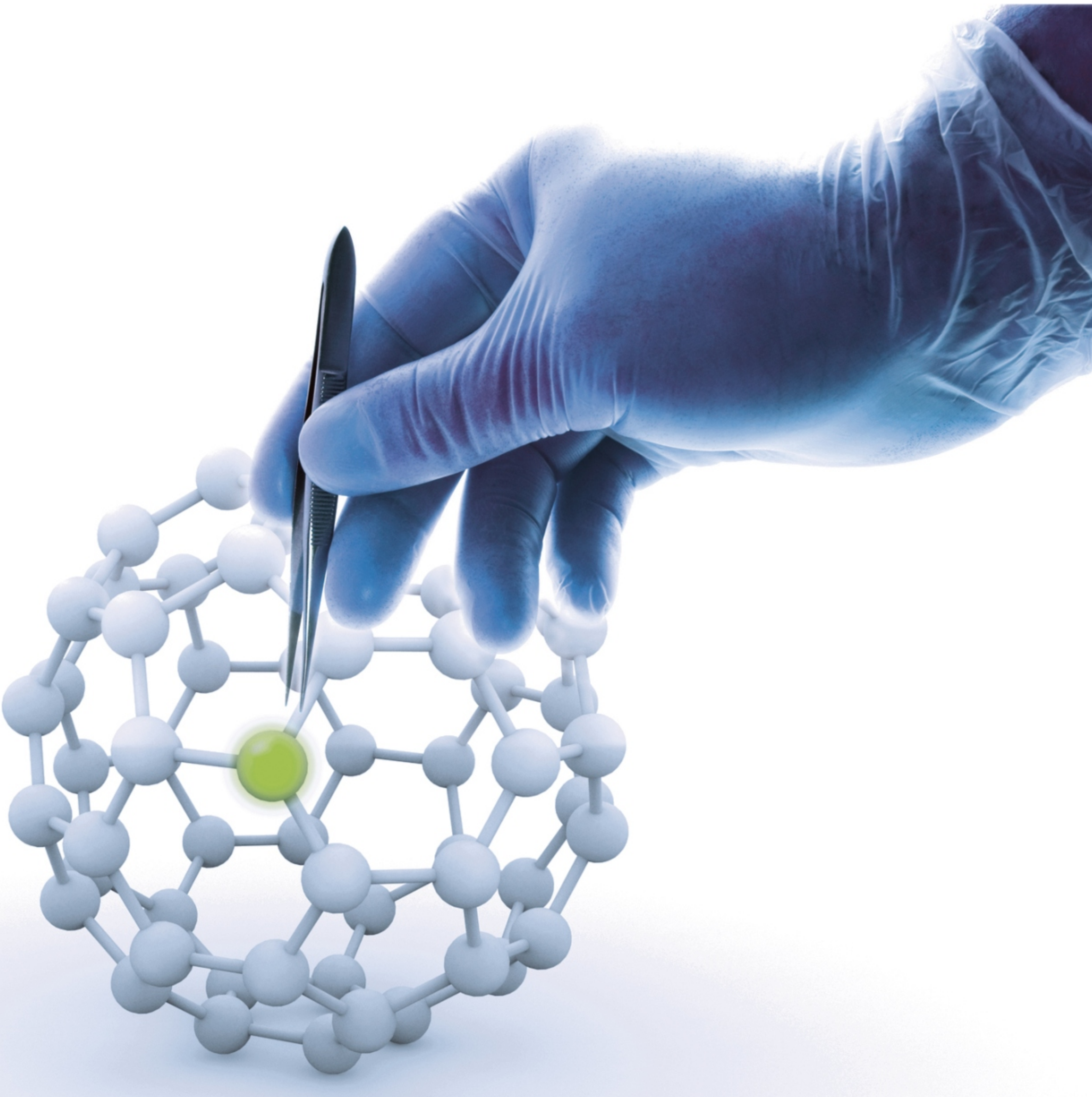
ORGANOMETALLIC COMPOUNDS

Manuel Huff



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Introduction

Organometallic compounds are defined as materials which possess direct, more or less polar bonds between metal and carbon atoms. Since Zeise synthesized in 1827 the first organometallic compound, $K[PtCl_3(CH_2{=}CH_2)]$, the organometallic chemistry has grown enormously although most of its applications have only been developed in recent decades.

Some of the key points in the fast expansion of organometallic chemistry are the selectivity of organometallic complexes in organic synthesis (discovered with Grignard reagents at the end of the 19th century) and the interesting role that metals play in biological systems (*e.g.* enzymes, hemoglobin, etc.). One of the most interesting things about organometallic compounds is that they can be used as homogeneous catalysts in processes where all the reacting partners are present in one phase, usually the liquid one.5

Transition metal complexes act in different ways within the catalytic reaction: they bring the substrates together, activate the substrates by coordinating to the metal and lower the activation energy of the reaction between substrates.

In general the use of a homogeneous catalyst in a reaction provides a new pathway, because the reactants interact with the metallic complex. These interactions make it possible for thermodynamically favoured reactions, which need long times to reach equilibrium, to be accomplished within hours. Therefore, homogeneous catalysts can be used to synthesize compounds which can hardly be obtained by conventional methods.

Although heterogeneous catalysts are widely used, particularly in oil processes, homogeneous transition metal catalysts are increasingly being applied in industrial processes to obtain fine chemicals and polymers. Some of these processes are: toluene and xylene oxidation to acids, oxidation of ethene to aldehyde, ester condensation to polyesters, carbonylation of methanol and of methyl acetate, polymerization of dienes to unsaturated polymers, hydroformylation of alkenes, oligomerization of ethene and propene, hydrocyanation of 1,3-butadiene, cyclodi(tri)-merization of 1,3-butadiene, asymmetric hydrogenation, asymmetric isomerization, asymmetric epoxidation, codimerization of 1,3-butadiene and ethene, hydrosilylation of alkenes, ring opening metathesis polymerization of dicyclopentadiene and norbornene, alternating copolymerization of ethene and carbon monoxide, etc. One interesting application of homogeneous catalysis is enantioselective (asymmetric) catalysis. It deals with the synthesis of enantiopure compounds, which are active ingredients of pharmatheuticals, agricultural products, flavours, fragrances and some advanced materials.

Life itself depends on chiral recognition because living systems identify the enantiomers as different substances and interact with them in different ways. For example, for many drugs only one of these enantiomers has a beneficial effect, being the other enantiomer either inactive or even toxic. Although the resolution of racemates is a way of obtaining enantiopure compounds, enantioselective synthesis enables just a single enantiomer to be obtained. The advantage that enantioselective catalysis has over stoichiometric synthesis is that one organometallic catalyst molecule can generate millions of chiral product molecules.

Catalytic synthesis also generates smaller amounts of chemical waste than stoichiometric organic synthesis. Therefore the search for homogeneous enantioselective catalysts that selectively react to give the desired product is one of the most interesting trends in organometallic chemistry. The success of organometallic catalysts lies in the easy modification of their environment by ligand exchange. A very large number of different types of ligands can coordinate to transition metal ions. Once the ligands are coordinated, the reactivity of the metals may change dramatically. In fact the rate and selectivity of a given process can be optimized to the desired level by controlling the ligand environment.

Understanding the role played by the different ligands coordinated to a metal is one of the main themes in homogeneous catalysis. Because organometallic complexes are highly soluble in organic solvents their behaiour throughout the catalytic reaction can be studied using different techniques to do in-situ measurements. Fundamental knowledge about the catalytic systems and studies about the steps of the catalytic processes can help to improve the efficiency of the catalysts. In this respect kinetic studies and stoichiometric model reactions with well-defined transition metal complexes are used to elucidate the steps of the catalytic cycle.

The use of labeled compounds allows the spectroscopic identification of intermediates. Palladium is one of the most extensively studied metals in organometallic chemistry because it is versatile and catalyzes a considerable number of organic reactions. The most important palladium-catalyzed reactions are those leading to C-C bond formation such as oligomerization and polymerization of alkenes, carbonylation of alkenes and organic halides, Wacker oxidation of alkenes, Heck reaction, allylic alkylation, Suzuki reaction, cross coupling reactions, polyamide synthesis, etc. The main steps in the mechanism of reactions catalyzed by palladium complexes are oxidative addition, reductive elimination, ligand substitution, transmetallation and migratory insertion. Migratory insertion is the fundamental step in coordination polymerization reactions such as the copolymerization of alkenes and carbon monoxide.

Organometallic chemistry at the threshold of a new millennium

The remarkable flowering of organometallic chemistry, notably of the transition metals, during the second half of the 20th century, has enriched and transformed chemical science to a degree and in ways that have few parallels in the history of the discipline. The full dimensions of this development cannot be easy to appreciate for anyone who was not around to witness the entire period. In 1950, the traditional branches of chemistry—physical, organic, and inorganic—already were mature disciplines, indeed, to the point that prompted many to wonder whether chemistry had already reached its full maturity with no really major new insights or discoveries remaining to be uncovered. At the time, organometallic chemistry was a fledgling discipline—hardly recognizable as such. A striking reminder of the state of the field is provided by the organometallic literature—or lack thereof—of the period.

Confronted with the massive current volume of literature on organometallic chemistry. The ensuing growth of the field—and of the organometallic literature—were dramatic. Updated and expanded editions of Coates' monograph followed in rapid succession, a 360-page second edition in 1960, and a two-volume 950-page third edition, co-authored by M. L. H. Green, P. Powell, and K. Wade, in 1971. At the same time, the fraction of space devoted to the organometallic chemistry of the transition metals increased dramatically from 14 per cent in the first edition of Coates to 68 per cent in Wilkinson's compendium.

Compounds: Covalent and Organic Compounds

While H_2 is not very reactive under standard conditions, it does form compounds with most elements. Millions of hydrocarbons are known, but they are not formed by the direct reaction of elementary hydrogen and carbon (although synthesis gas production followed by the Fischer-Tropsch process to make hydrocarbons comes close to being an exception, as this begins with coal and the elemental hydrogen is generated in situ). Hydrogen can form compounds with elements that are more electronegative, such as halogens (*e.g.*, F, Cl, Br, I) and chalcogens (O, S, Se); in these compounds hydrogen takes on a partial positive charge.

When bonded to fluorine, oxygen, or nitrogen, hydrogen can participate in a form of strong non-covalent bonding called hydrogen bonding, which is critical to the stability of many biological molecules. Hydrogen also forms compounds with less electronegative elements, such as the metals and metalloids, in which it takes on a partial negative charge. These compounds are often known as hydrides. Hydrogen forms a vast array of compounds with carbon. Because of their general association with living things, these compounds came to be called organic compounds; the study of their properties is known as organic chemistry and their study in the context of living organisms is known as biochemistry.

Hydrides

Compounds of hydrogen are often called hydrides, a term that is used fairly loosely. To chemists, the term "hydride" usually implies that the H atom has acquired a negative or anionic character, denoted H^-. The existence of the hydride anion, suggested by G.N.

Lewis for group I and II salt-like hydrides, was demonstrated by Moers with the electrolysis of molten lithium hydride (LiH), that produced a stoichiometric quantity of hydrogen at the anode. For hydrides other than group I and II metals, the term is quite misleading, considering the low electronegativity of hydrogen. An exception in group II hydrides is BeH_2, which is polymeric. In lithium aluminum hydride, the $AlH_4^{''}$ anion carries hydridic centers firmly attached to the Al(III). Although hydrides can be formed with almost all main-group elements, the number and combination of possible compounds varies widely; for example, there are over 100 binary borane hydrides known, but only one binary aluminum hydride.Binary indium hydride has not yet been identified, although larger complexes exist.

“Protons” and Acids

Oxidation of H_2 formally gives the proton, H^+. This species is central to discussion of acids, though the term proton is used loosely to refer to positively charged or cationic hydrogen, denoted H^+. A bare proton H^+ cannot exist in solution because of its strong tendency to attach itself to atoms or molecules with electrons.

To avoid the convenient fiction of the naked “solvated proton” in solution, acidic aqueous solutions are sometimes considered to contain the hydronium ion (H_3O^+) organized into clusters to form $H_9O_4^+$. Other oxonium ions are found when water is in solution with other solvents. Although exotic on earth, one of the most common ions in the universe is the H_3^+ ion, known as protonated molecular hydrogen or the triatomic hydrogen cation.

Biological Syntheses

H_2 is a product of some types of anaerobic metabolism and is produced by several microorganisms, usually via reactions catalyzed by iron- or nickel-containing enzymes called hydrogenases. These enzymes catalyze the reversible redox reaction between H_2 and its component two protons and two electrons. Evolution of hydrogen gas occurs in the transfer of reducing equivalents produced during pyruvate fermentation to water.

Water splitting, in which water is decomposed into its component protons, electrons, and oxygen, occurs in the light reactions in all photosynthetic organisms.

Some such organisms: Including the alga *Chlamydomonas reinhardtii* and cyanobacteria — have evolved a second step in the dark reactions in which protons and electrons are reduced to form H_2 gas by specialized hydrogenases in the chloroplast.Efforts have been undertaken to genetically modify cyanobacterial hydro-genases to efficiently synthesize H_2 gas even in the presence of oxygen.

Hydrogen as an Energy Carrier

Hydrogen is not an energy source, except in the hypothetical context of commercial nuclear fusion power plants using deuterium or tritium, a technology presently far from development.

The sun's energy comes from nuclear fusion of hydrogen but this process is difficult to achieve on earth. Elemental hydrogen from solar, biological, or electrical sources costs more in energy to make than is obtained by burning it.

Hydrogen may be obtained from fossil sources (such as methane) for less energy than required to make it, but these sources are unsustainable, and are also themselves direct energy sources (and are rightly regarded as the basic source of the energy in the hydrogen obtained from them). Molecular hydrogen has been widely discussed in the context of energy, as a possible carrier of energy on an economy-wide scale.

A theoretical advantage of using H_2 as an energy carrier is the localization and concentration of environmentally unwelcome aspects of hydrogen manufacture from fossil fuel energy sources.

Definitions of Terms

Any ion which contains more than one atom, as, for example, the sulfate ion $SO_4^{=}$, may be called a complex ion. Therefore a complex ion may be defined as an electrically charged radical or group of atoms, such as $Co(NH3)_6^{3+}$, which has been formed by the direct union of simple ions or by the direct union of a simple ion with neutral molecules.

Despite the foregoing definition, stable ions such as $SO_4^{=}$, ClO_3^{-}, and NO_3^{-} are usually regarded as simple ions, inasmuch as they are incapable of dissociation into their component parts under ordinary conditions.

Therefore we shall limit our definition of complex ions to those ions which are capable of some dissociation into their component parts at ordinary temperatures.

In view of this interpretation, complex-ion formation may be considered to be a reaction that is more or less reversible. Also, our concept of what constitutes a complex ion does not include lattice complexes consisting of certain double salts such as $FeSO_4 (NH_{4)})_2 SO_4^{-} 6H_2O$ and alums such as $KAl(SO_{4)})^2 12H_2O$, since these substances are complexes only in the solid state. In water solution these compounds usually break down into simpler substances or ions.

The term complex ion carries a broader meaning than that generally assigned to coordination compound. The latter term is usually reserved for those ions or compounds which contain coordinate linkages.

A coordination compound is a complex substance in which atoms or groups of atoms have been added beyond the number possible on the basis of electrovalent binding or covalent binding.

In such a compound both electrons of the additional linkages are furnished by the linked atom of the coordinated group. More simply, when a metal ion combines with an electron donor, the resulting substance is said to be a coordination compound.

For example, the cupric ion combines with four ammonia molecules, in which the nitrogen atom is an electron donor, to produce the ion $Cu(NH_{3)}^{4++}$. This definition is not without exceptions. We shall encounter coordination compounds which do not contain coordinate linkages. A typical exception is the hydrated aluminum ion, which is clearly a coordination compound, but whose components are held together by ion-dipole linkages.

The bonding between the central cation in a coordination compound and the surrounding particles may be essentially covalent or essentially ionic depending upon the nature of the components involved. The components of a coordination compound may be held together by electrostatic forces as well as covalent linkages. We shall learn that the components in the ion FeF_6^{3-} are held together by ionic linkages, whereas the components of the ion $Fe(CN)_6^{3-}$ are linked with covalent bonds.

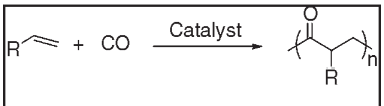
The discouraging observation that any attempt specifically to define the terms complex ion and coordination compound or to differentiate between the two is unsatisfactory because of the many meanings which have become attached to these expressions.

Alternating copolymerization of alkenes with carbon monoxide

The alternating copolymerization of carbon monoxide with alkenes to yield polyketones is an attractive reaction for various reasons. One of these is that carbon monoxide is an accessible and inexpensive monomer and so the final products are low cost polymers. Moreover, polyketones have interesting properties; they are thermal plastics, they are photo- and biodegradable and they can be starting material for a variety of functionalized polymers due to the chemical transformation of the carbonyl groups. Thermoplastics with high-performance properties are in increasing demand because of their strength, toughness, wear resistance, chemical resistance, UV stability, etc.

The applications of these materials include automotive components such as gears, fittings, containers, fibres, packaging, etc. Shell and more recently BP have commercialized polyketones as aliphatic terpolymers (CO/ alkene1/ alkene2) (Carilon and Ketonex, respectively).

The metal-catalyzed copolymerization reaction started when it was discovered that $K_2[Ni(CN)_4]$ catalyzed the alternating copolymerization of carbon monoxide and ethene. Homogeneous copolymerization catalysts provided greater control of the polymer properties than polymerization initiated via free radicals or rays, and gave a perfect alternation of the alkene and carbon monoxide. After nickel (II) other metal complexes containing rhodium (I) and palladium (II) were used as catalysts, always in severe conditions of pressure and temperature. The first catalyst that was active in the copolymerization of carbon monoxide and ethene, in mild conditions, was a palladium complex of formula $[Pd(PR_3)n(NCMe)_4\text{-}n][BF_4]_2$ with at least one molecule of phosphine ligand. However, the essential improvement to the efficient synthesis of polyketones at industrial level came with the discovery of the combined importance of using bidentate ligands and weakly coordinating anions in catalytic systems of the type PdX_2(L-L) where (L-L) is a bidentate phosphine and X a weakly or non-coordinating anion.



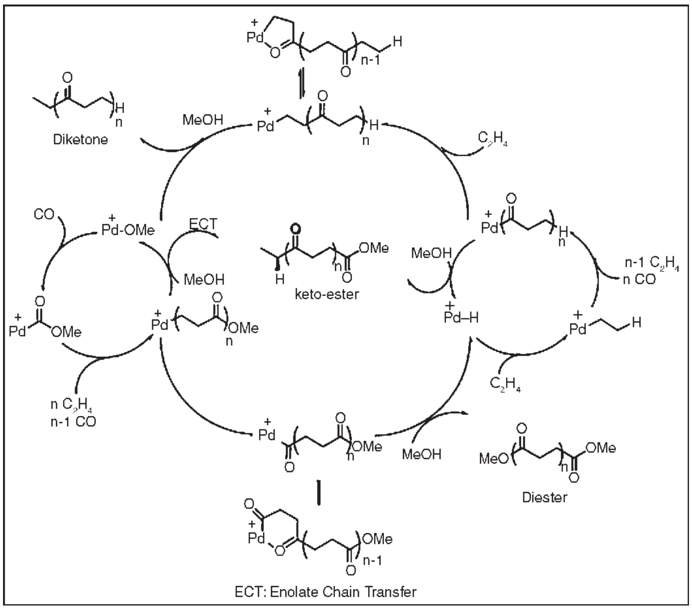
Alternating CO/Alkene Copolymerization

Copolymerization of ethene with carbon monoxide

In 1996 the copolymerization of ethene and carbon monoxide was extensively reviewed and the complete mechanism, which is applicable to other alkenes, proposed.

The alternating copolymerization of alkenes with carbon monoxide consists of the following steps:

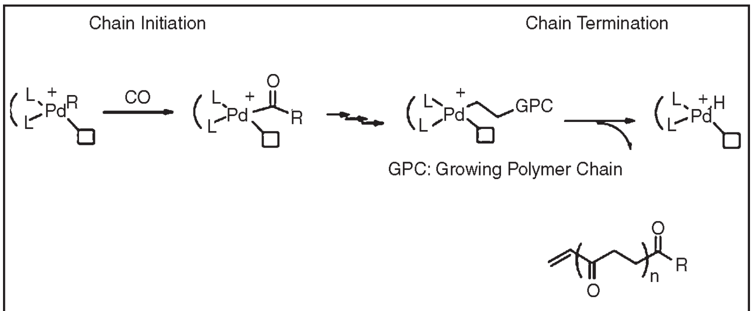
- The initiation of the chain growth;
- The propagation mechanism, with the perfect alternation of monomers;
- The termination of the chain together with the chain transfer, because of the importance for a polymerization catalyst of making more than one chain per metal center.



Proposed mechanism for the copolymerization of CO/ ethene in methanol. The analysis of the end groups of the polyketones enabled the initiation and termination steps of the mechanism to be understood.

Depending on the reaction conditions and on the nature of the alkene, the chain initiation process has different possibilities. It is generally accepted that for catalysts of the type PdX_2(L-L), made in-situ, or for the preformed ones [Pd(L-L)$(S)_2$][X_2] (S = solvent molecule), in alcoholic medium and under CO pressure, the mechanism starts with CO being inserted into a Pd- OMe bond or the alkene being inserted into a Pd-H species.23 Reaction of the palladium precatalyst in methanol with carbon monoxide generates the Pd-carbometoxy species (Pd-COOMe). The starting palladium hydride species might be formed by hydride elimination from a palladium methoxy species although the traces of water present in the reaction medium also lead to the formation of Pd-H species by -H elimination of the Pd-COOH species formed (shift reaction). H elimination reaction from a Pd-methoxyethyl complex (formed by a Wacker type reaction) also generates the Pd-H species. When the precatalyst is an alkyl complex, the insertion of CO into the Pd-alkyl bond is the initiation step. This alkyl complex is only the initiator species, and is not regenerated after the first copolymer molecule is made.

Generally, precatalysts of the type [PdR(LL)(S)][X] (where R is a methyl group) have been used, although recently it has been shown that an in-situ system formed by PdX_2(L-L) and a borane BR_3 (where R is the aryl group C_6F_5) is a good catalyst precursor due to the formation of the Pd-C_6F_5 species which inserts CO. When the copolymerization reaction is performed in non-protic solvents an alkylpalladium species is necessary so that the first monomer can be inserted.

