the stomach (whose function in part helps kill bacteria). In the initial study it was claimed that there were no metals in the enzyme. Fifty years later this was corrected when it was discovered that nickel ions were present and an integral part of the system.

The Nobel Prize in Physiology or Medicine for 2005 was awarded to Barry J. Marshall and J. Robin Warren "for their discovery of the bacterium Helicobacter pylori and its role in gastritis and peptic ulcer disease".

The display below shows the crystal structure found for a *Helicobacter Pylori* urease [published 2000]. The nickel ions can be identified by clicking the approriate button.



Highlight: the backbone x the Ni sites x spacefill x reset x

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