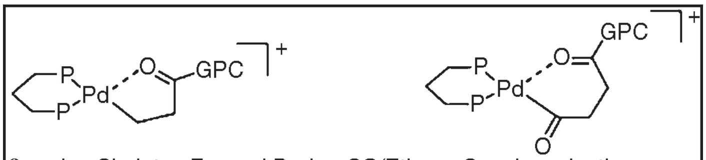


Initiation and Termination Stops using and Alkylpalladium Catalyst in a non-protic Solvent

The propagation mechanism consists of the successive migratory insertion of carbonyl into an alkylpalladium complex and of alkene into an acylpalladium complex, in an alternating way.

Cationic complexes with non-coordinating anions ensure the presence of accessible coordination sites and chelate ligands cause cis-coordination of the monomers and, thus, enable migratory insertion reactions. Errors in the alternation of the insertions have never been observed and it has been stated that they are not possible. The CO insertion into a Pd-acyl bond is thermodynamically not favoured and the insertion of an alkene into an alkylpalladium bond, although thermodynamically possible, is avoided because CO is more strongly coordinated and inserts faster in a Pd-alkyl bond than the alkene.

It has been shown that the growing polymer chain, σ-bonded to palladium, also coordinates internally to the metal by the last inserted carbonyl to form 5- or 6-membered ring metallacycles. This seems to help to the perfect alternation.



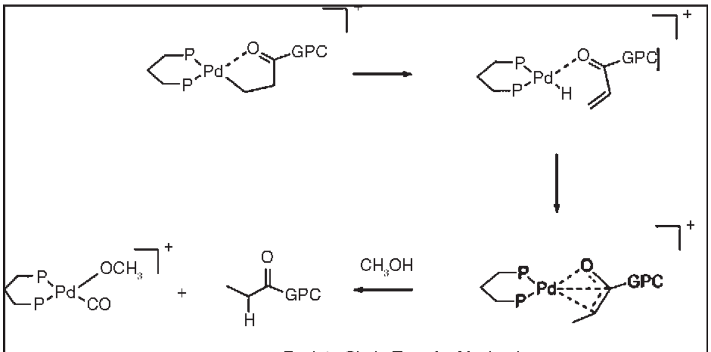
β-and γ- Chelates Formed During CO/Ethene Copolymerization

Several studies have been made about the detection and isolation of carbon monoxide and alkene insertion intermediates in the copolymerization reaction. Theoretical calculations have shown that there is a correlation with the experimental data in the perfect alternation of comonomers.

The termination step, like the initiation one, depends on the reaction conditions and on the alkene. When the reaction solvent is an alcohol, it acts as a chain transfer agent leading to two termination ways.

The alcoholysis of an acylpalladium species regenerates the Pd-H and gives an ester endgroup; while the protonolysis of an alkylpalladium bond regenerates Pd- COMe and forms a ketone end-group. Recently it has been shown that protonolysis does not imply the expected protonation of the alkylpalladium species. In fact, deuterium experiments have shown that previously hydrogen is - eliminated from the alkylpalladium species, to form an enolate, and is then reinserted.

The hydrolysis of an alkylpalladium bond, due to the water present in the reaction, has also been observed, giving carboxylic end-groups and regenerating the Pd-H species. Another possible termination pathway is the H elimination from an alkylpalladium species forming Pd-H bonds and unsaturated-end groups. This is the termination step in the reactions performed in non-protic solvents and in the case of other alkenes, like propene and styrene, is the main termination reaction.



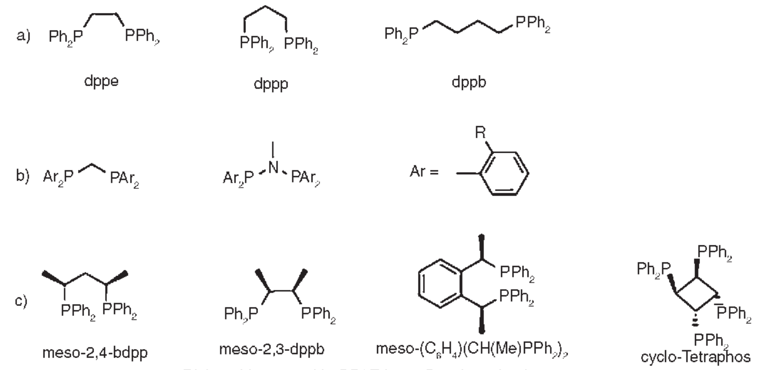
Enolate Chain Transfer Mechanism

Since the discovery of the efficiency of dppp (1,3-bis(diphenylphosphino)propane) as chelating ligand for the CO/ethene copolymerization reaction, many studies have been made of various diphosphine ligands as well as of modifications to the dppp backbone.

An interesting observation concerning diphosphines is that the size of the chelate ring dramatically affects productivity. Although it was stated that the most productive catalysts were those with a diphosphine containing a three-carbon backbone, it has been shown that four-membered diphosphine chelates may indeed lead to efficient catalysts if the ligands are sterically demanding enough.

Additionally modifications on the (1,3-bis-(diphenylphosphino)- propane) backbone creating chirality in the 1- and 3-centers by introduction of a methyl group (2,4-bis(diphenylphosphino)pentane) have led to a considerable increase of productivity. It has also been found that mesodiphosphines lead to higher activities than catalysts with similar ligands but without the meso structure.

The explanation seems to be that catalysts containing meso-diphosphines are more active since the metallacycles formed during the catalytic reaction are less stable. In agreement with this, calculations on the CO migratory insertion barriers for catalysts containing diphosphines with different chelate ring sizes showed that the larger the chelate ring size is, the faster the migratory insertion. Likewise, when the steric bulk of the ligand is increased the migratory insertion is accelerated.



Diphosphines used in CO/ Ethene Copolymerization

It has been said that Pd(II) complexes are the best choice for the copolymerization of carbon monoxide not only with ethene, but also with propene and with styrene. These alkenes may be considered as models for more complicated substrates like strained alkenes, 〈-alkenes substituted with polar groups, carbamates, alkynes, imines, amines, etc.

However, other late-metal catalysts such as nickel and rhodium74 have been used to a lesser extent in the copolymerization of alkenes with carbon monoxide. Monodentate ligands and bidentate ligands with relatively large bite angles are not used to avoid coordination in trans position in mono or bimetallic complexes, respectively.

Therefore, depending on the alkene involved in the catalysis, different types of chelating ligands are used, containing P-, N-, S-, O- or C- donor atoms.

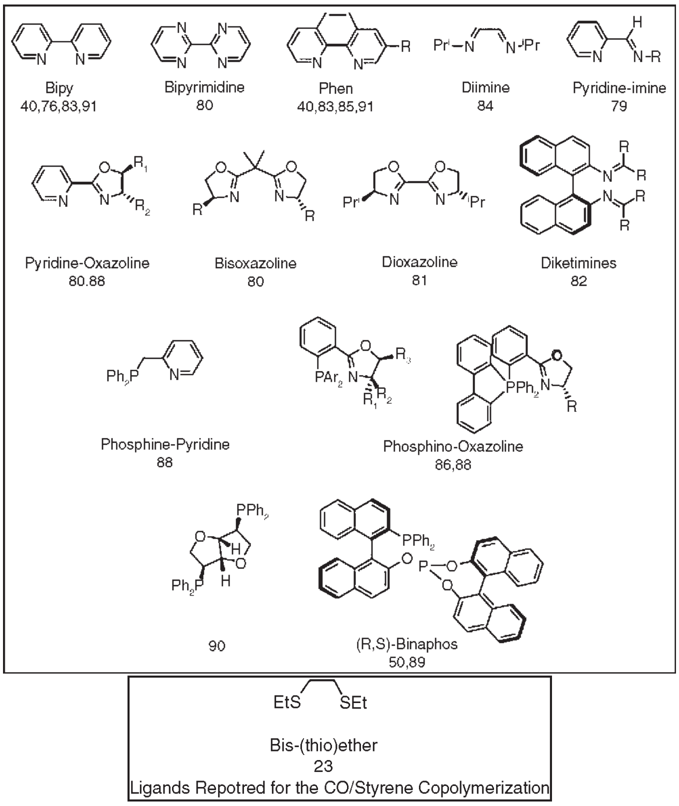
Copolymerization of styrene with carbon monoxide

As already stated for the copolymerization of ethene with carbon monoxide, palladium (II) complexes that contain both a non-coordinating anion and a chelating ligand are necessary if catalysts are to be active. Of the different anions tested, the BAr'_4 anion ($Ar' = 3,5\text{-}(CF_3)_2C_6H_3$) has been claimed to be the most appropriate because of its combination of bulkiness and low coordinating ability. For this anion, multinuclear NMR studies showed the weakest contacts with the cationic part of the catalysts. Preformed catalysts containing one or two molecules of chelating ligand have generally been used for CO/styrene copolymerization. Bisnitrogen-donating ligands have been mostly used for effective CO/styrene copolymerization. The combination of a phosphorous and a nitrogen-donating atom was also found to be active, although severer conditions of pressure and temperature are needed to obtain polyketones.

Unlike the co- and terpolymerization of ethene and propene with CO, catalysts containing diphosphine ligands are not active in the copolymerization of styrene (and its derivatives) with CO since only low molecular weight oligomers are obtained. It has been stated that when a phosphine is coordinated to palladium, H elimination is more favoured than polymer growth because of the higher electron density existing on the metal.

Moreover, the strongly stabilized benzylic intermediate formed after styrene insertion prevents subsequent carbon monoxide coordination and insertion.88 Surprisingly a palladium complex containing a phosphinephosphite ligand (BINAPHOS) has also shown activity. This was explained in terms of the reverse regiochemistry observed in the styrene. insertion (1,2-insertion). Very recently a palladium catalyst containing a diphosphine derived from L-iditol was reported to be active in the CO/styrene copolymerization, giving polymers with a highly regular microstructure. It seems that the iditol-derived diphosphine coordinates almost in a monodentate fashion (a strong coordination with one phosphorous and a weak one with the other, which can be exchanged during the catalysis) although the system has not been explained clearly. As well as nitrogen and phosphorous donating ligands, there is an example in the literature with sulfur-donating ligands, yielding polyketones with an irregular microstructure.

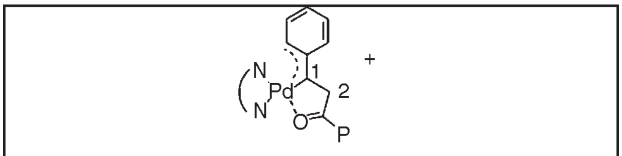
As well as having an effect on the activity of catalysts, ligands may influence the selectivity in which the copolymerization proceeds. When 1- alkenes are used as monomers, one important goal is the control of the regioand stereochemistry of the alkene insertion in the growing chain. It has been reported that in complexes containing bisnitrogen ligands, styrene insertion always takes place in a secondary fashion (2,1 insertion), because of the stabilization of the σ-benzylic intermediates



Ligands Repotred for the CO/Styrene Copolymerization

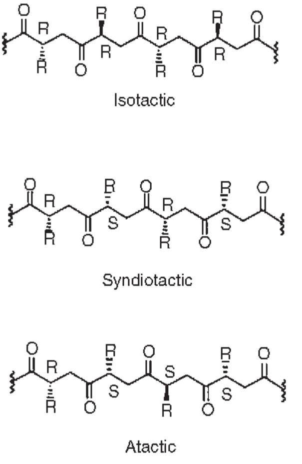
However, this situation changes when the ligand is varied: steric modifications in P-N ligands yield regioirregular polyketones containing some 1,2-inserted styrene units, while only 1,2- insertions were found in the regioregular copolymer obtained with the BINAPHOS ligand.

The reverse insertion of styrene, observed with the phosphine-phosphite ligand, prevents the ®-H elimination and might explain the activity of this ligand in CO/ styrene copolymerization.



π-Benzylic Intermediate Formed after 2,1 Insertion of Styrene in a Pd-Acyl Bond

The stereochemistry of the alkene insertion along the chain determines the copolymer tacticity: isotactic, syndiotactic or atactic. Two facts may be responsible for the control of the stereochemistry to give stereoregular (isotactic or syndiotactic) copolymers. On the one hand the enantioselective environment created by the chiral ligand may govern the stereoregularity of the alkene insertion, which is known as enantiosite control, and this leads to isotactic polymers. On the other hand the growing polymer chain, which is also chiral because of its successive stereogenic carbon centers, may lead to a controlled stereoregular insertion of styrene. This control is known as chain-end control, and it gives syndiotactic polymers.



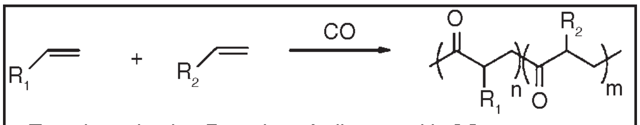
Tacticity of CO / Alkene Copolymers

C_2- and C_{2v}- achiral ligands give completely stereoregular syndiotactic copolymers due to the chain-end control.For C_2-symmetrical chiral ligands, enantiosite control overrides the effect of the growing chain to give isotactic polymers.However, for C_1-symmetrical ligands the relative influence of both effects cannot be inferred a priori. There are examples reported where the use of C_1-symmetrical ligands led to isotactic syndiotactic or even atactic copolymers.

Terpolymerization of styrene and ethene with carbon monoxide

The CO/alkene copolymer chains are packed together in an orderly fashion giving highly crystalline materials. This makes polyketones to be very strong but also very brittle. To avoid this problem, another alkene, *e.g.* propene, can be introduced in the chain to disturb somehow the crystal packing.

Inserting a second alkene into the palladium-catalyzed CO/alkene copolymerization reaction gives strictly alternating CO/alkene polyketones in which two different units are obtained (CO/alkene1) and (CO/alkene2). The relative amount of both units inside the polymer chain depends on the conditions of the reaction as well as on the different reactivity of each alkene.



Terpolymerization Reaction of Alkenes with CO

Different alkenes have been terpolymerized with CO using cationic palladium catalysts although combinations of ethene and 1-alkenes have been more studied.59,79,92-94 Recently some reports have appeared on terpolymerization of 1-alkenes and vinylarenes with CO.

Pathways of Organometallic Catalysis

Recognition of the basic reactions was followed almost immediately by appreciation of their potential role as component steps in the pathways of an extensive array of catalytic processes in organic chemistry.

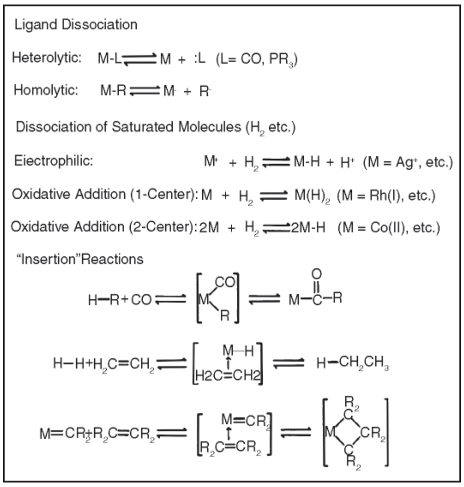


Fig. Basics Steps in Organometallic Catalysis.

The mechanistic scheme of essentially that proposed by Heck and Breslow in 1961 to depict the pathway(s) of cobalt carbonyl-catalyzed hydroformylation is prototypical.

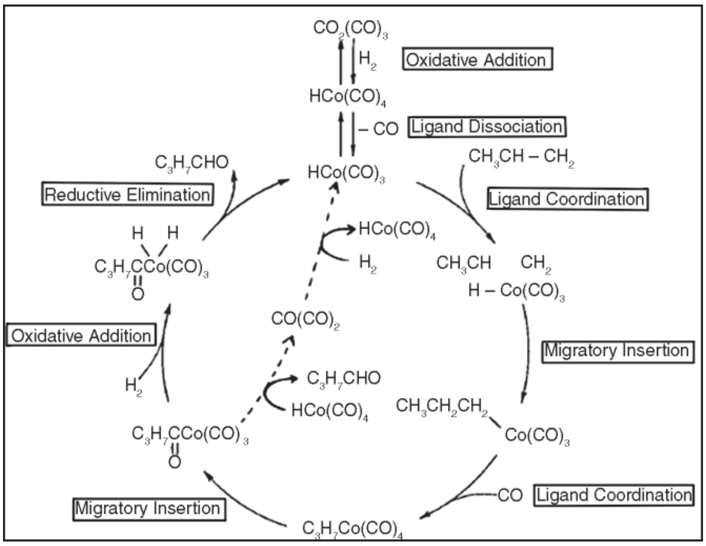


Fig. Heck-Breslow Mechanism of the Coblt Carbonyl-Catalyxed Hydroformylation of Propylene.

While details of the mechanisms still await substantiation and the possible involvement of additional pathways still cannot be excluded, the essential features of this interpretation have withstood the test of time and analogous mechanistic schemes have been proposed, and come to be accepted, for most of the other catalytic reactions exemplified.

$$RCH=CH_2+H_2+CO \rightarrow RCH_2CH_2CHO$$

Notwithstanding this basic understanding of the mechanistic framework of organometallic catalysis, the elucidation of the mechanisms of such reactions continues to be an active field of research with many challenges remaining to be surmounted. Increasingly detailed knowledge and understanding of such mechanistic pathways continue to be achieved through enhanced appreciation of the basic underlying chemistry, as well as increasingly powerful tools for elucidating elusive mechanistic details. Among the tools that are providing such important insights, are in situ spectroscopic methods, notably infrared and NMR, for identifying and structurally characterizing species present in solution, fast reaction methods such as flash photolysis that permit the detection of short-lived transient species and determination of the rates of their reactions in real time and application of the chemically induced dynamic nuclear polarization (CIDNP) technique that permits identification of intermediates that do not accumulate in sufficiently high concentrations to be detected directly.

Illustrative of the progress that has been achieved is the evolution of our appreciation of the mechanism of olefin hydrogenation catalyzed by $[RhCl(PPh_3)_3]$ (Wilkinson's catalyst) one of the earliest, and most widely applied, homogeneous hydrogenation catalysts.

Our current understanding of the mechanisms of this reaction, while retaining the essential steps originally proposed by Osborn, Jardine, Young, and Wilkinson, encompasses additional intermediates and an additional, previously unsuspected, pathway which, under certain conditions, accounts for most of the catalytic rate. The prospect cannot be excluded that further investigations will reveal yet additional mechanistic pathways.

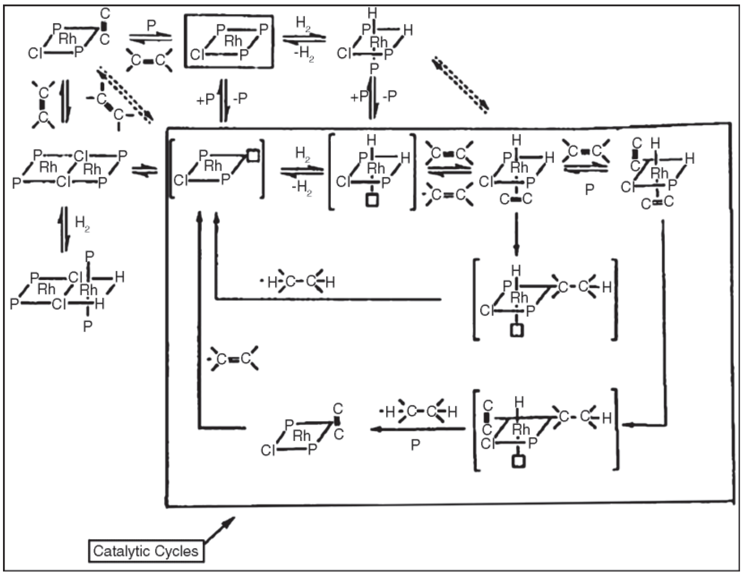


Fig. Mechanistic Scheme for the “RhCl(PPh$_3$ $_3$”-Catalyzed Hydrogenation of Olefins.

This system illustrates some of the challenges associated with the elucidation of the pathways of such catalytic reactions. The superposition of parallel multi-step sequences involving many species, often in rapid equilibrium, drastically curtails the extent and reliability of mechanistic information that can be deduced from measurements of the kinetics of the overall catalytic reaction.

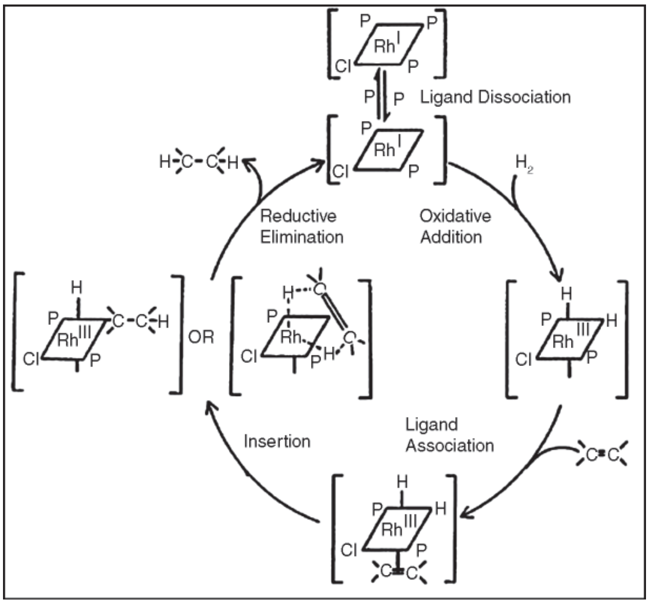


Fig. Wilkinson Mechanism of the "RhCl(PPh$_3$)$_3$"-Catalyzed Hydrogenation of Olefins.

Misleading leads also may be provided by identification of the predominant species present in solution under reaction conditions.

Thus, in the system under consideration none of the several species that have been directly identified as being present in solutions of the catalyst precursor, [RhCl(PPh$_3$)$_3$], or under conditions of the catalytic reactions, actually lie within the catalytic cycle, details of which must be inferred from less direct criteria.

Asymmetric Catalysis

Asymmetric catalysis, whereby complexes containing chiral ligands catalyze the conversion of achiral substrates to chiral products with high enantiomeric excess, must be counted as one of the major triumphs of organometallic chemistry. The earliest such systems, reported in the early 1970s, and exemplified by eq. 2, involve the asymmetric hydrogenation of á-acetamidocinnamic acid derivatives, using rhodium catalysts containing chiral phosphine ligands.

$$R_1CH = C[COOR_2][NHC(=O)R_3] + H_2 \rightarrow R_1CH_2C^*H[COOR_2][NH(C = O)R_3]$$

This system, developed by scientists at Monsanto, found almost immediate application in the manufacture of the anti-Parkinson drug, L-Dopa, and has been followed by many other asymmetric catalytic systems, commonly based on organometallic chemistry, which are transforming not only the methodologies for synthesizing pharmaceuticals and other chiral compounds, but also our conceptual framework of understanding of the origin of catalytic entantioselectivity.

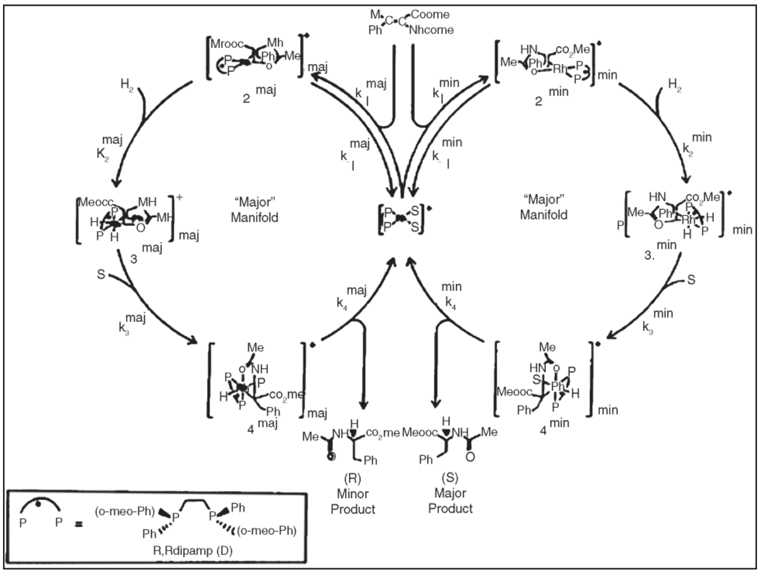


Fig. Mechanistic Scheme for the Asymmetric Hydrogenation of Methyl-(Z)-a-Acetamidocinnamate, Catalyzed by {1,2-bis (Phenyl-o-Anisoylphosphino)-Ethane}Rhodium(I).

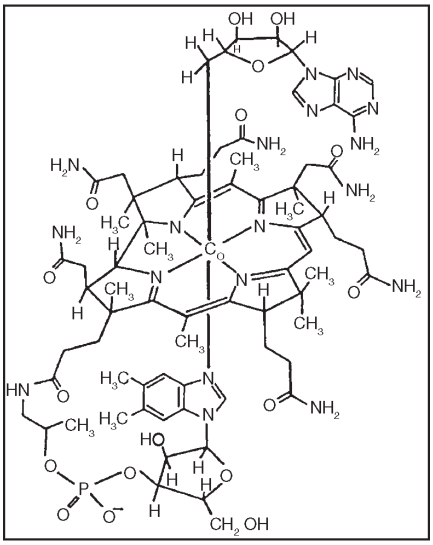
The mechanism of the reaction depicted has been elucidated in exquisite. While the basic features of the mechanism are conventional, comprising the familiar sequence of oxidative addition, migratory insertion and reductive elimination steps, elucidation of the mechanism revealed a remarkable, totally unexpected, feature. Contrary to the generally accepted prior view, it turned out that formation of the preferred product enantiomer results not from preference of the initial mode of binding of the olefinic substrate to the catalyst; instead, the predominant product enantiomer is derived from the minor, less stable, diastereomeric form of the catalyst-substrate adduct by virtue of its much higher reactivity towards H_2. This finding raises significant questions about the widely held “lock and key” interpretation of catalytic selectivity, with implications that extend considerably beyond organometallic chemistry.

ORGANOMETALLIC CHEMISTRY IN BIOLOGY

The totally unexpected finding in 1961, revealed by X-ray crystallography, that the biologically active forms of vitamin $B_{12,}$ 5´-deoxydenosylcobalamin (coenzyme $B_{12)}$ and the corresponding methylcobalamin, are organometallic compounds containing covalent cobalt–carbon bonds, opened up a new field, bioorganometallic chemistry, spanning organometallic chemistry and biology, the full scope of which still is unfolding.

Coenzyme B_{12} is distinctive, not only because of its unprecedented metal–carbon bond, but also because the class of enzymatic reactions for which it serves as a cofactor, depicted schematically are unprecedented in non-biological organic chemistry. The common feature of these reactions is the 1,2-interchange of a H atom and another substituent on adjacent saturated carbon atoms, which also depicts schematically the mechanism that has been deduced for these reactions through a combination of eznymatic and chemical studies. The key stop in this mechanism is the enzyme-induced homolytic cleavage of the Co–C bond leading, ultimately, to formation of a substratederived radical which rearranges to the corresponding product radical.

Organometallic chemistry also has been invoked to interpret the biological roles of some recently identified nickel-containing enzymes, notably methyl-coenzyme M reductase and carbon monoxide dehydrogenase (CODH). The mechanistic scheme that has been proposed for the biosynthesis of acetyl-coenzyme A, CoAS, (which undergoes hydrolysis to acetate) is depicted. The evolution of the field of organometallic chemistry, with particular attention to lessons learned from its biological component, prompts two general observations.



First, the significance and impact of the discoveries that have marked this rapidly evolving field often extend beyond their immediate context and even beyond the broader landscape of organometallic chemistry.

Thus, the immediate consequence of elucidation of the mechanistic features of coenzyme B_{12}-dependent reactions, was the unfolding of the extensive and distinctive chemistry of a previously unrecognized class of organocobalt compounds. Beyond that, the search for understanding of the factors that influence cobalt–alkyl bond dissociation energies and contribute to the enzyme-induced Co–C bond weakening and dissociation that triggers the coenzyme B_{12}-dependent rearrangements has provided much of the motivation for measurements of transition metal–alkyl bond dissociation energies and has contributed significantly to our present extensive knowledge and understanding of such energies.

Finally, this system has revealed previously unrecognized dimensions of organic and organometallic free-radical chemistry, added to our understanding of free radical rearrangements, and uncovered new applications of free-radical chemistry in organic synthesis and polymerization.

A second observation concerns the changing landscape of organometallic chemistry within which new discoveries are made. The structural characterization of coenzyme B_{12} in 1961 and its identification as an organocobalt compound provided virtually no insights into its role or mechanism of action, requiring them to be deduced from detailed enzymatic and chemical studies on the coenzyme, on its reactions, and on model systems. In contrast, when carbon monoxide dehydrogenase was characterized as a nickel-containing enzyme 20 years later, and found to exert its role in combination with a B_{12}-related cobalt-corrinoid, our knowledge and understanding of the organometallic chemistry of nickel and cobalt, and of the catalytic pathways of carbonylation reactions, had evolved to the point where a plausible mechanistic scheme. The proposed scheme parallels closely the previously deduced pathway of the Monsanto Rh/I-catalyzed synthesis of acetic acid from CO and methanol developed in the early 1970s and employed today to produce most of the world's acetic acid.

Because we are always seeking to exploit our understanding of how biological systems work to devise more effective approaches to achieve chemical goals, it is reasonable to speculate whether an understanding of the mechanism of action of carbon monoxide dehydrogenase, had this understanding preceded discovery of the Monsanto acetic acid process, would have helped to guide that discovery. Possibly—but my suspicion is that it might well have had the opposite effect by encouraging attention to be focused on nickel, rather than rhodium, as a potential catalyst—an option that appears, in retrospect, to be much less promising.

Current Directions and Future Outlook

Modern organometallic chemistry was shaped in many important respects during the three-decade "golden age" of the discipline, extending from about 1950 through the 1970s. As documented much of the conceptual framework of the field evolved during this period, including: discovery of most of the basic metal–ligand combinations and elementary reaction steps that constitute the "building blocks" of organometallic chemistry; recognition of the role of organometallic chemistry in biology; discovery of many important organometallic-based catalytic processes, such as Ziegler–Natta catalysis, Wacker oxidation of ethylene, rhodium-catalyzed carbonylation of methanol, and olefin metathesis; as well as considerable progress towards the understanding of the mechanisms of these and related processes. The ensuing evolution of organometallic chemistry has served to refine, extend, and exploit these groundbreaking discoveries and, thereby, to sustain the importance, distinctiveness and vitality of the field.

Notable recent advances and promising areas of current research include, but are not limited to, the following:

- Catalysis. Applications of organometallic catalysis to organic synthesis continue to expand, along with our understanding of their mechanistic pathways and our ability to design and "fine tune" catalytic activities and selectivities. "Traditional" catalysts are being supplanted by new generations, for example Ziegler–Natta and olefin metathesis catalysts by significantly superior "single- site" variants. At the same time, challenging targets, for example, the useful selective catalytic functionalization of alkanes, remain to be effectively achieved.
- Theoretical studies. The theoretical study of organometallic compounds and reactions employing extended Hückel and ab initio molecular orbital (MO) approaches, continues to be actively pursued. The impact of such studies to date has been only moderately encouraging, restricted, for the most part, to rationalizing known structures and reactivity patterns with only limited predictive power, particularly at the quantitative level. Discriminating among plausible alternative accessible reaction pathways with comparable rates, a common feature of organometallic reactions, is a particularly

challenging task. Nevertheless, with the rapid pace of increasing computing power, this is likely to continue to be an active research field, and significant advances may be anticipated.

- Mechanistic studies. Increasingly powerful tools, notably spectroscopic techniques for identifying and structurally characterizing species in solution, as well as time-resolved infrared and optical spectroscopic methods for monitoring short-lived intermediates, are significantly enhancing our knowledge and understanding of the mechanistic aspects of both elementary and complex organometallic reactions. This continues to be an active and productive area of research.
- "Unconventional" media. Increasingly, reaction media, other than traditional organic solvents, are being employed as solvents for organometallic reactions. Such "unconventional" media include highly electrophilic solvents, aqueous solutions (using ligands with solubilizing substituents), supercritical CO_2 and other fluids as well as multiphase systems. Apart from practical advantages (*e.g.*, environmental impact or superior separation properties) such media often significantly modify organometallic reactivities, thereby providing yet another tool for "tuning" catalytic systems. It is likely that this will continue to be an active and fruitful area of research and application.
- Materials and supramolecular assemblies. Mononuclear and polynuclear transition-metal centers are characterized by distinctive and potentially tunable

electronic, magnetic and optical properties. Embedding such centers in, or attaching them to, organic matrices, or connecting them through organic bridges of specified architecture or electronic attributes, affords possibilities for the design of new organometallic materials with distinctive and useful characteristics. This currently is an active area of research that promises to expand significantly both the scientific framework and range of applications of organometallic chemistry. Recently reported examples of such compounds or materials include: mononuclear or polynuclear metal centers linked

- Through conjugated polyalkynylene bridges ("molecular wires"); supramolecular constructs exemplified by dendrimeric assemblies by arrays of metal-containing moieties coordinated to sites on a fullerene surface and by organometallic supracyclopentadienyl derivatives "molecular magnets", exemplified by tetracyanoethylene (TCNE)-linked arrays of metallocene units and organometallic materials with non-linear optical properties. This field is still at a relatively early stage, with promise of playing a prominent role in the future evolution of organometallic chemistry.
- Bioorganometallic chemistry. Although only a few roles of organometallic chemistry in biology have thus far been uncovered, the distinctive nature of these and the fact that their recognition was totally unexpected, suggests that such roles are considerably more widespread. Among other systems in which roles for

organometallic chemistry (*i.e.*, for metal–carbon bonds) have been suggested are several involving iron-containing enzymes. The systems that have been identified thus far have yielded important new insights, for both chemistry and biology, and it is likely that this will continue to be an active and fruitful area of organometallic chemistry. In the circumstances, there is every reason to anticipate that the extraordinary momentum and pace of discovery that have characterized organometallic chemistry during the past half century, and contributed so much to the vitality of chemical science during this period, will extend well into the new millennium.

2

Basic Theory of Coordination Compounds

When aqueous ammonia is added to a solution of cobalt dichloride, $CoCl_2$, a blue precipitate forms of the corresponding hydroxide, $Co(OH)_2$, which dissolves on the addition of an excess of ammonia to give a solution that immediately begins to absorb oxygen and turn brown. From the oxidized solution, the following compounds can be isolated:

	Composition	**Colour**
(I)	$CoCl_3{\cdot}6NH_3$	Orange-yellow
(II)	$CoCl_3{\cdot}5NH_3{\cdot}H_2O$	Pink
(III)	$CoCl_3{\cdot}5NH_3$	Purple

A great many other compounds of this type can be prepared, (i) by starting with other cobalt salts, and (ii) by carrying out further reactions with the compounds first obtained. Among these other compounds are two other chlorides:

(IV)	$CoCl_3 \cdot 4NH_3$	Violet
(V)	$CoCl_3 \cdot 4NH_3$	Green

At first sight, the properties of compounds (I) – (V) are very puzzling:

i. All of them fail to give a brown precipitate of $Co(OH)_3$ when treated with sodium hydroxide solution - a property expected of compounds containing the Co^{3+} ion. Only on boiling does a precipitate form.

ii. All of them fail to give ammonium chloride when treated with concentrated hydrochloric acid - a reaction that would be expected of a compound containing ammonia. Only on boiling with sodium hydroxide is ammonia evolved.

iii. While all of them give a precipitate of silver chloride when treated with silver nitrate in aqueous solution, the amount that is precipitated in the cold is in some cases less than expected. In these cases the full amount is only obtained by leaving the solution to stand for a long time or by boiling it.

iv. The five compounds give different numbers of ions in solution, as judged from
   a. The electrical conductivities of their solutions in comparison with those of other electrolytes,
   b. The extent to which they depress the freezing point of water.

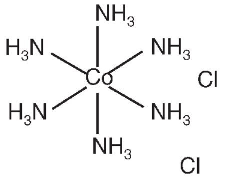
	Moles of AgCl precipitated per mole	**Number of ions present in solution per $CoCl_3$**
(I) $CoCl_3 \cdot 6NH_3$	3	4
(II) $CoCl_3 \cdot 5NH_3 \cdot H_2O$	3	4
(III) $CoCl_3 \cdot 5NH_3$	2	3
(IV) $CoCl_3 \cdot 4NH_3$	1	2
(V) $CoCl_3 \cdot 4NH_3$	1	2

These properties, and those of many other compounds of a similar kind, were brilliantly rationalized by Alfred Werner in 1893. In this year, at the age of only 26, he proposed what is now referred to as his "coordination theory", for which he was awarded a Nobel prize in 1913. Its principal postulates are as follows:

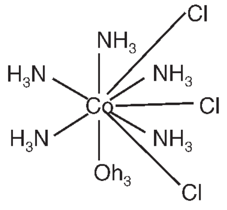
1. An atom exhibits two types of valency, its ordinary valency (*V*), and a valency that determines the number of neighbouring atoms to which it is bound (the "coordination number").
2. An atom's ordinary valency is satisfied by other atoms or radicals; its coordination number is satisfied by atoms, radicals, or molecules.
3. Bonds to neighbouring atoms are directed towards fixed positions in space.

On the basis of postulates (1) and (2), Werner formulated compounds (I)-(V) as shown diagrammatically below. Ordinary valency bonds are designated by black lines (—) and bonds between neighbouring atoms by green lines (.....).

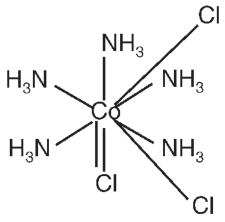
The cobalt atoms have their ordinary valency of three (as in CoF_3) and are given a coordination number of six. The other atoms are given coordination numbers to match (four for the nitrogen atom in NH_3, leaving one for the cobalt).



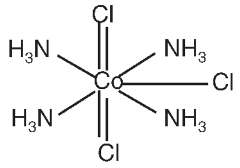
$CoCl_3.6NH_3$



$CoCl_3.5NH_3.H_2O$



$CoCl_3.5NH_3$



$CoCl_3.4NH_3$

Now if in these formulations the black lines are taken to be ionic bonds, and the green and double lines are taken to be bonds of a non--ionic character, the properties of compounds (I) - (V) given above are fully explained.

Thus (I) and (II) would be expected to give three Cl^- ions in solution, (III) only two, and (IV) and (V) only one. This leads to the customary formulations:

1. $[Co(NH_3)_6]Cl_3$ containing the $[Co(NH_3)_6]^{3+}$ ion;
2. $[Co(NH_3)_5H_2O]Cl_3$ containing the $[Co(NH_3)_5H_2O]^{3+}$ ion;
3. $[CoCl(NH_3)_5]Cl_2$ containing the $[CoCl(NH_3)_5]^{2+}$ ion;
4. $[CoCl_2(NH_3)_4]Cl$ containing the $[CoCl_2(NH_3)_4]^+$ ion.

The existence of two isomers of $[CoCl_2(NH_3)_4]Cl$ was explained by Werner on the basis of postulate (3). Indeed, the fact that only two isomers of this formula were known led him to propose that the arrangement of atoms around the cobalt atom is an octahedral one, since other arrangements would lead to more than two isomers.

Known isomers vs. the number theoretically possible for three different structures

The absence of a third isomer of $[CoCl_2(NH_3)_4]Cl$ does not of course prove that the octahedral structure is correct. The third isomer may simply be much less stable or more difficult to isolate.

Werner was able to prove, however, that the octahedral structure is the correct one by preparing a compound that would be expected to exist in optically active forms if the structure were octahedral, but not if it was planar or a trigonal prism, and showing that the compound can indeed be resolved into optically active isomers. This conclusion has been verified by X-ray crystallography.

Complex type	**Number of known isomers**	**Number of isomers theoretically possible**		
MA_5B	One	One	One	One
MA_4B_2	Two	Three (1,2; 1,3; 1,4)	Three (1,2; 1,4; 1,6)	Two (1,2; 1,
MA_3B_3	Two	Three (1,2,3; 1,2,4; 1,2,5)	Three (1,2,3; 1,2,4; 1,2,6)	Two (1,2,3; 1,2,6)

Most metals can form some coordination compounds, but few form as many as trivalent cobalt. Others that do include trivalent chromium, and bi- and quadri-valent platinum.

Trivalent chromium and quadrivalent platinum have the same coordination number and geometry as trivalent cobalt; bivalent platinum has a coordination number of four with the groups around it arranged in a square.

The complex part of a coordination compound may be a cation, an anion, or an uncharged molecule. For example:

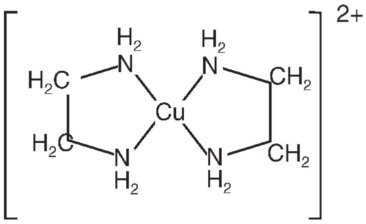
Complex cation	$[Co(NH_3)_6]^{3+}$
Complex anion	$[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$, $[Co(NO_2)_6{}^{3-}]$
Neutral complex	$[CoCl_3(NH_3)_3]^0$, $[Co(NO_2)_3(NH_3)_3]^0$

Neutral complexes are frequently more soluble in non-polar organic solvents than they are in water. When they do dissolve in water, they behave as non--electrolytes.

Terminology of coordination compounds

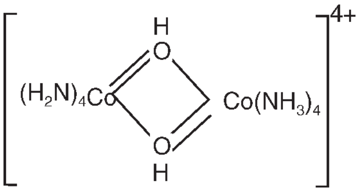
A species like $[Co(NH_3)_6]^{3+}$ is called a “coordination entity”. The atom in the middle is called the “central atom”, the attached groups are called “ligands” (Latin, *ligare*, bind), and the atoms by which they are attached, “coordinating” or “ligating” atoms. The ligands are said to be “coordinated” or “ligated” to the central atom. They are also said to be in the “coordination sphere” of the central atom. Following Werner, the number of coordinating atoms around the central atom is called the “coordination number” of the central atom. This term is also used by crystallographers. However, the latter use it to describe a particular structure, whereas Werner used it more as a valency. A better term for this purpose would be “coordinate valency”.

A ligand containing more than one coordinating atom is called a multidentate (literally “many-toothed”) ligand, the number of coordinating atoms being indicated by the terms “unidentate”, “bidentate”, etc. An example of such a ligand is ethylenediamine, usually abbreviated en: $H_2N–CH_2–CH_2–NH_2$.



This can coordinate through its two nitrogen atoms in the same way as two molecules of CH_3NH_2 or NH_3. Thus, just as the addition of ammonia to a solution containing Cu^{2+} leads to the formation of the deep blue $[Cu(NH_3)_4]^{2+}$ ion, so the addition of ethylenediamine leads to the formation of the dark blue-violet $[Cu(en)_2]^{2+}$:

A multidentate ligand is said to function as a "chelate" ligand when it attaches itself to a central atom through more than one of its coordinating atoms, as in the example above. The resulting species is called a chelate. This comes from the Greek word for a crab's claw and describes the way in which the ligand grasps the central atom between two or more of its coordinating members. A ligand is said to function as a "bridging" ligand when it is attached to more than one coordinating centre. An example is the hydroxide ion in



Coordination entities of this sort are described as "polynuclear", the number of central atoms being designated by the terms "mononuclear", "dinuclear", etc.

Pseudo-Binary Compounds

A great many compounds of ternary or higher order behave as if they were compounds of binary order, with a group of atoms acting as if it was a single atom. Such a group is called a "radical". A classical example is provided by the cyanides, some of which are described below:

Hydrogen cyanide, HCN. This is manufactured by passing a mixture of methane and ammonia over a platinum catalyst at 1200 °C:

$$CH_4 + NH_3 \rightarrow HCN + 3H_2$$

It is a colourless liquid, boiling at 26 °C to a colourless gas. It is a poor conductor of electricity. Like most cyanides, it is extremely poisonous.

Sodium cyanide, NaCN: This is manufactured by absorbing gaseous hydrogen cyanide in aqueous sodium hydroxide or sodium carbonate. The compound is a colourless solid, melting at 564 °C to a colourless liquid. The liquid conducts electricity with the formation of sodium at the cathode and a colourless gas at the anode. This gas is cyanogen, C_2N_2.

Potassium cyanide, KCN: This is similar to sodium cyanide.

Cyanogen, C_2N_2. This is a colourless gas, condensing at –21 °C to a colourless liquid.

Cyanogen chloride, ClCN: This is made by passing chlorine into aqueous hydrogen cyanide:

$$HCN + Cl_2 \rightarrow HCl + ClCN$$

It is a colourless gas, condensing at 13 °C to a colourless, mobile liquid. From the above descriptions, it is clear that there is a close resemblance between cyanides and halides, both in composition and in character:

Composition		**Character**
Cyanide	*Chloride*	
HCN	HCl	Nonmetallic
NaCN	NaCl	Salt-like
KCN	KCl	Salt-like
ClCN	ClCN	Nonmetallic

This resemblance extends to the parent substances:

$(CN)_2$ Cl_2 Nonmetallic

So close is this resemblance that cyanogen is called a pseudo-halide. A second example is provided by ammonium compounds, *e.g.* ammonium chloride, NH_4Cl. These are very similar to alkali metal compounds. Indeed, ammonium compounds and potassium compo-unds often form mixed crystals with each other.

Furthermore, electrolysis of ammonium chloride solution with a mercury cathode at 0 °C gives a grey mass that is similar in character to sodium or potassium amalgam. Thus it reduces copper dichloride solution to copper, zinc chloride to zinc, etc.

On warming it decomposes into ammonia and hydrogen in the proportions required by the equation,

$$2NH_4(\text{amalgam}) \rightarrow 2NH_3 + H_2$$

the NH_4 radical is thus very much like an alkali metal atom in its behaviour.

The nature of pseudo-binary compounds: The nature of pseudo-binary compounds follows from our discussion of binary compounds. The bonding between radicals and radicals or radicals and atoms is the same as the bonding between atoms and atoms.

For example:

- The molecules HCN, ClCN, and $(CN)_2$ are held together with essentially covalent bonds:

  H–CN, Cl–CN, NC–CN

- The compounds NaCN and KCN are ionic:

  $Na^+[CN]$, $K^+[CN]^-$

- Ammonium chloride is ionic: $[NH_4]^+Cl^-$d.
- Ammonium amalgam presumably contains:

  $[NH_4]^+e^-$

Bonding *within* radicals is of a covalent character. Thus the full bond formula of the HCN molecule is H–C°N while that of the $[CN]^-$ ion is $^-$C°N Ions like $[CN]^-$ and $[NH_4]^+$ are called “molecular” ions. The square brackets indicate that the charge is somewhere on the radical as a whole, but they are often omitted:

$$CN^- \text{ and } NH_4^+.$$

This should not be misinterpreted as implying, for example, that the charge on the cyanide ion is located on the nitrogen atom.

radicals

Formula of radical	Name as electropositive constituent of compounds	Name as electronegative constituent of compounds

Non-metal-like

Table.Forming one Covalent Bond or a Singly Charged Anion

OH		Hydroxide
NO_2	Nitryl	Nitrite
NO_3		Nitrate
CN	cyanogen	Cyanide
SCN	thiocyanogen	Thiocyanate
CH_3CO_2		Acetate
CH_3 (Me)	methyl	Methyl
C_6H_5 (Ph)	phenyl	Phenyl

Table. Forming two Covalent Bonds or a Doubly Charged Anion

CO_3	Carbonate
SO_3	Sulfite
SO_4	Sulfate

Table.Forming three Covalent Bonds or a Triply Charged Anion

PO_4	Phosphate

Metal-like

Table. Forming a singly charged cation

NH_4	Ammonium
NMe_4	Tetramethylammonium

- All the non-metal-like radicals form covalent bonds with sufficiently electronegative atoms or radicals. This includes nitrate and sulfate, *e.g.* in $MeNO_3$ and Me_2SO_4.
- All the non-metal-like radicals form anions with sufficiently electropositive elements. This includes methyl and phenyl, *e.g.* in Na^+Me^- and Na^+Ph^-.
- The NMe_4 radical forms a similar amalgam to NH_4.

Nomenclature of radicals

The names given above are based on those recommended by IUPAC – the International Union of Pure and Applied Chemistry Though not very systematic, they reflect long established usage.

The use of the endings –ite and –ate to indicate a lower and higher oxo-anion (*e.g.* nitrite, nitrate) parallels the use of –ous and –ic to indicate a lower and higher cation. British schools teach different names as advised by the Association for Science Education (ASE):

IUPAC	ASE
Nitrite	Nitrate(III)
Nitrate	nitrate(V)
Sulfite	Sulfate(IV)
Sulfate	Sulfate(VI)
Acetate	Ethanoate

The ASE names are derived from IUPAC rules for naming less common ions. These names, however, are only used in British schools. Everywhere else in the world (in the chemical literature, chemical industry, other sciences, and other countries) IUPAC names are used.

Metallic Compounds

The nature of these is more difficult to determine. However, we can get so far along the following line:

- Metals conduct electricity without electrolysis taking place. The carriers of electricity cannot therefore be ions. They must either be some kind of charged entity that can travel through a conductor without affecting it or else a component of the atoms making up the conductor, which, by a process of successive displacement from one atom to another, can effectively be transferred from one end of the conductor to the other.
- When an electric current is passed through a tube of gas at low pressure, rays can be seen to emerge from the negative electrode (the cathode). These rays are drawn towards a plate carrying a positive charge, and must therefore be carrying negative charge. They are likewise deflected by a magnet. From measurement of these deflections, the ratio of the charge to the mass can be determined for the particles making up the rays, and this is found to be the same, irrespective of the particular gas in the tube or the particular metal forming the cathode. This suggests that the particles are a common constituent of matter, and that they not only carry electricity through the gas, but also through the metal that supplies the electricity to the gas, the particles streaming without change from one into the other.
- Measurement of the charge on these particles gives a value identical in magnitude with the charge on the sodium ion worked out above, *viz.* F/L. This gives us our terminology for the particle ("electron") and mode of conduction ("electronic"): it also gives us something

else. It suggests that metal atoms may be thought of as being composed of metal ions and electrons, sodium atoms being Na^+ with one electron, magnesium atoms Mg^{2+} with two, and so on.

- A simple model of a metal, therefore, is that of a collection of metal ions, held together by the appropriate number of electrons situated between them, the electrons being readily made to move by supplying further electrons at one point of the metal and taking electrons away at another. In the solid, the electrons hold the ions together in a rigid assembly: in the liquid the ions are free to move.
- The constitutional formulae of metals can thus be written in the same way as the constitutional formulae of salts. The latter are properly written as exemplified by $(Na^+Cl^-)_n$, with n a very large number, but this is usually abbreviated to Na^+Cl^-, that is, to one unit of the complete assembly. In an analogous way, metallic sodium can be written Na^+e^-, metallic magnesium $Mg^{2+}(e^-)_2$, etc. A metallic compound like Cs_7O may similarly be written $(Cs^+)_7(e^-)_5O^{2-}$.
- Support for these formulations is provided by the latent heats of vaporization of metals:

	ΔH
Sodium, Na^+e^-	90 kJ mol^{-1}
Magnesium, $Mg^{2+}(e^-)_2$	130 kJ mol^{-1}
Aluminium, $Al^{3+}(e^-)_3$	290 kJ mol^{-1}

These values are for the vaporization of the liquid at the boiling point into gaseous atoms.

It can be seen that the strength of binding increases as the number of opposite charges increases.

The vapours of metals are, as we have seen, quite different from the solids and liquids.

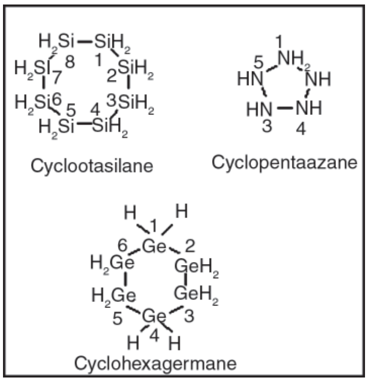
In general, metals vaporize into a mixture of atoms and diatomic molecules, the proportion of the latter diminishing with increase of temperature.

Thus sodium metal just above the boiling point contains about 99 per cent of sodium atoms and 1 per cent of Na_2 molecules. On vaporization of a metal, therefore, the individual ions or pairs of ions become separated from each other, carrying their electrons with them. The mechanism for the conduction of electricity accordingly breaks down, and metallic properties disappear.

Homogeneous Hydrides Other than Hydrocarbons or Boron Hydrides

A compound having a single saturated ring of identical heteroatoms is named by adding the prefix "cyclo-" to the name of the saturated unbranched chain containing the same number of identical atoms.

Examples:



Cyclootasilane

Cyclopentaazane

Cyclohexagermane

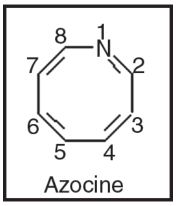
Heterogeneous Hydrides Other than Heteropolyboron Hydrides

- Monocyclic compounds with no more than 10 ring members and containing one or more heteroatoms, may be named by using the extended Hantzsch-Widman system.

  The name is formed by combining the “a” prefix(es) for the heteroatom(s) with a stem indicating the size of the ring.

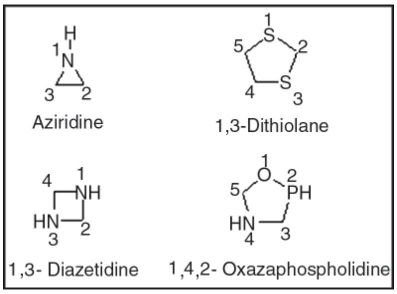
  The prefixes designating heteroatoms are cited in the order of their appearance; and the heteroatoms of the structure are numbered in the same order.

Examples of Hantzsch-Widman names



Azocine

- The position of a single heteroatom determines the numbering in a monocyclic compound. *Example:*

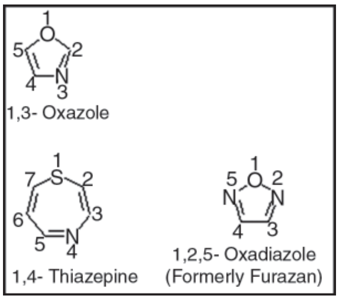


Aziridine

1,3-Dithiolane

1,3- Diazetidine

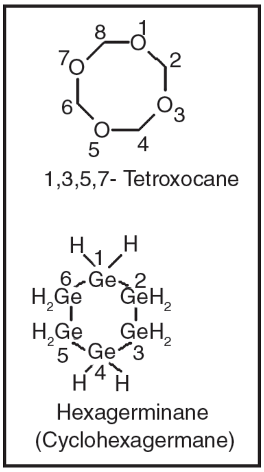
1,4,2- Oxazaphospholidine



1,3- Oxazole

1,4- Thiazepine

1,2,5- Oxadiazole (Formerly Furazan)

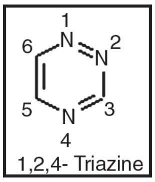


1,3,5,7- Tetroxocane

Hexagerminane (Cyclohexagermane)

- When the same heteroatom occurs more than once in a ring, the numbering is chosen to give the lowest locants to the heteroatoms.

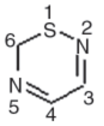
  Example:



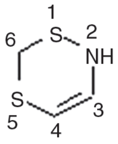
1,2,4- Triazine

- When heteroatoms of different kinds are present, the locant 1 is given to a heteroatom which appears earliest. The numbering is then chosen to give the lowest locants to the heteroatoms, first considered as a set without regard to kind; if a choice still remains.

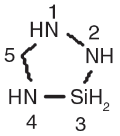
  Examples:



6H- 1,2,5- Thaidiazine
(not: 2,1,4- Thiadiazine)
(not: 1,3,6- Thiadiazine)



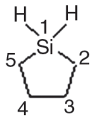
2H,6H- 1,5,2- Dithiazine
(not: 1,3,4- Dithiazine)
(not: 1,3,6- Dithiazine)
(not: 1,5,4- Dithiazine)



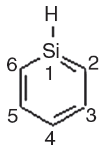
1,2,4,3- Traizasilolidine
(For the N Atoms, the Set
1,2,4 is Prefferred to 1,3,4)

- Heteromonocyclic compounds may be named by replacement nomenclature. However, replacement nomenclature for heteromonocycles with 10 or fewer members has usually been applied only to silicon-containing rings.

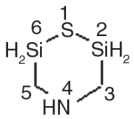
  Examples:



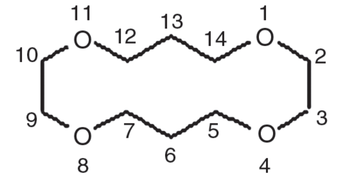
Silacyclopentane



Silabenzene



1- Thai-4-aza-2,6- disilacyclohexane

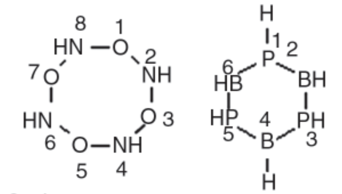


1,4,8,11 - Tetraoxacyclotetradecane

- Saturated monocyclic systems consisting of repeating units of two different skeletal atoms may be named by citing successively the prefix “cyclo-” followed by a multiplying infix denoting the number of repeating units, the “a” terms of the atoms of the repeating unit in the reverse order, and the suffix “-ane”.

The terminal letter “a” of an “a” term is elided when followed by a vowel; the terminal vowel of a numerical prefix is not elided even when the “a” term begins with the same vowel..

Examples:



Cyclotetraazoxane Cyclotriboraphosphane

Parent Hydrides and their Derived Substituent Groups

A “parent hydride” is the structure which is named before the addition of affixes denoting substituents to yield the name of a specific compound. Its name is understood to signify a definite population of hydrogen atoms attached to a skeletal structure. Acyclic parent hydrides are always unbranched, for example pentane and trisilane; although a few trivial names for branched acyclic hydrocarbons are retained, their use for naming substitutive derivatives is not recommended. Cyclic parent hydrides are usually either fully saturated, for example, cyclopentane, cyclotrisiloxane, azepane, bicyclooctane, and spirodecane, or fully unsaturated, *i.e.*, they contain the maximum number of non-cumulative double bonds, for example, pyridine, 1,3-oxazole, 1*H*-phenalene, phenanthroline, and benzo[*a*]anthracene.

Also, there are parent hydrides that are partially saturated, for example, 1,4-dihydro-1,4-ethanoanthracene and spiro[1,3-dioxane-2,1'-[1*H*]indene], and that are combinations of cyclic and saturated acyclic structures having retained trivial names.

Substituent Prefix Names Derived from Parent Hydrides

The presence of one or more free valence(s) derived from the loss of one or more hydrogen atoms from a parent hydride is denoted by suffixes such as "-yl", "-diyl", "-ylidene", "-triyl", "-ylidyne".

Monovalent	Divalent	Trivalent	Tetravalent	etc.
–Yl	–Diyl –Ylidene	–Triyl –Ylidyne –Ylylidene	–Tetrayl –Ylylidyne –Diylidene –Diylylidene	etc.

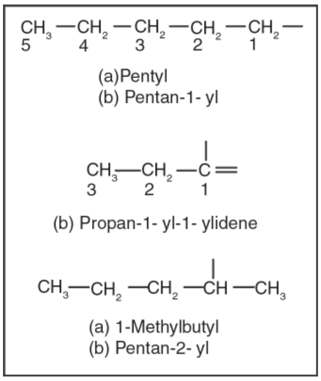
Note: In these recommendations, the suffixes "-ylidene" and "-ylidyne" are used only to indicate the attachment of a substituent to a parent hydride or parent substituent by a double or triple bond, respectively.

These suffixes are used according to two methods as follows:

- The suffixes "-yl", "-ylidene", and "-ylidyne" replace the ending "-ane" of the parent hydride name. The atom with the free valence terminates the chain and always has the locant "1", which is omitted from the name. This method is recommended only for saturated acyclic and monocyclic hydrocarbon substituent groups and for the mononuclear parent hydrides of silicon, germanium, tin, lead, and boron.

- *More general method.* Any of these suffixes may be added to the name of the parent hydride with elision of a terminal "e", if present, before suffixes beginning with "y". The atoms with free valences are given numbers as low as is consistent with any established numbering of the parent hydride; except for the suffix "-ylidyne", the locant number "1" must always be cited.

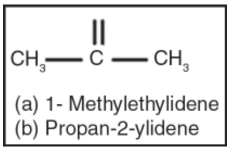
  Examples:



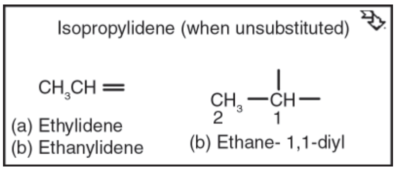
(a)Pentyl
(b) Pentan-1- yl

(b) Propan-1- yl-1- ylidene

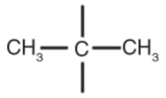
(a) 1-Methylbutyl
(b) Pentan-2- yl



(a) 1- Methylethylidene
(b) Propan-2-ylidene


Isopropylidene (when unsubstituted)

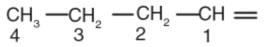
(a) Ethylidene
(b) Ethanylidene
(b) Ethane- 1,1-diyl



(a) 1- Methylethane- 1,1- diyl
(b) Propane-2,2-diyl

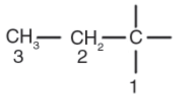
$-CH_2-CH_2-CH_2-$

(b) Propane- 1,3-diyl



$CH_3-CH_2-CH_2-CH=$

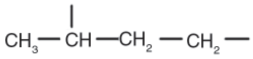
(a) Butylidene
(b) Butan-1-ylidene



(b) Propane-1,1,1-triyl

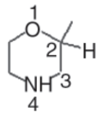
$CH_3-CH_2-C\equiv$

(a) Propylidyne
(b) Propanylidyne



(b) Butane-1,3-dlyl

(a) Cyclohexyl
(b) Cyclohexan-1-yl



(b) Morphin-2- yl

The contracted names adamantyl, naphthyl, anthryl, phenanthryl and furyl, pyridyl, isoquinolyl, quinolyl, piperidyl are retained. The trivial names vinyl, allyl, and phenyl and thienyl, furfuryl, and thenyl are retained for use with no limitation on substitution; other trivial names are retained but only with limited or no substitution.

Limiting types of Chemical Bond

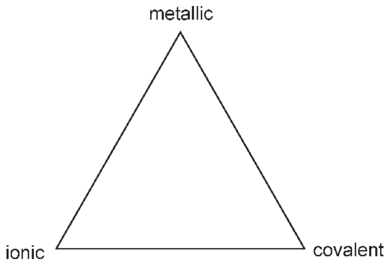
Corresponding to the three limiting types of binary compound there are three limiting types of chemical bond. These are named as follows:

Type of binary compound	**Type of chemical bonding**	
	Original name	**Modern name**
Metallic	Metallic	Metallic
Nonmetallic	Nonpolar	Covalent
Salt-like	Polar	Ionic

The character of these may be inferred from the nature of metallic, non-metallic, and salt-like compounds:

- *Ionic bonding* involves the transfer of electrons from metal atoms to non-metal atoms and the binding together of the ions produced by the attraction of opposite charges.
- *Metallic bonding* involves the binding together of metal ions by electrons instead of anions.
- *Covalent bonding* involves some other kind of interaction between atoms, with neither the electrical polarization that is involved in ionic bonding nor the mobility of electrons that is possible with metallic bonding.

Between these limiting types are bonds of intermediate character, corresponding to the intermediate types of binary compound:



Ionicity

To determine the degree of ionic character (*i*) of a bond, we need to measure the charges on the atoms. This is in general difficult. Indeed, according to the quantum theory, this is something that cannot be done precisely even in principle. However, we saw earlier that the charges on the atoms in a diatomic molecule (AB) can be approximately determined from its dipole moment (m). If there is transfer of charge from atom A to atom B to give $A^{x+}B^{x-}$, the value of x is approximately given by,

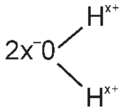
$$m = xer$$

where r is the internuclear distance. The value is approximate because there may be displacement of charge *within* the atoms contributing to m.

In the table below, values of x are given for hydrogen halide molecules, as calculated from m and r. These give the values of i shown in the last column.

r/Å	**m/10^{-30} C m**	**x**	**i**	
HF	0.917	6.07	0.41	41%
HCl	1.275	3.60	0.18	18%
HBr	1.41	2.74	0.12	12%
HI	1.600	1.47	0.06	6%

This method can be extended to other molecules. For example, to the same approximation, the charge distribution in the water molecule can be pictured as follows:



The dipole moment associated with each bond is then xer, where r is the O-H distance, and the dipole moment associated with the whole molecule is given by

$$m = 2xer \cos \tfrac{1}{2}q$$

Where q is the H-O-H angle. From the observed values of r (0.957 Å), q (104.5°), and m (6.17×10^{-30} C m), x is calculated to be 0.33. The charge distribution is thus $O^{0.66-}(H^{0.33+})_2$, and the ionic character of each bond 33 per cent.

The considerable polarity explains many of the unusual properties of water.

This method rests on the assumption that there is little displacement of charge within the atoms concerned. Quantum-mechanical calculations support this assumption for the above molecules, giving similar values of x:

$HF \sim 0.5$ $HCl \sim 0.2$ $HBr \sim 0.1$ $HI \sim 0.05$ $H_2O \sim 0.4$

However, the assumption does not hold for all molecules.

For bonds in solids, assessing the degree of ionic character is more difficult. That this can vary, however, is clear enough. For example, cadmium chloride ($CdCl_2$) has a less ionic kind of structure than sodium chloride. In the latter, as we have seen, cations are surrounded by anions and anions by cations. In $CdCl_2$, however, while the cations are surrounded by anions the anions only have cations on one side, to give a layer structure. Mercury dichloride ($HgCl_2$) has an even more covalent type of structure, in which there are discrete, linear $HgCl_2$ units, similar to the molecules in the vapour.

Metallicity

The degree of metallic character of a bond in a binary compound is best measured by the electrical conductivity of the compound. Strictly speaking, the property is not of an isolated bond (as in Na_2) but of bonds in concert.

Types of Formula

Empirical formulae: The empirical formula of a compound is the simplest possible formula indicating the relative numbers of different atoms in it. The formula is determined from the composition of the compound.

Molecular Formulae

The molecular formula of a compound indicates the total numbers of different atoms in a molecule of it.

For molecular compounds, the molecular formula is determined from the empirical formula and the molecular mass of the compound. For non-molecular compounds, it is set at the empirical formula multiplied by infinity.

In practice, a mixture of empirical and molecular formulae are used – NaCl alongside C_2H_6. Even hybrid formulae are used, *e.g.* Na_2O_2 (as this compound contains O_{22}- ions). Ideally, the different formulae should be distinguished, *e.g.* with brackets:

$$(NaCl)\ [C_2H_6]\quad (Na_2[O_2])$$

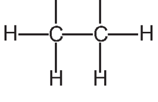
Structural formulae: The structural formula of a compound indicates the way in which the atoms are united in the molecule.

There are two main types:

1. *Constitutional formulae*,
2. *Descriptive formulae*.

1. *Constitutional formulae*:
   a. *Covalent compounds: Bond formulae* These are determined from the valencies of the atoms and such structural information as is required.

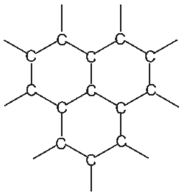
Example:



b. *Ionic compounds: Ion formulae* These are determined from the charges on the ions. Example: Na^+Cl^-

2. *Descriptive formulae*: These do not attempt to give any indication of the bonding.
   a. *Single stroke formulae*: These are formulae in which bonded atoms are connected up with a single stroke, with no indication of bond number or polarity. They are usually used for compounds in which the bonds have an intermediate bond number or polarity. An example is the following representation of one layer of graphite:

   Example:



   This kind of representation is also used in referring to bond distances in a compound, as in the statement "the C–C bond length in graphite is 1.42 Å". Care needs to be taken not to confuse formulae of this kind with bond formulae.

   b. *Descriptive formulae of crystals:* If the crystal structure of a non-molecular compound is known, the arrangement of atoms can be represented in the form $[\mathrm{AB}_{x/y}]_{¥}$, or more generally

   c. $[\mathrm{AB}_{x/y}\mathrm{B}¢_{x¢/y¢}\ldots]_{¥}$, where x is the number of nearest neighbours B to A, and y is the number of nearest neighbours A to B–$1/y$ being the share atom A has of each neighbouring atom B.

   Example: $[\mathrm{NaCl}_{6/6}]_{¥}$

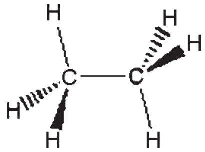
This indicates that in crystalline sodium chloride each sodium atom (ion) is surrounded by six chlorine atoms (ions), each of which is shared between six sodium atoms (ions), giving an empirical formula NaCl.

Crystallographers call the number of nearest neighbours the “coordination number”.

Geometrical Formulae

The geometrical formula of a compound represents the geometrical arrangement of the atoms in the molecule. It is determined from the structure of the compound. To represent the geometry properly really requires a three-dimensional model, but we have to try to do this in two dimensions.

Example:



3

Classification of Organometallic Elements

During the nineteenth century much time and effort on the part of chemists were devoted to seeking an arrangement for the known elements which would emphasize similarities in properties and thereby facilitate their systematic study. The culmination of this search was the discovery of the periodic law, which may be concisely stated as follows: The properties of the elements are periodic functions of their atomic weights. The formulation of this law has been attributed by many writers to Dmitri Mendeleev, but most certainly the same idea was also expressed in the writings of both Beguyer de Chancourtois and John Newlands.

The discovery of this law permitted an orderly classification of the elements and a prediction of certain missing elements. The use of a periodic system for the methodical arrangement of the elements has made it possible for students to assimilate a great deal of knowledge about all the elements by studying the general properties of groups of related elements.

Since all the missing elements have been discovered, the periodic system is no longer a guide in this respect. However, its use in teaching the properties of the various different atoms and their ions, in relation to their positions in such a classification, will always be important. For this reason it is worthwhile to trace the history and development of the methods of classification and to examine some of the more important present-day periodic systems for the elements.

HISTORICAL

The earliest attempts to classify elements date back to the discovery of metals and the recognition that such substances were elementary in character.

According to an early classification metals were divided into those which were noble and those which were base. The former included gold and silver and the latter copper, iron, lead, tin, and mercury.

However, it was not until after the establishment of the atomic theory of Dalton that chemists became concerned to seek a relation between the properties of the elements and their atomic weights.

In 1815 William Prout suggested that the atomic weights of all the elements were exact multiples of the atomic weight of hydrogen. Although this theory was disproved by subsequent accurate determinations of atomic weights, it did represent one of the first attempts to correlate the structure of matter with atomic weights.

Döbereiner's Triads

The first recognition of a significant relation between the atomic weights and the properties of the elements was noted by Johann Wolfgang Döbereiner.

Table. Döbereiner's Triads

Triad	**Atomic weights**	**Average of first and third element**	**Difference between consecutive elements**
Calcium	40.08		
Strontium	87.63	88.72	47.55
Barium	137.36		49.73
Lithium	6.940		
Sodium	22.997	23.020	16.057
Potassium	39.100		16.103
Sulfur	32.066		
Selenium	78.96	79.84	46.85
Tellurium	127.61		48.65
Chlorine	35.457		
Bromine	79.916	81.183	44.459
Iodine	126.91		46.994

In 1817 Döbereiner observed that several groups of three closely related elements, which he called *triads,* existed in which the central, or middle, element had an atomic weight almost the arithmetical mean of the other two elements. Moreover the differences between the atomic weights of the three related elements were approximately constant.

Among the groups of elements indicated as triads by Döbereiner were: calcium, strontium, and barium; lithium, sodium, and potassium; sulfur, selenium, and tellurium; and chlorine, bromine, and iodine.

Using present-day atomic weights, which are more accurate than those of the time of Döbereiner, the numerical relationships existing in the so-called triads are indicated in table.

The apparent regularity in atomic weight averages and differences, indicated by the elements of Döbereiner's triads, stimulated other investigators to seek additional and wider numerical relationships. However, the many attempts to classify the elements prior to 1858 failed, largely because atomic weights were not evaluated on a sound basis. In 1858 Statilslao Cannizzaro published his *"Sketch of a Course of Chemical Philosophy,"* in which he established the relations among equivalent weight, atomic weight, and molecular weight upon the basis of Avogadro's hypothesis. It was after the publication of this treatise that the real advances in the classification of the elements were made.

The Telluric Screw of De Chancourtois

The first truly periodic arrangement of the elements should be credited to Beguyer de Chancourtois. It was in 1863 that Chancourtois, an engineer and a geologist, published the first of a series of papers in which he emphasized the fact that when the elements are arranged in the order of their ascending atomic weights there is a recurrence of elements with similar properties. De Chancourtois plotted the values of the atomic weights on a helical curve described on a vertical cylinder.

The convex surface of the cylinder was divided into 16 equal parts, with lines drawn parallel to the axis. The number 16 was selected because it represented the atomic weight of oxygen. The curve was drawn by starting at the base and ascending the cylinder at an angle of 45°. In this graphic representation each intersection of the spiral curve with one of the vertical lines represented a unit of atomic weight, and each crossing of a given generatrix was a multiple of 16.

This curve, which De Chancourtois called the *telluric screw,* produced an arrangement whereby related elements fell upon the same vertical line. An "unfolded" portion of the telluric screw is given in figure. The similarity among vertically arranged elements caused De Chancourtois to suggest that "the properties of substances are properties of numbers."

Newlands' Law of Octaves

Without knowledge of De Chancourtois' work a somewhat similar system of classification for the elements was developed by John A. R. Newlands in England between 1863 and 1865. Upon arranging the known elements in the order of their atomic weights, he noticed that in many cases there was a repetition of chemical properties in each eighth element. Elaborating on this idea, he published a series of papers in the Chemical News during this period. In one of these papers he stated: "The difference between the number of the lowest member of a group and that immediately above it is 7; in other words, the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of an octave in music."

In 1866 Newlands delivered a paper entitled *"On the Law of Octaves"* before the Chemical Society of London.

Table: Newlands' table of the E'lements in Octaves

H	1	F	8	Cl	15	Co and Ni	22
Li	2	Na	9	K	16	Cu	23
G	3	Mg	10	Ca	17	Zn	24
Bo	4	Al	11	Cr	18	Y	25
C	5	Si	12	Ti	19	In	26
N	6	P	13	Mn	20	As	27
O	7	S	14	Fe	21	Se	28
Br	29	Pd	36	Te	32	Pt and Ir	50
Rb	30	Ag	37	Cs	44	Os	51
Sr	31	Cd	38	Ba and V	45	Hg	52

Ce and La	32	U	39	Ta	46	Tl	53
Zr	33	Sn	40	W	47	Pb	54
Di and Mo	34	Sb	41	Nb	48	Bi	55
Ro and Ru	35	I	42	Au	49	Th	56

In this paper he proclaimed his discovery of the numerical relationship among the elements to be a law which he termed the law of octaves. However, his comparison of the recurrence of chemical properties among the elements with the repetition of musical notes in an octave was unfortunate.

His paper was received with ridicule and derision by members of the Chemical Society, and they refused to permit his paper to be published in the journal of this scientific organization. It is said that one member, G. C. Foster by name, asked Newlands sarcastically “whether he had ever examined the elements according to the order of their initial letters.” As a lesson in the history of science it might be added that Professor Foster’s foolish question is the only reason that his name is still remembered.

Newlands’ arrangement of the elements as it appeared in the *Chemical News* is reproduced in table. This classification was obviously imperfect. It provided no spaces for elements still to be discovered. Several of the heavier elements were transposed to account for chemical similarities, and some elements, which had no apparent connection with one another, were placed in corresponding positions in different octaves. Despite the table’s many serious defects it did indicate more clearly than any other previous work the recurrence of similar properties among the elements. In 1887 the Royal Society awarded Newlands the Davy medal for his discovery of the periodicity existing among the elements.

Lothar Meyer

Credit for the development of the periodic system of the elements is usually given jointly to Lothar Meyer of Germany and Dimitri Mendeleev of Russia. Meyer seems to have arrived at his classification through an analysis of those relations among the elements which were based upon their physical properties, whereas Mendeleev appears to have been more influenced by the relations exhibited as chemical properties. The first edition of Lothar Meyer well-known textbook *"Moderne Theorien der Chemie"* was published in 1864. This book contained an incomplete periodic table in which the elements were arranged horizontally according to their atomic weights, and in such a manner that elements with similar properties and valence fell under one another. In 1870 Meyer published an expanded version of this table in an article entitled *"Nature of the Elements as Functions of Their Atomic Weights."* The latter table differed from the first in that the consecutive atomic weights were not arranged horizontally but vertically.

Meyer's periodic system was probably developed a little earlier than the one published by Mendeleev, and in many respects the two tables are almost identical. However, the views expressed by Meyer in his publications indicate that he had a much less clear picture as to the nature of the periodicity among the elements than did Mendeleev. He failed to recognize the importance of differentiating the elements into even and odd series, and his first table made no provision for a separate grouping for the transition elements.

Meyer is less remembered for his periodic table than for the curves he drew, which indicated that certain physical properties such as fusibility, volatility, malleability, and brittleness are periodic functions. This physical periodicity is shown in a modern version of one of his curves given in figure.

Dimitri Mendeleev

In March, 1869, Mendeleev transmitted to the Russian Chemical Society his first paper on the classification of the elements, which bore the title *"The Relation of the Properties to the Atomic Weights of the Elements."* This table was published in Russian, from which the English version is reproduced in table Similar elements within this classification were arranged horizontally, which seemed to be the customary arrangement in the earlier tables.

Mendeleev's first periodic system was practically identical with those proposed by New lands and Meyer, although it is fairly certain that all three systems were original and independent of each other. The superiority and difference in the Mendeleev table over all previous and contemporary tables were its predictions that certain atomic weights had been incorrectly determined and that new elements would be discovered to fit into vacant spaces occurring in the classification. These predictions are indicated in the table by question marks.

Mendeleev's first paper also contained certain conclusions he had reached concerning the periodicity of the elements, and these statements may be regarded as containing the fundamental principles of the *periodic law.* In view of the meagre, and somewhat inaccurate, chemical information available to Mendeleev in 1869 the extent of his knowledge as to the properties of the elements is no less than amazing.

For that reason, it seems worthwhile to include these conclusions, which have been translated as follows:

1. The elements, if arranged according to their atomic weights, exhibit an evident periodicity of properties.
2. Elements which are similar as regards their chemical properties have atomic weights which either are of nearly the same value (*e.g.*, platinum, iridium, osmium) or increase regularly (*e.g.*, potassium, rubidium, cesium).
3. The arrangement of the elements, or groups of elements, in the order of their atomic weights corresponds to their so-called “valences” as well as, to some extent, to their distinctive chemical properties — as is apparent, among other series, in the series of lithium, beryllium, barium, carbon, nitrogen, oxygen, and iron.
4. The elements which are most widely diffused have small atomic weights.
5. The magnitude of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.

Table. Mendeleev’s Predictions Versus Observed Properties For An Element

Property 1871	**Predicted for germanium**	**Observed for 1886**	**ekasilicon**
Atomic weight	72.0	72.3	
Specific gravity	5.5	5.469	
Atomic volume	13.0 cc	13.22 cc	

Colour	Dark gray	Grayish white
Specific gravity of oxide	4.7	4.703
Boiling point of chloride	100°C	86°C
Specific gravity of chloride	1.9	1.887
Boiling point of ethyl derivative	160°C	160°C
Specific gravity of ethyl derivative	0.96	1.0

6. We must expect the discovery of many yet unknown elements, for example, elements analogous to aluminum and silicon, whose atomic weights would be between 65 and 75.
7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements. Thus the atomic weight of tellurium must lie between 123 and 126 and cannot be 128.
8. Certain characteristic properties of the elements can be foretold from their atomic weights.

An improved version of Mendeleev's table appeared in 1871 in which the arrangement of the elements was altered to the now familiar form of vertical groups and horizontal series. In this table, reproduced in tableemphasis is laid on the relationship between atomic weight and chemical properties, including valency. Members of the main groups, for the first time, were divided into two subgroups, the division being based largely upon whether the members of the subclasses belonged to series with odd or with even number.

For instance, Group II is composed of two subgroups, the first of which contains beryllium, calcium, strontium, and barium in the series of even number and the second magnesium, zinc, cadmium, and mercury in the series of odd number. In his writings Mendeleev not only presented the best periodic table of his time, but he made so bold as to venture into the field of prophecy and not only predicted that certain new elements would be discovered to fit into vacant spaces in his system but even foretold with incredible accuracy the properties of some of the undiscovered elements. Three of these elements, which he designated as ekaboron, ekaaluminum, and ekasilicon, were discovered soon after and are now known as scandium, gallium, and germaium. Table presents a comparison of Mendeleev's predictions, with the actual determined properties for one of these elements.

Periodic Functions of the Elements

Many types of periodic tables have been developed for the purpose of classifying the elements into groups with somewhat similar properties. The development of these tables resulted in the formulation of the *periodic law,* which was originally stated as follows: *The properties of the elements are periodic functions of their atomic weights.* We now know that this is a somewhat inexact statement, inasmuch as atomic weight is a nuclear property and not directly related to the electronic structure of an atom. From the results of Moseley's investigations it is now recognized that the chemical and most of the physical properties depend on the number and arrangement of the extranuclear electrons, rather than on the atomic weight. However, there is a fairly close relation between mass number and atomic number and, during the latter part of the nineteenth century, the original statement of the periodic law was sufficiently accurate to serve as an invaluable aid in smoothing out certain imperfections in the classification of the known elements and as a prophetic guide in predicting the properties of those elements to be discovered.

The designation *periodic* in most of the classifications of the elements serves to indicate that certain characteristic properties reappear at definite intervals. Thus, when the elements are arranged in the order of their atomic numbers, there appears a periodicity, not only in their chemical properties, but also in their physical properties and in their electronic structures.

Two structural properties, the size and the ease with which electrons may be removed, largely determine the chemical behaviour of the atoms. Moreover the close relationship between these two fundamental properties prevents the discussion of the effect of one of these properties upon chemical behaviour without including the other.

Density

The densities of the elements in the solid state vary periodically with their atomic numbers, as is shown in table.

Table The Densities of the Elements of the Second and Third Periods

Na	Mg	Al	Si	P	S	Cl			
0.97	1.74	2.74	2.42	2.20	2.07	1.51			
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
0.87	1.54	2.5	4.5	5.96	6.92	7.42	7.8	8.9	8.9
Cu	Zn	Ga	Ge	As	Se	Br*			
8.93	7.15	5.91	5.47	5.73	4.8	2.97			

The periodicity varies in a regular manner from member to member within a period and reaches a maximum in the central members.

The change in density with atomic number for the lighter elements is indicated graphically in figure.

Melting Point

Another periodic property of the elements is indicated graphically in figure in which the melting points of the lighter elements are plotted against their atomic numbers.

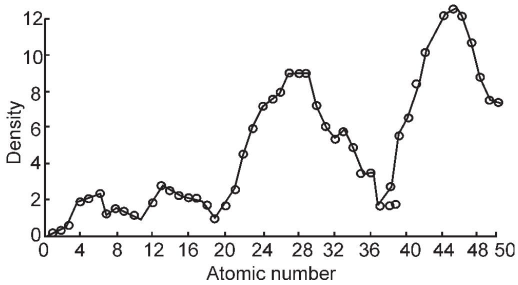


Fig. Periodicity of density for elements 1 to 50.

From this plot it may be observed that melting point occurs as a minimum (or near minimum in the case of neon) in the inert gases and as a maximum in Group IV (for the lighter elements) and Group VI (for the heavier elements). Also it may be noted that members of the same family of elements occupy similar positions on the ascending or descending portions of the curve.

Atomic Volume

It was stated that Lother Meyer apparently arrived at his classification of the elements through an analysis of certain relationships which were based upon physical properties. Moreover we are indebted to Meyer for many curves which represent graphically certain physical periodicities. Of these graphical representations the most famous is his atomic-volume curve, in which he sought to relate the mass of the atoms to their atomic volumes. This he showed by plotting atomic volume against atomic weight. The resulting curve takes the form of a series of well-defined loops, upon which similar elements are found occupying analogous positions.

It is of interest that the ascending slopes of these loops contain the electronegative elements and the descending slopes the electropositive ones, whereas the alkali metals occupy the maximum positions on the curve. A modern version of Lothar Meyer's curve is given in figure. In the more modern interpretation atomic number is substituted for atomic weight.

Atomic volume is defined as the volume occupied by 1 gram atom of an element; mathematically, it is the atomic weight divided by the density. According to this definition the atomic volume is the volume of 1 gram atom; by Avogadro's hypothesis, it is the volume occupied by 6.023 X 1023 atoms of an element. Therefore the atomic volumes of the elements should be the volumes occupied by the same number of atoms. However, the latter conclusion is somewhat erroneous because of certain variable factors, which, for the most part, are connected with the way atoms are packed in various elements.

Among the conditions that may affect the reliability of the atomic volume curve are the following:

1. Many elements exist in more than one allotropic form, and the densities of the allotropes differ considerably. For instance, the densities of diamond and graphite are 3.52 and 2.25, respectively, and the former falls very low on the atomic-volume curve, whereas the latter, with a greater atomic volume, falls into its normal position upon the graph. However, the selection of graphite as the standard is quite arbitrary. In many cases it is impossible to justify the choice of one allotrope over another.

2. No very reliable comparison can be made between the atomic volumes of elements existing in different physical states. Thus it is impossible to compare the atomic volume of an element in the gaseous state with one in the solid state. For those cases in which densities in the solid state are not reliably known, it is necessary to compromise and use densities in the liquid state. Even so, a comparison between the atomic volume of elements such as liquid oxygen and solid sodium is more or less meaningless because of the wide differences in the amount of free space between atoms or molecules.
3. Any reliable comparison between the atomic volumes of two or more elements must be made from values obtained at corresponding temperatures. This necessity arises as a result of the change in density with temperature. Theoretically the most favourable temperature for such a comparison is absolute zero, but for experimental reasons it is impossible to determine the densities of the elements at this temperature. Furthermore it is unfortunate that insufficient data are available at other temperatures which might be used for correlations, such as the freezing points and boiling points.
4. The various elements have several different types of crystal lattices, and the distance between atoms or molecules in a lattice depends upon the packing arrangement. Consequently, unless elements possess identical lattices, there will be an error in comparing their atomic volumes.

5. Molecules among the elements contain a varying number of atoms. For instance, the molecules of a metal are monoatomic, whereas the molecules of most common gases are diatomic. In the case of rhombic sulfur, which is a solid, there are apparently eight atoms in each molecule. However, in the latter case, there is no justification for the assumption that the atomic-volume of sulfur is equal to one-eighth of its molecular volume. Despite the many factors which indicate the unreliable basis upon which the atomic volume curve is constructed, it is nevertheless surprisingly regular in its representation of the periodicity of atomic volume as well as other properties in the elements.

Of interest is the position of the rare earths (lanthanons) on the atomicvolume curve. Beginning with lanthanum, these elements are unusual in that they are formed by a progressive increase in mass and charge upon the nuclei; yet the differentiating electrons go, not into the valence shell, but into the third from the outermost shell. Since the volume of an atom is determined by the distance from the nucleus of the outer quantum group, this form of atom building becomes significant. In the rare earths the increasing atomic number (charge on the nucleus) causes the valence electrons to become more and more firmly held, despite the screening effect of the added electrons.

Furthermore, as the attractive force of the nucleus for the valence electrons becomes progressively larger, each successive lanthanon contracts in size. This shrinkage is known as the *lanthanide contraction.* Hence the rare earths show diminishing atomic volumes with increasing atomic numbers, as evidenced in figure. Moreover the effect of the lanthanide contraction continues in those elements immediately succeeding the lanthanons. This accounts for the fact that the expected periodic increase in atomic volume for elements beginning with hafnium does not appear. The effect of the lanthanide contraction upon post-lanthanon elements also explains the existence of pairs of elements, located on the atomic-volume curve before and after the lanthanons, which have almost identical volumes and the same number of valency electrons.

As might be expected, these pairs of elements are remarkably similar in their chemical properties. Thus the lanthanide contraction can be held responsible for the close chemical similarity of the post-lanthanon elements hafnium, tantalum, and tungsten to the corresponding pre-lanthanon elements zirconium, niobium, and molybdenum.

Other Physical Properties

Almost any physical property of the elements, if plotted against the atomic numbers, will show a periodicity, and usually the curve so obtained closely parallels the atomic-volume curve. Among these periodic properties which have not already been discussed are hardness, malleability, compressibility, coefficient of expansion; thermal conductivity, and electrical resistance. Likewise, the physical properties of analogous compounds of the elements, such as melting point, boiling point, stability, colour, and solubility, are often periodic. However, of most im portance to the chemist is the fact that these periodic similarities occurring among the elements and their compounds have greatly simplified the task of organizing the extensive mass of knowledge relating to inorganic materials.

Not only do the physical properties of the elements and their compounds show periodic changes within the limits of each series, but there is also a gradation of properties within a given group or family. In other words, although the properties of the first element in a family reappear in other elements within the family, there is also a more or less regular change in these similar properties in passing from the lowest to the highest member in the group. For instance, the boiling points of the inert gases increase as the atomic number increases. Furthermore the gradation in properties frequently follows the course indicated in the atomic-volume curve, since this curve is fairly representative of the periodicity of most physical properties. This gradation within groups is illustrated more emphatically by the data presented in Table.

Table. Gradation of Physical Properties of Elements Within Groups

Boiling pionts of the inert gases, °C		**Specific heats of the alkali metals, cal/g**		**Densities of Group IV ele- ments, g/cc**		**Melting points of the halogen elements, °C**	
He	-268.9	Li	0.837	C	2.25	F	-223
Ne	-245.9	Na	0.297	Si	2.42	Cl	-101.6
A	-185.7	K	0.192	Ge	5.35	Br	-7.3
Kr	-152.9	Rb	0.079	Sn	7.28	I	113.6
Xe	-140.0	Cs	0.048	Sb	11.34	At	?
Rn	-71	Fr	?				

Atomic Radii

The term *radius* for an atom or ion is usually considered as the distance from the centre of the nucleus to the outer shell of the atomic particle. It is obviously impossible to isolate an individual atom or ion and determine its radius, especially since its size or radius is affected by the association with other particles.

According to J. A. Campbell atomic radii in compounds depend largely on:

1. The multiplicity of the bond, *i.e.*, whether the bond is single, double, or triple;
2. The oxidation number of the atoms, which indicates the number of electrons involved in the bonding;
3. The extent to which the bonding is ionic or covalent, *i.e.*, the percentage ratio of the bond types;
4. The coordination number of the atoms; and
5. The repulsive forces between atoms not directly bonded. As might be expected from these five variable factors, the atomic radius of an atom of a particular element may differ from one substance to another. Some of the variations produce relatively little effect on the apparent atomic radii, and fortunately all the factors are so interrelated that it is possible to use only the first two as criteria in the calculations of the relative sizes of atoms.

X-ray investigations of crystals have furnished data for assessing the radii of various elements, in both their ionic and their atomic form. In using these data it has been necessary to assume that an atom or ion behaves as an effective sphere which is barely in contact with another atom or ion in the crystal. Thus the distance between the centres of two adjacent atoms or ions is equal to the sum of their characteristic radii, or, in other words, the radius of the atom or ion is one-half of the single-bond distance between the nuclear centres of the two particles. X-ray measurements have been made on a number of crystals in which the binding is known to be covalent and the atomic distances obtained.

The values for a few atoms, such as carbon and sulfur, whose crystal structures are known, have served as starting points for the measurements and calculations of other atomic radii. For example, the single-bond distance between carbon to carbon has been measured in diamond as 1.54 A, and in normal and cyclic hydrocarbons, which contain series of CH_2 groups linked together, the distance has been found to vary between 1.52 and 1.55 A.

This constancy of bond length indicates that any appreciable deviation from 1.54 A for a carbon-to-carbon linkage must result from a different arrangement of electron sharing. Moreover, if it is assumed that the carbon atoms are spheres barely in contact with each other, the atomic radius of the carbon atom is one-half of the carbon-to-carbon bond, or 0.77 A. To continue our illustration, the single-bond distance between atoms in pure silicon has been measured as 2.34 A, and it may be assumed that the radius of the silicon atom is 1.17 A.

The arithmetical sum of the values for the radii of the carbon and silicon atoms is 1.94 A, indicating that the C-Si bond distance in silicon carbide is of this value. Conversely it is possible to assign to the elements values for covalent radii, the sums of which give the length of the covalent bonds between adjacent atoms in various substances. Thus, if the C-F single-bond distance is measured as 1.41 A, it may be deduced that the atomic radius of the fluorine atom is 0.64

A by subtracting the value of the atomic radius of carbon from the bond distance.

It must be admitted that the foregoing explanation of the methods used in assigning values for the atomic radii of the various elements is an oversimplification of the true procedures. As has been stated in an earlier paragraph, atomic radii are affected by a number of variables, and where possible these effects must be taken into consideration in calculating the size of atomic particles.

Frequently the term *single bond* is qualified by a descriptive word or phrase to indicate a variation which may change the bond length. This is exemplified by the *tetrahedral* bond, which describes a bond as being one of four covalent bonds attached to an atom in an sp^3 bonding. The tetrahedral radius may vary slightly from a *normal* radius, the latter being a term to denote the atomic radius for an element exhibiting its normal valence but in which the coordination number is less than 4.

Hence the atomic radius of an atom may have a number of slightly varying values depending upon whether the bonding is normal, tetrahedral, square, or octahedral. Other radii are designated as *metallic,* indicating the bonding of atoms occurring in metals.

This term is necessary for describing radii for those active metals which do not form covalent compounds. Fortunately metallic and covalent radii are so closely related that the terms and values may be used interchangeably. Furthermore it is generally agreed that the sizes of free atoms and those values obtained for the same atoms occurring in covalent compounds are apparently the same.

Table. Tetrahedral Atomic Radii

	Be	**B**	**C**	**N**	**O**	**F**
	1.07	0.89	0.77	0.70	0.66	0.64
	(1.11)					
Mg	Al	Si	P	S	Ci	
1.40	1.26	1.17	1.10	1.04	0.99	
(1.60)	(1.43)					
Cu	Zn	Ga	Ge	As	Se	Br
1.35	1.31	1.26	1.22	1.18	1.14	1.11
(1.28)	(1.33)	(1.22)	(1.21)	(1.17)	(1.14)	
Ag	Cd	In	Sn	Sb	Te	I
1.53	1.48	1.44	1.40	1.36	1.32	1.28
(1.44)	(1.62)	(1.41)	(1.37)	(1.33)		
Au	Hg	TI	Pb	Bi		
1.50	1.48	1.47	1.46	1.46		
(1.44)	(1.55)	(1.71)	(1.75)	(1.51)		

Therefore, from the subsequent discussion, it may be rightfully inferred that it is usually possible to use the terms *atomic radius, covalent radius, normal radius, and tetrahedral radius* synonymously, since such use rarely involves an appreciable error.

Values of the tetrahedral covalent radii for many of the common elements are given in Table. These values were derived from interatomic distances in crystals in which the atoms form four sp^3 tetrahedral bonds.

In those elements where the normal radii differ from the tetrahedral, the former are shown in parentheses. In the previous section it was suggested that almost any physical property of the elements is a periodic function of their atomic numbers. This implication may be extended to include the size of atoms of the elements.

Although the periodicity in relation to size among the elements is not so pronounced as the periodicities for some other physical properties, it is nevertheless present. A comparison of table with a modern version of Mendeleev's periodic table of the elements discloses two periodic regularities in connection with atomic size.

First of all, there is a progressive decrease in size along each series (or rovv) from left to right as the atomic number increases. For example, the first member of the second series listed in tableis magnesium with an atomic radius of 1.40 A, and the sizes of the atoms in this series decrease progressively through chlorine, which has an atomic radius of 0.99 A.

This general decrease in size is due to a corresponding increase in the atomic number for the elements concerned. Since atomic number denotes the magnitude of the positive charge on the nucleus, it is evident that, as this charge increases, the electrons are attracted more strongly to the nucleus, resulting in a decrease in atomic size.

This decrease in size has a pronounced influence on the metallic properties of the atoms. As a general rule, the larger the atom, the farther from the nucleus are the valence electrons, and, consequently, the more metallic is the atom. It might also be stated that, if two atoms have approximately the same size, the one with the larger atomic number (greater nuclear charge) is less metallic.

In other words, nonmetallic elements are those with small atoms and large nuclear charge. Returning to our original statement in regard to the progressive decrease in size within a given series with increasing atomic number, it should also be pointed out that this decrease is less pronounced as the atomic weight increases.

To illustrate this statement with values from table the difference in size between magnesium and chlorine in the second series is greater than that between cadmium and iodine in the fifth series. The second periodic regularity, in relation to atomic size, occurs within a given family (or column) of the elements. This periodicity is manifested as a tendency on the part of the elements in any one family to increase in size as the atomic number increases.

The number of electrons in the valence layer of the elements in a given family remain constant, but the total number of electron layers increase with atomic number, and this latter augmentation causes a progressive expansion in size as the atomic number becomes larger. However, the increment in size within a family is less pronounced as the atomic number becomes greater. These statements may be verified from values in table for example, there is a large increase in size in going from beryllium, with an atomic radius of 1.07 A, to magnesium, with a radius of 1.40, whereas there is no difference in the radii of cadmium and mercury in the lower part of the same family.

At this point it seems pertinent to restate the fact that the metallic properties of large atoms are more pronounced than those of small atoms. Again, we may use table to illustrate our point by calling attention to the difference in metallic properties between the relatively small atoms in the upper series and the larger atoms in the lower series. The latter are decidedly more metallic in nature.

Valency

Periodicity in valence among the elements was first recognized by Mendeleev. In fact he pointed out that the number of a group corresponds with the valency of the elements in it. The valence of an element, commonly referred to as *valence number,* or *oxidation number,* was originally defined as the combining capacity of an element and, in terms of the original definition, is equal to the number of atoms of hydrogen that an element will combine with or replace.

Table. Abegg's Conception of Valency of the Elements

	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Normal valences	+1 -7	+2 -6	+3 –5	+4 –4	–3 +5	–2 +6	–1 +7
Contravalences							

A more frequently used term than valence is that of oxidation number, which may be defined as the number of electrons lost or gained by an atom as the result of combining with other atoms to form an ionic compound, or the number of electrons shared by an atom with other atoms in the formation of a covalent compound.

Table. Periodicity of the Elements With Respect to Valence

	Groups						
	I	**I**	**III**	**IV**	**V**	**VI**	**VII**
Series 1	LiCl	$BeCl_2$	BCl_3	$ClC_{4;}$	NH_3	H_2O	HF
	Li_2O		B_2O	CH_4	$_2$		
	NaCl	BeO_3	AlCl $_3$	CO_2	O_5PH_3	H_2S	HCL Cl
	Na_2O	MgCl	Al_2O_3	$SiCl_{4;}$	P_2O_5	SO_3	$_2O_7$
		$_2$ MgO		SiH_4			
				SiO_2			

As early as 1904 Abegg stated that every element possessed a maximum valency of 8, this number being made up of positive and negative components, sometimes designated as normal valences and contravalences. The first series of the periodic table of the elements is used in tableto illustrate Abegg's idea of valency. From Abegg's conception of valency was developed the rule of eight and the octet theory, both of which refer to the erroneous idea, once widely believed, that all atoms enter into chemical combination to attain an outermost structure containing eight electrons. The periodicity in chemical nature of the first two series of the periodic table towards chlorine and hydrogen follows Abegg's conception of normal valency. Towards oxygen, however, the elements exhibit a valence ascending from I through 7. Periodicity of valency is illustrated by the different valences exhibited by elements in the various compounds listed in table. Using the compounds given in table as criteria, it can be stated that in progressing from left to right in the periodic classification, along any series of typical elements, the hydrogen valency increases from 1 to 4 and then decreases again to 1, whereas the oxygen valency increases from 1 to 7.

Ionic Radii

The radii of atoms are altered by the addition or loss of electrons. Since the charge on the nucleus remains the same during these alterations, the change in size resulting from an atom being converted into an ion can be attributed either directly or indirectly to the change in number of electrons.

Table. Decrease in Size of Atoms in Producing Various Cations

Element Atomic radius, A	Fe 1.26	Mn 1.29	Pb 1.75
Ion Ionic radius, A	Fe^{++} 0.75	Mn^{++} 0.80	Pb^{++} 1.21
Ion Ionic radius, A	Fe^{2+} 0.60	Mn^{4+} 0.52	Pb^{4+} 0.84

When an atom loses electrons, a positive ion is formed, which is appreciably smaller than the neutral atom. This smaller size is due to a concentration of the attractive force of the nucleus upon a smaller number of electrons, holding them more tightly, and causing a contraction in the volume occupied by the remaining particles. On the other hand, when a negative ion is formed, the opposite process takes place.

In this case the electrostatic force exerted by the nucleus is distributed over a greater number of electrons than were present in the neutral atom; consequently there is an expansion in volume to accommodate the increased number of negative charges. Hence it is possible to frame a general rule to the effect that the ionic radius of any cation is smaller than the radius of the neutral atom, whereas the radius of the anion is always greater.

Furthermore, if an element exhibits more than one positive valence, *i.e.*, if different numbers of electrons can be stripped from the atom to form more than one ion, then the radius decreases progressively with loss of electrons. The change in size of atoms with successive losses of electrons is illustrated in table.

If two oppositely charged ions are brought together, they are attracted to each other by electrostatic attraction as predicted by Coulomb’s law of electrostatic force; however, as they approach close to one another, the attractive force is counteracted by a repulsive force produced by the two electronic systems. At some point, or interionic distance, the two opposing forces will just balance each other, and this might be called the equilibrium distance. The electrostatic force exerted by an ion is not spatially directed; consequently the radius of any given ion is not constant but varies with the number of unlike charges around it.

By X-ray methods it is possible to determine distances between the centres of two oppositely charged ions, and since such ions are packed in crystals as if they were spheres of characteristic sizes, it is also possible to assign “ionic radii” to the ions.

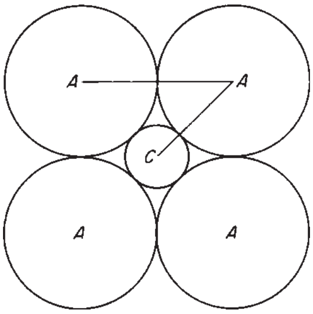


Fig. Method for the Calculation of Ionic Radii from Interatomic Distances in Crystals with the Sodium Chloride Structure.

The ionic radii so assigned are not actual radii, but instead represent the effective or apparent radii of the ions packed within a crystal. In other words, the apparent ionic radii of two oppositely charged ions are values so chosen that the sum of the two radii will be equal to the equilibrium distance between the two ions in contact with each other within the crystal. Ionic distances, therefore, are always fractions of interionic distances so chosen that they may be used to predict other interionic distances in other crystals.

The coordination number of an ion in the majority of ionic crystals is determined by the number of surrounding ions of opposite charge; *i.e.*, the sodium ion is surrounded by six chloride ions in the sodium chloride lattice. By means of X-ray measurements the distance between the sodium ion and the chloride ion can be measured, but it is impossible to decide what part of this distance should be assigned as the radius of the sodium ion and what part for the chloride ion.

Fortunately many positive ions are small as compared with the negative ions packed around them. Thus, in figure the small central cation may be represented as *C* with four large anions designated as A packed around it. If it is assumed that the anions are in contact with one another, then the radius of one anion is half the distance between two anions. Furthermore the radius of the cation may be deduced by subtracting the radius of the anion from the interionic distance between the oppositely charged ions. By this method of analysis many oxides show a minimum distance between oxygen centres of about 2.7 A. In 1923 J. A. Wasastjerna calculated the ionic radii of $O^=$ and F^- ions to be 1.32 and 1.33 A, respectively. Using these values as standards, V. M. Goldschmidt has worked out a fairly complete set of ionic radii by substitutional methods from measured interionic distances. Some of his values are given in table.

Pauling has derived a theoretical set of radii based on the general idea that the radii of ions with the same electronic configuration, such as Na^+ and F^-, are inversely proportional to the effective charges on the ions. The effective nuclear charge is assumed to determine the distribution of the outer electrons and, consequently, the size of the ion.

Table. Radii Angstroms, of Ions With Inert Gas Configurations

	$\mathbf{H}^{-}$	$\mathbf{Li}^{+}$	$\mathbf{Be}^{++}$	$\mathbf{B}^{3+}$	$\mathbf{C}^{4+}$	$\mathbf{N}^{5+}$	$\mathbf{0}^{6+}$	$\mathbf{F}^{7+}$
	1.54	0.60	0.31	0.20	0.15	0.11	0.09	0.07
$\mathbf{O}^{-}$	$\mathbf{F}^{-}$	$\mathbf{Na}^{+}$	$\mathbf{Mg}^{++}$	$\mathbf{A1}^{3+}$	$\mathbf{Si}^{4+}$	$\mathbf{P}^{5+}$	$\mathbf{S}^{6+}$	$\mathbf{C1}^{7+}$
1.40	1.36	0.95	0.65	0.50	0.41	0.34	0.29	0.26
$\mathbf{S}^{-}$	$\mathbf{Cl}^{-}$	$\mathbf{K}^{+}$	$\mathbf{Ca}^{++}$	$\mathbf{SC}^{3+}$	$\mathbf{Ti}^{4+}$	$\mathbf{V}^{5+}$	$\mathbf{Cr}^{6+}$	$\mathbf{Mn}^{7+}$
1.84	1.81	1.33	0.99	0.81	0.68	0.59	0.52	0.46
$\mathbf{Se}^{=}$	$\mathbf{Br}^{-}$	$\mathbf{Rb}^{+}$	$\mathbf{Sr}^{++}$	$\mathbf{Y}^{3+}$	$\mathbf{ZI}^{4+}$	$\mathbf{Nb}^{5+}$	$\mathbf{Mo}^{6+}$	$\mathbf{Te}^{7+}$
1.98	1.95	1.48	1.13	0.93	0.80	0.70	0.62	
$\mathbf{Te}^{=}$	$\mathbf{I}^{-}$	$\mathbf{Cs}^{+}$	$\mathbf{Ba}^{++}$	$\mathbf{La}^{3+}$	$\mathbf{Hf}^{4+}$	$\mathbf{Ta}^{5+}$	$\mathbf{W}^{6+}$	$\mathbf{Re}^{7+}$
2.21	2.16	1.69	1.35	1.15	0.79	0.71	0.65	0.50

It is defined as the actual nuclear charge *Ze* minus the screening eff effect *Se* of the remaining electrons in the ion. The screening factor is deduced experimentally from spectral data. Thus the screening factor *S* for ions with the neon structure is interpreted as a value of 4.52; therefore the effective nuclear charges of the Na^+ and F^- ions are their actual nuclear charges less 4.52, or 6.48*e* and 4.48*e*, respectively. If the interionic distance 2.31 A between these two ions is apportioned. in the inverse ratio of the effective nuclear charges, the values so obtained are 0.95 A for the radius of the sodium ion and 1.36 A for the fluorine ion. In a similar manner Pauling has evaluated the radii of the alkali and halogen ions. These values have been used to obtain the radii of other ions with the same number of electrons, but with different effective charges, by assuming that the electron atmosphere (volume of the ion) is inversely proportional to the effective charge. Some of the values calculated by Pauling are given in table.

From the foregoing explanations as to the methods for estimating ionic radii it is obvious that the magnitudes of individual radii are dependent upon the method used to apportion observed interionic distances between the ions involved in the measurements. This also accounts for the variance among these values as listed in the chemical literature; however, these differences are usually no more than a few hundredths of an angstrom, which represent no real significance. We are particularly interested in the change of ionic radii with atomic number, and values obtained by almost any method show a definite periodicity.

In table are listed values of ionic radii for some ions with inert gas configurations. It should be pointed out that those ions indicated as bearing high positive charges, on the right side of the table, do not exist as simpleions. These values simply represent magnitudes for the particular ions in coordination compounds. A comparison of this table with a modern version of Mendeleev's periodic classification of the elements indicates the same periodic regularities in relation to size, except they are more pronounced. Thus, in going from left to right along any series, there is a pronounced and progressive decrease in ionic radii. This decrease is to be expected since the attraction of the nucleus for remaining electrons increases with the number of electrons lost. The other periodicity, similar to that among atomic radii, is manifested as an increase in size in passing from the top to the bottom of the table among any one family. The increase may be attributed to the added electron layers in progressing from one element to another within any particular family. It should also be noted that in any series of isoclectronie ions, *i.e.*, ions with the same configuration of orbital electrons, the radii decrease rapidly with decreasing positive charge. This decrease may be illustrated in the fluoride, sodium, magnesium, and aluminum ions, where the over-all change in radius is from 1.36 A in the fluoride ion to 0.50 A in the aluminum ion.

The size of an ion is obviously a physical property, but this property is so closely interlinked with chemical behaviour that any discussion of one must include some mention of the other. An analysis of the various forces which may operate between atoms and ions will be presented in Chap, but it seems pertinent to mention at this point that the so-called "chemical linkages" are frequently dependent upon, or related to, size. Thus, as we shall learn later the extent of hydration of cations in aqueous solutions and the consequent acidities of such solutions are directly related to the radii of the ions involved. Furthermore, according to

Fajan's rules the tendency to form ionic or covalent linkages is related to the deformability of the electron shells of the reacting ions; and the extent of the deformation that may be produced is directly dependent upon the radii of the cation and anion which are in contact.

Ionization Potentials

Probably the most fundamental property of an atom that we are able to measure is its *ionization potential.* The term, more properly called the *first ionization potential,* is defined as the work necessary to remove the most loosely held electron from a normal atom, leaving it positively charged. The amount of energy required to perform this work may be evaluated either in kilocalories or in electron volts, the latter unit being the one most frequently used. A curve showing the periodic variations of the first ionization potentials with atomic numbers, for the different elements, is given in figure. The periodicity which is indicated in this curve is quite pronounced and corresponds identically with the periods of the Mendeleev table. Consequently the atomic numbers of those elements occurring at the peaks of the curve are the inert gases, which are also the elements at the end of each period in Mendeleev's classification.

The first ionization potential is measured for the outermost electron or electrons, whereas each row in the periodic table is made up of elements in the order in which their outermost shells are filled with electrons. In progressing along any row the ionization potentials tend to increase from left to right. This tendency may be attributed to a rising nuclear charge as the atomic number is increased, and is culminated at the end of each row. Furthermore, in the building up of any particular row, there is a slight decrease in the radii of the atoms involved. These two factors, the increase in nuclear charge and the decrease in radius, operate to bind each added electron more tightly to the nucleus. Still other factors are involved in holding the outer elctrons. to an atom, but, before continuing with them, our explanation up to the present may become clearer by examining tablein which certain related periodicities for the first row of the periodic table are tabulated.

Table. Some Related Periodicities in the First Row of the Periodic Table

	Elements							
	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Nuclear charge	3 1	4 2	5 3	6 4	7 5	8 6	9 7	10 8
Number of outermost electrons	1.52	1.07	0.89	0.77	0.70	0.66	0.64	1.12
Radius, A First ionization potential	5.39	9.32	8.30	11.26	14.54	13.64	17.42	21.56

If we retain the Bohr conception of the atom, it is possible to describe at least four factors which affect, the magnitude of ionization potentials.

These influences may be designated as:

1. The size of the nuclear charge;
2. The atomic radius;
3. The screening effect of inner electron shells; and
4. The ellipticity of the electron's orbit. All these various as ects are related to atomic structure and were described at some length in; therefore the present discussion will avoid repetition of this material as much as possible.

According to Coulomb's law the force operating between two electric charges is directly proportional to the product of their magnitudes and inversely proportional to the square of the distance between them. However, within the atom various disturbing influences prevent more than approximate adherence to the law of electrostatic attraction. In fact the law serves only as a rough prediction of the effect of the first two factors, listed in the preceding paragraph, upon the size of the ionization potentials. The first ionization potential increases somewhat irregularly in progressing along a row in the periodic table. The irregular increase must be attributed to disturbances resulting from the other factors just mentioned.

The periodicity among ionization potentials is produced by the sudden increase in average distance between the nucleus and the beginning of a new shell. At the same time there is a corresponding decrease in the effective nuclear charge due to the shielding effect of the electrons in the inner shells. If electrons are arranged in shells about the nucleus of all atom, it may be assumed that an inner shell acts as a screen, or shield, to decrease the attractive force of the positively charged nucleus for an electron or electrons beyond the shell.

Therefore each inner shell existing between the nucleus and the outermost shell produces a shielding effect which weakens the force holding the outer electrons to the atom. Furthermore it is believed that the screening effect is related to the magnitude of the electric charges involved and is an inverse function of the distance between the screening electrons and the nucleus.

If an electron is at a great distance from the nucleus and its path is beyond the orbits of the inner shell or shells, the effective charge of the nucleus is *(Z-N)e*, where *Z* is the atomic number, *N* is the number of electrons in the screening shell, and e is the charge of the electron.

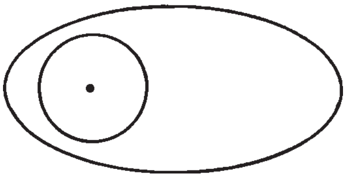


Fig. A Three-electron Atom with the Third Electron Occupying a Non-penetrating Orbit.

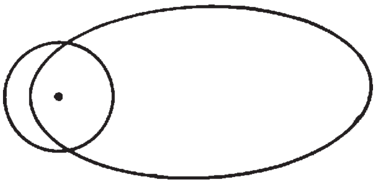


Fig. A Three-electron Atom with the Third Electron Occupying a Penetrating Orbit.

This being true, we can modify Eq., which denotes the total energy of the electron in the hydrogen atom, to fit the energy requirements of an electron of the foregoing description. The equation then becomes,

$$E^n = -\frac{2\pi^2 (Z-N)^2 e^4 m}{n^2 h^2}.$$

If it is assumed that the third electron in the lithium atom follows a path outside both the nucleus and the orbits of the two first-quantum electrons, the effective charge of the nucleus may be postulated as consisting of the nucleus proper plus the two inner electrons. Considered from this structural viewpoint, the outer electron moves about a nucleus which has a single positive charge and which is equivalent to that of the hydrogen nucleus. A diagrammatic representation of such a nonpenetrating orbit is given in figure.

Should the third electron in the lithium atom follow a path which penetrates the orbits of the two first-quantum electrons, the effective charge of the nucleus will no longer be +1. As the electron penetrates the orbitals of the inner electrons, the latter's screening effect is decreased and the attractive force of the nucleus becomes greater than+1. On the other hand, the effective charge of the nucleus will never be+3, which is the actual value of the nuclear charge of the lithium atom, because the outer electron will move part of the time outside the orbits of the two inner electrons. The greater the amount of penetration, the stronger is the attractive force exerted by the nucleus; consequently the greater will be the ionization potential. The effective nuclear charge will be a value less than +3 but greater than + 1. A schematic representation of a penetrating orbit is given in figure.

Electronegativity

The attraction of a neutral atom in a stable molecule for electrons is a property that Pauling designates as electronegativity. From heats of formation of the most common elements in their compounds Pauling has set up an arbitrary electronegativity scale for the atoms of the elements. This scale varies from 0.7 for cesium to 4.0 for fluorine. From the relative positions of the elements on this scale a prediction can be made as to the ease with which the atoms of the elements lose their valence electrons.

Table. Electronegativities of the Elements

Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	CI

0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca	Se	Ge	As	Se	Br
0.8	1.0	1.3	1.8	2.0	2.4	2.8
Rb	Sr	Y	Sn	Sb	Te	1
0.8	1.0	1.3	1.7	1.8	2.1	2.5
Cs	Ba					
0.7	0.9					

Electronegativity is a property of the elements which is a periodic function of their atomic numbers. Table is an arrangement of some of the common elements in the order in which they fall in the Mendeleev periodic classification and includes Pauling's values for the electronegativities of these particular elements. It can be seen that the periodicity of electronegativity follows the pattern of most of the other periodic properties. Upon progressing from left to right along any row of these elements the magnitude of the electronegativity increases, whereas, in passing from the top downward in any group, there is a progressive decrease in the values for electronegativity.

Other Chemical Properties

As we have said before, there are two structural properties, the size of atoms (or ions) and the ease of removal of electrons, which largely determine the chemical properties of the elements. The periodic nature of these fundamental properties has been described in detail in the preceding sections. However, we shall attempt to summarize some of the more important relationships indicated by the periodic table in connection with chemical properties.First of all, as we progress across the periodic table from left to right, we find that the metallic character of the elements in any period decreases, whereas the nonmetallic properties increase. Thus, as the radii of the atoms of the elements decrease, in passing along a given period, they tend to hold their outer electrons more tightly. As a general rule, large atoms are found in elements that are metals, and small atoms are found in elements that are nonmetals. Consequently the best reducing elements are the metals which lose electrons easily to f orm positive ions, and the latter form basic hydroxides because of their relatively small attraction for electrons.

In general the electronegative character of the elements increases along any series. Hence the metals on the left of the periodic table form basic oxides, and conversely the nonmetals, on the right, form acidicoxides. This accounts for the fact that the positive ions may exist in water solution with hydroxide ions and the negative ions may be found in water solution with a high concentration of hydronium ions. A less accurate description would classify the metals as base-forming elements and the nonmetals as acid-forming elements.

It is also true that, when an element exhibits two or more valences, the ion of the element in its lowest valence is less electronegative than in a higher valence. For example, the stannous ion is more basic in its properties than the stannic ion, as indicated by the fact that stannic sulfide will dissolve in potassium hydroxide solution, whereas stannous sulfide will not.The metallic character of the elements increases in passing from the top to the bottom of the periodic table. Probably the best illustration of this tendency is found in Group V, in which nitrogen, a nonmetallic element, occurs at the top and bismuth, a metal, is found at the bottom. In other words, the more acid-forming elements are found at the top of the table, and the stronger base-forming elements occur at the bottom of the table. Again in Group V, the hydroxide of phosphorus is definitely an acid, whereas the hydroxide of bismuth must be classified as a base.The size of an atom and the ease with which it loses electrons may also determine the type of ‘bond that is formed when the element enters into chemical reaction.

Types of Element

The classification of elements into metals and nonmetals, with the intermediate category of semimetal, is a fundamental one in inorganic chemistry.

Metallic elements are characterized by the following properties under ordinary conditions:

- High lustre, high opacity over the visible spectrum;
- High electrical and thermal conductivity.

Nonmetals are characterized by:

- No lustre, high transparency over the visible spectrum;
- Low electrical and thermal conductivity.

Semimetals are characterized by:

- High opacity over the visible spectrum, little or no lustre;
- Intermediate electrical conductivity.

“High opacity over the visible spectrum” is a way of saying that the substance absorbs light strongly over the whole range of the visible spectrum, or at least over the whole range beyond the red. If it is not lustrous, therefore, the substance appears black to the eye, or very dark brown.

“High transparency over the visible spectrum” is a way of saying that the substance absorbs light weakly over the greater part of the visible spectrum, if not over all of it. If no light is absorbed, the substance appears colourless or white. (Colourless substances look white when finely divided because light is scattered from the many crystal faces. Similarly, coloured substances become paler on grinding.) If some light is absorbed, the substance appears coloured, the colour being the complementary one to the colour of the light that is absorbed.

The complementary colours to the main spectral colours (red, orange, yellow, green, blue, and violet) are obtained by writing the colours in order round a circle. Those appearing opposite each other are complementary.

Electrical Conductivity

$$\kappa = 1/\rho$$

The resistivity is defined by the equation:

$$R = \rho(l/A)$$

where R is the resistance of a uniform conductor, l is its length, and A is its cross sectional area. The SI unit of ρ is ohm meter (Ω m) and its value is equal to the resistance that a meter cube of the substance offers to the passage of electricity from one parallel face to another.

The SI unit of k is thus Ω^{-1} m^{-1}*.On the basis of their ability to transmit an electric current, materials can be divided into four main classes*:

- *Ordinary conductors*, characterized by having conductivities greater than about 10^5 $\Omega^{-1}m^{-1}$ at room temperature, which fall with increase of temperature.
- *Semiconductors*, characterized by having conductivities between about 10^{-7} and 10^5 $\Omega^{-1}m^{-1}$ at room temperature, which rise with increase of temperature, and are highly sensitive to traces of impurity.

- *Electrolytic conductors*, characterized by the chemical decomposition that takes place at the points at which a direct current enters and leaves the material. (The words “electrolysis”, “electrolyte”, “electrolytic”, come from the Greek *lyo*, to loosen.)
- *Insulators*, characterized by conductivities of less than about $10^{-7}\ \Omega^{-1}m^{-1}$ at room temperature, rising with increase in temperature.

In these terms, metals are conductors, semimetals are semiconductors, and nonmetal s are insulators.

It is necessary to specify “under ordinary conditions” because, under extreme conditions, the character of a substance can change profoundly.

Thus:

- Gases at very low pressures become good conductors of electricity, as in a discharge tube at low pressure;
- Metals at high temperatures vaporize, and lose their metallic properties completely (*e.g.* mercury boils at 357°C to give a colourless vapour, which is a poor conductor of electricity at ordinary pressures);
- Semimetals and nonmetals at very high pressures become metallic in character (*e.g.* at 150 atmospheres iodine becomes a very good conductor of electricity).

A further characteristic of metals that is usually given is that, in the solid state, they are malleable (easily hammered into sheets) and ductile (easily drawn into wires). By contrast, nonmetals in the solid state are brittle and easily powdered. In practice, however, while the majority of elements that are metallic according to the above criteria are indeed malleable and ductile, there are a few that do not have this property, even when ultra-pure. (Slight traces of impurity can produce brittleness in metals. Thus, ordinary commercial tungsten is so brittle that it can only be worked with difficulty, whereas the ultra-pure metal can be cut with a hacksaw, turned, drawn, or extruded.) Since the exceptional elements include some whose metallicity has never bee questioned - *e.g.* manganese, cobalt, and zinc - it seems better *not* to make malleability and ductility a characteristic of metals, but rather a property possessed by most of them.

Zinc is a particularly interesting case, because it is malleable at some temperatures and brittle at others. Thus, it is brittle at room temperature, but softens above 100°C. At 205°C, however, it becomes brittle again, and can then be powdered in a mortar.

Assignment of Elements to Classes

The clear-cut nonmetals are: hydrogen, nitrogen, oxygen, fluorine, sulfur, chlorine, bromine, and the inert or noble gases (helium, neon, argon, krypton, xenon).

The clear-cut semimetals are: boron, silicon, germanium, tellurium. The clear-cut metals constitute all of the remaining elements, with the exception of the problem cases discussed below.

Carbon

Under ordinary conditions, carbon exists in two common forms, graphite and diamond, of which graphite is the more stable. Diamond is definitely nonmetallic, but graphite has properties on the borderline between a semimetal and a metal. Thus it is a shiny, black solid, readily separated into flakes, with a metallic conductivity in the plane of the flakes, and a semimetallic conductivity perpendicular to the plane. Other forms include black, petrol-soluble “fullerenes”. When pure, these are insulators.

Phosphorus

This exists in a number of different forms: one white, several red, and several black. The white form can be made by condensing the vapour. It melts at 44°C and boils at 280°C. A red form is obtained when the white form is heated to just below its boiling point. A black form can be obtained by heating the white form under a very high pressure, or in the presence of a mercury catalyst. The yellow and red forms are insulators; the black forms are semiconductors. The most stable form under ordinary conditions is black; all forms, however, melt to a colourless liquid.

Arsenic

This can be obtained in several forms, ranging from a yellow one, which is similar to white phosphorus, to a grey one, which is a metal. The metallic form is the most stable under ordinary conditions; the yellow one is very unstable.

Antimony

This can also be obtained in several forms, ranging from yellow to metallic. The metallic form is again the most stable, with the yellow very unstable.

Selenium

This exists in three red forms, one black form, and one grey. The red and black forms are insulators; the grey is a semiconductor. The latter is the most stable.

Iodine

Iodine crystallizes in blackish-grey opaque scales, with an almost metallic lustre. In the plane of the scales it has the conductivity of a semiconductor; perpendicular to the plane it is an insulator.

Volatilities of Metals and Nonmetals

The volatility of a substance is the ease with which the substance is vaporized. It is conveniently measured by the temperature at which the substance boils or sublimes at atmospheric pressure.

A broad generalisation concerning the relative volatilities of metals and nonmetals is the following: Metals are generally involatile, *i.e.* they have boiling points in excess of 500 °C. Only mercury has a boiling point below 500 °C, this being at 357°C. Most metals have their boiling point somewhere between 1000°C and 4000°C. The highest value is for tungsten, at 5660°C.

Nonmetals vary from being very volatile to very involatile. All the definite nonmetals listed above have boiling points below 500 °C, and most are gases at room temperature. The least volatile is sulfur, boiling at 445°C. If, however, we include carbon among the nonmetals, as surely we should, this lies at the opposite extreme of volatility, boiling at 4830 °C.

Chemical Properties of Metals and Nonmetals

There are many chemical differences between metals and nonmetals.

Some elements have very similar properties and are grouped into families.

These include:

- *Alkali metals:* Li, Na, K, Rb, Cs
- *Alkaline earth metals:* (Mg,) Ca, Sr, Ba
- *Halogens:* F, Cl, Br, I
- *Inert or noble gases:* He, Ne, Ar, Kr, Xe

”Alkali” is an Arabic word meaning “the ash” (ash from plants contains sodium and potassium carbonates).

“Halogen” means “producer-of (-gen) salt (Greek *hals*)”.

Some chemists class magnesium as an alkaline earth metal as it is quite similar to calcium, often occurring with it in nature.

The gases He, Ne, Ar, Kr, and Xe were called “inert” when they were thought to be completely inactive. Their name was changed to “noble” after the xenon fluorides were discovered in 1962. This was because metals having a low activity (but nevertheless some activity) like gold and platinum are sometimes called “noble” as they are used for noble purposes. The change was inept. “Inert” need not imply complete inactivity, and “noble” is hardly apt (commoners breathe in these gases no less than nobles!).

The Isotopic Constitution of the Elements

Over 1,000 isotopes, natural and artificial, have been identified of the known elements. Of this number approximately 320 occur in nature, of which at least 40 are radioactive. For the present we shall confine our discussion to the stable, naturally occurring isotopes of the various elements. Later, in Chap, we shall examine the radioactive isotopes in some detail. However, we should add that, of the more than 280 so-called “stable” isotopes, 3 are radioactive and 6 or 7 exhibit feeble radioactivity; the first 3 are Th^{232}

U^{235}, and U^{238}; and the latter 6 or 7 are K^{40}, Rb^{87}, In^{115}, Sm^{152}, Lu^{176}, Re^{187}, and possibly V^{50}. In table are listed the mass numbers of the naturally occurring stable isotopes of the elements.An analysis of the figures in table reveals certain facts and relationships relevant to the structure and stability of the atomic nucleus. Some of these items have been mentioned before, but they will be restated in the form of rules, for the purpose of emphasis:

1. *The masses of all stable nuclei are, except for H_1 and H_3, never less than twice their atomic numbers.* Among the lighter elements, up to calcium, the mass number is usually twice the atomic number, indicating that the nucleus is composed of equal numbers of protons and neutrons. Beyond calcium the ratio of neutrons to protons increases, but for naturally occurring isotopes this ratio rarely exceeds 1.2.

Table: Mass Numbers of The Stable Isotopes of the Elements

Element	Atomic number	Mass numbers, in order of abundance
H	1	1,2
He	2	4, 3
Li	3	7, 6
Be	4	9
B	5	11, 10
C	6	12, 13
N	7	14, 15
O	8	16, 18, 17
F	9	19
Ne	10	20, 22, 21
Na	11	23
Mg	12	24, 25, 26
Al	13	27
Si	14	28, 29, 30
P	15	31
S	16	32, 34, 33
Cl	17	35, 37
A	18	40, 36, 38

K	19	39, 41, 40
Ca	20	40, 44, 42, 43, 48, 46
Sc	21	45
Ti	22	48, 46, 47, 50, 49
V	23	51, 50
Cr	24	52, 53, 50, 54
Mn	25	55
Fe	26	56, 54, 57, 58
Co	27	59
Ni	28	58, 60, 62, 61, 64
Cu	29	63, 65
Zn	30	64, 66, 68, 67, 70
Ga	31	69, 71
Ge	32	74, 72, 70, 73, 76
As	33	75
Se	34	80, 78, 76, 82, 77, 74
Br	35	79, 81
Kr	36	84, 86, 82, 83, 80, 78
Rb	37	85, 87
Sr	38	88, 86, 87, 84
Y	39	89
Zr	40	90, 92, 94, 91, 96
Nb	41	93
Mo	42	98, 96, 95, 92, 97, 94, 100
Te	43	None
Ru	44	102, 104, 101, 88, 100, 96, 98
Rh	45	103
Pd	46	106, 108, 105, 110, 104, 102
Ag	47	107, 109

Table. Mass Numbers of the Stable Isotopes of the Elements (Continued)

Element	**Atomic number**	**Mass numbers, in Order of Abundance**
Cd	48	114, 112, 110, 111, 113, 116, 106, 108
In	49	115, 113
Sn	50	120, 118, 116, 119, 117, 124, 122, 112, 114, 115
Sb	51	121, 123
Te	52	130, 128, 126, 125, 124, 122, 123, 120
I	53	127
Xe	54	129, 132, 131, 134, 136, 130, 128, 126, 124
Cs	55	133
Ba	56	138, 137, 136, 135, 134, 130, 132

La	57	139
Ce	58	140, 142, 138, 136
Pr	59	141
Nd	60	142, 144, 146, 143, 145, 148, 150
Pm	61	None
Sm	62	152, 154, 147, 149, 148, 150, 144
Eu	63	151, 153
Gd	64	158, 160, 156, 157, 155, 154, 152
Tb	65	159
Dy	66	164, 162, 163, 161, 160, 158, 156
Ho	67	165
Er	68	166, 168, 167, 170, 164, 162
Tm	69	169
Yb	70	174, 172, 173, 171, 176, 170, 168
Lu	71	175, 176
Hf	72	180, 178, 177, 179, 176, 174
Ta	73	181
W	74	184, 186, 182, 183, 180
Re	75	187, 185
Os	76	192, 190, 189, 186, 187, 184
Ir	77	193, 191
Pt	78	195, 194, 196, 198, 192
Au	79	197
Hg	80	202, 200, 199, 201, 198, 204, 196
Tl	81	205, 203
Pb	82	208, 206, 207, 204
Bi	83	209
Th	90	232
U	92	238, 235

Elements with even atomic numbers (protons) are more abundant, more stable, and richer in isotopes than those of odd atomic numbers. Not only does this rule hold true for the number of nuclei, but also for their percentage of abundance in nature. Of additional interest in connection with this rule is the fact that those elements whose existence in nature has been questioned, namely, technetium, promethium, astatine, and francium, all have odd atomic numbers.

Elements with even atomic numbers may have numerous stable isotopes but only one or two with odd mass numbers.

If two isotopes with odd mass numbers do exist, they will differ by two mass units. The one exception to this rule is the occurrence of three stable tin isotopes with odd mass numbers, $_{50}Sn^{115}$, $_{50}Sn^{117}$, and $_{60}Sn^{119}$.

Nuclei composed of even numbers of neutrons are more abundant, more stable, and richer in isotopes than those with odd numbers of neutrons. This rule is a corollary of rule 2, and it might be advantageous to consider the two rules collectively. Thus, it is possible to classify nuclei according to whether they contain even or odd numbers of protons and neutrons. Under such a classification there are four possible types of nuclei. These four types, their distribution, and abundance in nature are given in table.

Table. Types of Naturally Occurring Stable Isotopes and Their Abundance

Constitution Protons	**of nucleus stable isotopes**	**Number of**	**Abundance,%, in earth's crust**	**Neutrons**
Even Even	Even Odd	162 52 56 4	87.4 10.8 1.8 0.0007	
Odd Odd	Even Odd			

Stable nuclei with even mass numbers have an even number of protons and an even number of neutrons. As indicated in table0 there are four exceptions to this rule, $_{1}H^{2}$, $_{3}Li^{6}$, $_{5}B^{10}$, and $_{7}N^{14}$, all of which are very light nuclei where large fluctuations in binding energy may be expected. The isotopes $_{23}V^{50}$ might also be added to these exceptions, but this isotope is probably radioactive.

Elements with odd atomic numbers (protons) have only one or two stable isotopes. The mass numbers of these elements are always odd, and if there are two isotopes, their mass numbers differ by two units. The only exceptions to this last statement are the five odd-odd nuclei indicated under rule 4. In these five exceptions the mass numbers of the isotopes differ by one unit.

An element with an odd mass number is represented by only a single stable nucleus with an odd atomic number. No exceptions to this rule are known. An example is fluorine, with a mass number of 19 and an atomic number of 9.

The number of isotopes of an element and their range of mass numbers apparently have definite limits. Since the atomic number (number of protons) determines the chemical properties of an element and these properties are not altered by the addition of neutrons, there is no arithmetical reason why neutrons may not occur in indefinite numbers within the nucleus, to produce any number of isotopes. However, the largest number of isotopes for an element, known for a certainty, is 10 in the case of tin. The exact limit for neutron addition is not known, but the theory of a shell structure for the nucleus postulates that definite numbers of protons and neutrons are required to fill certain energy levels within the nucleus.

Isotopes, Isobars, Isotones, and Isomers

Originally the meaning of the term isotope was unambiguous, but with the discovery of the existence of other nuclear species it is sometimes given a wider and looser meaning than was originally intended. The shifting of the meaning from an exact term with a specific definition to a more generalized expression is unfortunate. For this reason we shall redefine the word isotope and list with explanations those other atomic species which are sometimes improperly described as isotopes in an unrestricted interpretation of the term.

Isotopes are atoms of the same element whose nuclei contain the same number of protons but different numbers of neutrons. Also by definition we know that the atomic number of an element is the number of protons in the nucleus; therefore isotopes of the same element have the same atomic number. Furthermore, we know that the chemical properties of an element are dependent upon its atomic number, and not upon any other variable factor. Consequently isotopes of the same element may vary in mass number, but they have the same atomic charges and the same chemical properties.

Isobars are atomic species having the same mass number but different atomic numbers (protons). A few examples are $_{32}Ge^{76}$ and $_{34}Se^{76}$; $_{52}Te^{130}$, $_{54}Xe^{130}$, and $_{56}Ba^{130}$; $_{81}Tl^{210}$, $_{82}Pb^{210}$, $_{83}Bi^{210}$, and $_{84}Po^{210}$. As indicated by these symbols, isobars are atoms of different elements and therefore have different physical and chemical properties. The atoms simply happen to have the same mass.

Isotones are atoms having the same number of neutrons but different mass numbers. In other words, the variable factor in the nuclei of these atoms is the number of protons (atomic number); consequently such atoms have different chemical and physical properties. For example, $_{14}Si^{30}$, $_{15}P^{31}$, and $_{16}S^{32}$ are isotones, since each of these atoms contains 16 neutrons in its nucleus.

Isomers are atomic species with the same mass number and the same atomic number but with different radioactive properties. Atoms of this description are believed to have nuclei which are composed ultimately of the same number of protons and the same number of neutrons but which differ in their energy levels. The different energy states result from a variable arrangement of protons and neutrons in the shell structure of the nucleus, thereby producing dissimilar radioactive properties. A pair of nuclear isomers occurring in nature is uranium X_2 and uranium Z, which are found in the uranium-radium decay series (Chap. 8). These isomers are identical in that both have an atomic number of 91, both have a mass number of 234, and both are atoms of protactinium.

4

Nature of Coordinating Groups

According to Sidgwick any coordinating group must attach itself by sharing with the central ion a “lone” pair of electrons. Furthermore, he states that all such groups which are capable of entering into a complex in this way can be shown to possess the necessary lone pair.

However, there is a considerable difference in the ease with which coordinating groups attach themselves to the central ion, and, consequently, there is also a difference in the stabilities of the coordination compounds which are produced.

Since only the more electronegative elements can act as electron donors, coordinate bonds are largely limited to atoms of carbon, nitrogen, oxygen, sulfur, and the halogens. Donor groups containing these atoms, and the resulting complexes. However, many complexes, particularly those formed with the fluoride ion, are largely ionic in nature rather than covalent.

Owing to the complex nature of coordination compounds it is difficult to assign with any exactness the particular affinity of different coordinating groups for the central ion. In tablethe related donor groups are listed in the order of their relative stabilities. It must be emphasized that this order is decidedly approximate, and there are probably as many exceptions as there are examples which conform to the order of the stability sequence.

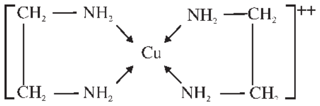
Cyclization

A complex containing a ring structure results whenever a single group or molecule occupies two or more coordination positions on the same atom. A cyclic compound of this type is termed a *chelate* from the Greek word *chele,* meaning *claw.* The name is applicable to these ring systems because of the clawlike character of the associating molecule.

Table. Some Electron Donors which May Enter into Complex Formation

Donor atom	Donor groups in approxi- mate stability sequence	Complexes formed	Examples
C	CN^-, CO	Cyanide Carbonyl	$Cd(CN)_4^=$ $Ni(CO)_4$
N	NH_3, NO_2 NO_2^-	Ammine Nitroso	$Cu(NH_3)_4^{++}$ $Co(NH_3)_5$
		Nitrito	NO^{++} $Co(NO^2)^{63-}$
O	H_2O, OH^-,	Aquo Hydroxide	$Cr(H_2O)_6^{3+}$ $C_2O_4^=$, $CO_3^=$ $Zn(OH)_4^=$
		Oxalato Carhonato	$Fe(C_2O_{4)2}^{3-}$ $Co(CO_3)_2^=$
S	CNS, $S_2O_3^=$, $S^=$ $Ag(S_2O_3)_2^{3-}$	Thiocyanate Thiosulfate Sulfide	$Hg(CNS)_4^=$ $SnS_3^=$
	Halogen $CuCl_4$	F^-, Cl^-, Br^-, I^-	Fluoride Chloride FeF_6^{3-} Bromide Iodide$^=$ $PbBr_4^=$ $HgI_4^=$

Groups which are able to occupy two or more coordination positions are usually organic molecules. A typical molecule of this description is ethylenediamine, NH_2 CH_2 CH_2 NH_2, which contains a donor nitrogen atom at both ends of the molecule and, consequently, may attach itself in two coordination positions to a central metal ion. In forming the copper chelate two molecules of ethylenediamine attach themselves to the cupric ion in a caliperlike manner to form two live-membered rings. The structure of this cyclic complex may be indicated as



In general a chelated complex is more stable than a complex which is similar but nonehelated. This generality may be verified by examining table in which are listed the stability constants of zinc, cupric, and nickel chelates of ethylenediamine as compared with the corresponding stabilities of the simple ammines. An additional proof is the fact that ethylamine, C_2 H_5 NH_2, which possesses only one coordinating group, forms complexes with many of the transitional metals, and these complexes are much less stable than those formed by ethylenediamine with its two coordinating groups.

Table. Stability Constants of Three Metal Ammines

Complex	**Consecutive complexity constants**	**Log dissociation constant**
$\mathrm{Zn(NH_{3})_{4}^{++}}$	$k_1 k_2 k_3 k_4$	9.46
$\mathrm{Zn(Cn)_{2}^{++\dagger}}$	$k_1 k_2$	11.07
$\mathrm{Cu(NH_{3})_{4}^{++}}$	$k_1 k_2 k_3 k_4$	12.67
$\mathrm{Cu(en)_{2}^{++}}$	$k_1 k_2$	20.03
$\mathrm{Ni(NH_{3})_{6}^{++}}$	$k_1 k_2 k_3 k_4 k_5 k_6$	6.74
$\mathrm{Ni(en)_{3}^{++}}$	$k_1 k_2 k_3$	18.61

Types of Binary Compound

Corresponding to the two limiting types of element, metal and nonmetal, there are three limiting types of binary compound:

- *Metallic*: These are formed principally by the combination of a metal with a metal, and have the characteristics of a metal.
- *Nonmetallic*: These are formed principally by the combination of a nonmetal with a nonmetal, and have the characteristics of a nonmetal.
- *Salt-like*: These are formed principally by the combination of a metal with a nonmetal, and constitute a new class of material.

Metallic Compounds

An example is the compound Mg_2Sn. This is made by fusing together a mixture of magnesium and tin of the appropriate composition, and cooling the resulting melt. The product is homogeneous, as can be seen by cutting and polishing it, and examining the polished surface under a microscope.

If more magnesium or tin is used than required by the formula Mg_2Sn, the product ceases to be homogeneous - crystals of Mg_2Sn can be seen embedded in a matrix of smaller crystals containing the excess of magnesium or tin. The compound Mg_2Sn is a bluish-white lustrous solid, having all the properties of a metal.

Metal-metal systems vary in character between the following extremes:

- Those in which the two metals are able to form solid solutions with each other over the whole composition range from 100% of one to 100% of the other. An example of such a system is that between silver and gold.

- Those in which the two metals are completely immiscible with each other, even in the liquid state. An example of such a pair of metals is iron and lead.
- Those in which a number of compounds are formed.

Metallic compounds fall into one of two categories of compound:

- *Stoicheiometric compounds*: These are compounds that obey the law of constant composition to very high accuracy, e.g. CH_4, NaCl, Mg_2Sn. They are also called "definite" compounds or "Daltonides". [The word "stoicheiometric" comes from "stoicheiometry", the name given to the measurement of the proportions of elements in compounds]
- *Non-stoicheiometric compounds*: These have a variable composition within certain limits. They are also called "indefinite" compounds or "Berthollides".

  Examples of non-stoicheiometric compounds are provided by the copper-tin system.

The three compounds referred to above have the following compositions at 300 °C $CuZn_{0.85-0.95}$, $CuZn_{1.4-2.0}$, and $CuZn_{2.5-6.2}$.

The same compositions are obtained at room temperature if the solids are cooled fairly quickly. The first compound, however, is metastable at room temperature, and when cooled very slowly, decomposes at about 250 °C into a mixture of the second compound and $CuZn_{0\text{-}0.5}$, a solid solution of zinc in copper (brass).

The formulae of compounds of this type are normally written in terms of some kind of idealized formula, using a *circa* ("round about") sign ~. The choice of idealized formula is based upon structural or theoretical considerations, and is not without arbitrariness. In the case of copper-zinc compounds, the idealized formulae are CuZn, Cu_5Zn_8, and $CuZn_3$, and the compounds are written ~CuZn, $\sim Cu_5Zn_8$, and $\sim CuZn_3$.

Nonmetallic Compounds

Pure silica also forms colourless crystals, melting to a colourless liquid at about 1600 °C and boiling at about 2400 °C. Both compounds are insulators. Conductivity measurements have also been made on liquid silica, in which state it remains a poor conductor.Nonmetallic compounds are generally formed by the combination of a nonmetal with a nonmetal, but combinations of a metal and a nonmetal can also be nonmetallic if the influence of the nonmetal predominates.

This occurs:

- When the ratio of metal atoms to nonmetal atoms is relatively low,
- When the metallic character of the metal is relatively weak, or
- When both circumstances pertain.

Good examples of nonmetallic compounds of metals are provided by the highest oxides of chromium and manganese. These have the formulae CrO_3 and Mn_2O_7, and are also similar to the highest oxides of sulfur and chlorine, SO_3 and Cl_2O_7. Thus CrO_3 is a red solid melting at 196 °C, and Mn_2O_7 is a dark red oil. Further, electrical measurements on CrO_3 show this to be an insulator in both the solid and liquid state. Both compounds decompose below their boiling point, Mn_2O_7 explosively.

Salt-Like Compounds

These represent a new class, characterized by the following properties:

- No lustre, high transparency over the visible spectrum,
- Either
  - Low electrical conductivity in the solid state, but high conductivity in the molten state and in aqueous solution, conduction being of the electrolytic type, or
  - High electrolytic conductivity in both the solid and the liquid state.

Bonding In Polyatomic Molecules

In the formation of covalent bonds between atoms in polyatomic molecules, the conditions that atomic orbitals distort so that maximum overlap may be achieved when bonding occurs produces more extensive changes of orbital geometry than is the case with diatomic molecules.

It will be remembered that the changes which result in a d bond formation in diatomic molecules are a distortion of the s orbitals or p lobes so that strongest bond formation results from the maximum overlap between the two joined nuclei.

For polyatomic molecules extensive alterations in the spatial disposition of atomic orbitals do occur, and very often the unique orbital geometry of the original atomic orbitals is completely lost. It is sometimes convenient to view these alterations as occurring in each atom prior to bonding by a process involving the mixing, or hybridization, of atomic orbitals.

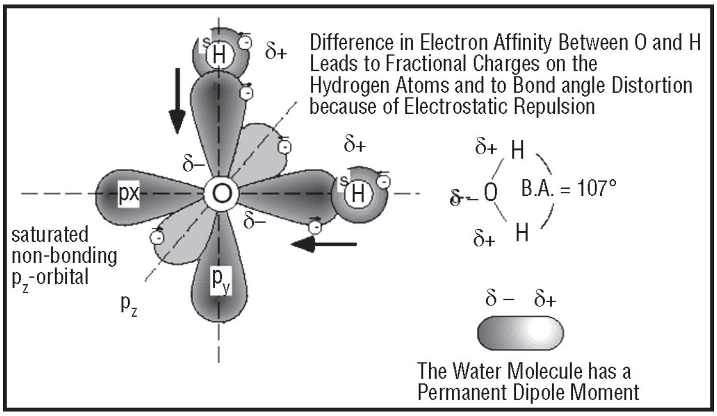


Fig. Bonding In Polyatomic Molecules.

Bonding Involving Carbon

In methane (CH_4) the four outer, or valence, electrons of carbon are shared with the electrons of hydrogen; there is spin-pairing (resulting in bond formation) between each individual hydrogen electron and one of the carbon valence electrons.

The noble gas structure is thus attained by each nucleus: the carbon nucleus "sees" eight outer electrons and each H nucleus "sees" two electrons. Consider now the orbitals which are involved in more detail. Each hydrogen has one spherical valence orbital (the 1s orbital) containing one electron, and covalent bond formation results from its distortion, overlap with the valence orbitals of carbon and spin-pairing.

According to the Aufbau principle and Hund's rule, in its ground state carbon has two electrons in the filled K shell and four electrons in the L shell: two 2s electrons and two 2p electrons in singly occupied orbitals which are capable of covalent bond formation.

This configuration provides, in principle, only two orbitals (2px, 2py) for covalent bond formation. However, with two covalencies carbon will not yield the desirable octet configuration.

Such a configuration can be obtained if one of the two 2s electrons is "promoted" into the empty 2pz orbital since this process results in four singly occupied orbitals - all of which, being singly occupied, are capable of bond formation.

The dissimilar singly occupied orbitals can assume (and therefore will assume) upon bond formation a lower energy configuration involving a process called hybridization whereby the four orbitals (of two different types) hybridize into four identical orbitals of maximum equal spacing from each other.

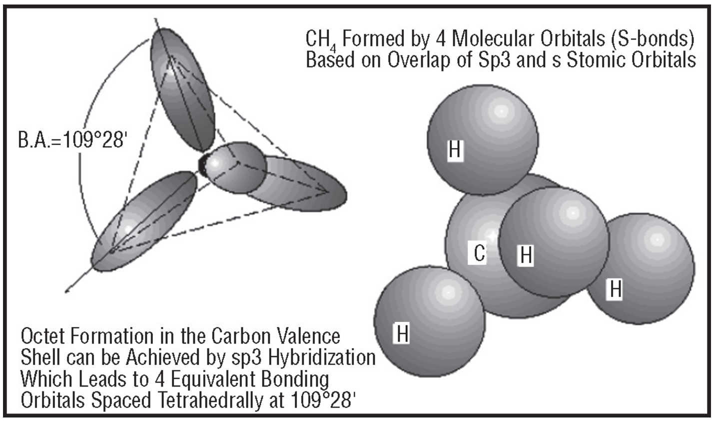
Thus the hybridized orbitals (sp^3 hybrids) are lobes emanating from the carbon atom into the corners of a tetrahedron, forming bond angles of 109°28'. sp^3 hybridization is characteristic for carbon; however, other types of hybridization, sp^2 and sp, are encountered in other elements as well.

Boron, for example, will tend to promote one of its two 2s electrons into a 2p state and, by hybridization, form three equivalent sp^3 orbitals which assume planar orientation with band angles of 120°. Beryllium forms sp hybrid orbitals of linear orientation (the bond angle is 180°). All hybrid orbitals are capable of σ bond formation. The great diversity of carbon compounds (it forms more compounds than all the rest of the elements in the Periodic Table) can be attributed to the hybridization capability of the carbon orbitals (sp^3, sp^2 and sp).

As a consequence, carbon forms not only axisymmetric d?bonds (through axial orbital overlap), but also σbonds (through lateral orbital overlap).

In the compound ethane ($H_2C = CH_2$), the interactive carbon atoms undergo sp^2 hybridization for a dbond by overlap of two sp^2 hybrid orbitals and form, in addition, a σ bond by lateral overlap of the remaining non-hybridized π orbitals. (Double bonds involve one σ and one π bond.)

In acetylene (HC ≡ CH), we find sp hybridization and, by axial overlap, bond formation as well as lateral overlap of the remaining non-hybridized px and py orbitals which form two bonds.



CH_4 Formed by 4 Molecular Orbitals (S-bonds) Based on Overlap of Sp3 and s Stomic Orbitals

Octet Formation in the Carbon Valence Shell can be Achieved by sp3 Hybridization Which Leads to 4 Equivalent Bonding Orbitals Spaced Tetrahedrally at 109°28'

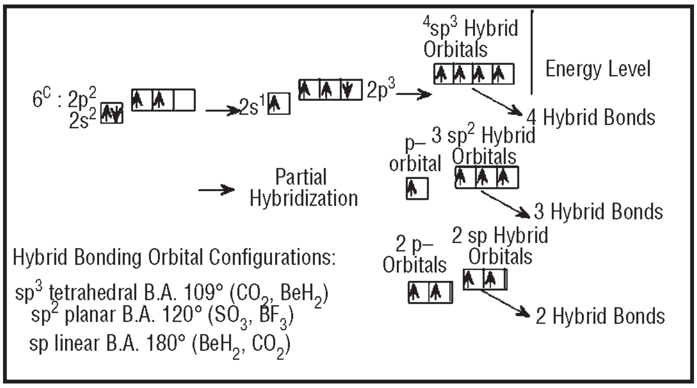


Fig. Hybrid Bonding Orbital Configuration.

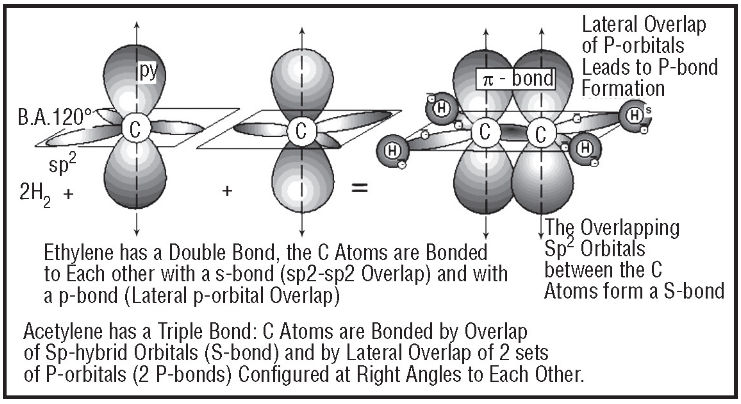


Fig. Triple Bond of Acetylene.

METALLIC BONDING

The stability of both covalent and metallic bonds may be regarded as arising from the potential energy lowering experienced by valence electrons under the influence of more than one nucleus. In metals, where the valence electrons are not as tightly bound to their ion cores, we cannot expect the formation of strong electron-pair bonds.

The bond energies of known diatomic molecules of metallic elements are, in fact, smaller than those consisting of nonmetallic elements: 104 kJ/mole for Hg_2. Only diatomic molecules of the semi–metals have relatively high binding energies (385 kJ/mole for As_2, 293 kJ/mole for Sb_2 and 163 kJ/mole for Bi_2). These values reflect multiple bonding. Much greater stability is possible in larger aggregates of atoms such as bulk metals.

The known properties of metals, such as low electrical resistance and malleability, support the conceptual view that the valence electrons in metals never remain near any particular atom very long, but drift in a random manner through the lattice of ion cores. We may therefore visualize metals as a lattice of ion cores being held together by a gas of free electrons

SECONDARY (van der WAALS) BONDING

Primary bonding (ionic, covalent and metallic) is strong and the energies involved range from about 100 to 1000 kJ/mole. In contrast, secondary bonding is weak, involving energies ranging from about 0.1 to 10 kJ/mole. While this type of bonding, also referred to as “residual”, is weak, it is essential in the functioning of our environment. Coke would likely be gaseous and not a bubbly, refreshing brew were it not for secondary bonding, nor would catalytic converters function.

The energy difference between the liquid and vapour states of a given system is given by the heat of vaporization, i.e. the heat required to convert a given liquid into a vapour (normally) at the boiling point temperature at 1 atm pressure.

The energy difference is due to intermolecular attraction between molecules at close distance of separation. This phenomenon of attraction through secondary bonding can best be considered between a single pair of molecules, but recognizing that the forces are of longer range. Four types of intermolecular forces can be identified.

- *Dipole-Dipole Interaction*: Molecules with permanent dipoles (such as water, alcohol and other organic compounds with functional groups) exert a net attractive force on each other as a result of varying degrees of alignment of oppositely charged portions of the molecules. For two polar molecules with a dipole moment of (μ) separated by a distance of (r), the energy of attraction can be quantified as:

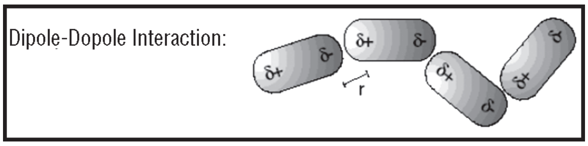


Fig. Dipole - Dipole Interaction.

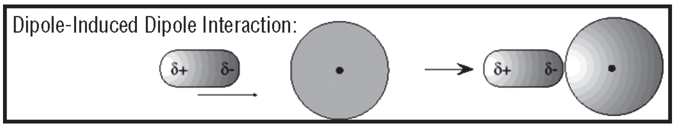
$$E_{\text{Dipole-Dipole}} = \frac{2}{3}\frac{\mu^4}{Dr^6} \times \frac{1}{kT}$$

where μ is the dipole moment, r is the distance of approach of the oppositely charged molecular portions, k is the Boltzmann constant and T is the absolute temperature in K.

The molar energies of attraction associated with dipole-dipole interaction range from 0 to about 10 kJ/mole. These forces are primarily responsible for the liquid state (at room temperature) of most polar organic molecules; they are a contributing factor for H_2O to be liquid at room temperature, and are responsible for alcohol being a liquid.

- *Dipole-Induced Dipole Interaction*: A dipole in one molecule can interact with and polarize the electrons of a neighboring non-polar molecule, thus generating an induced dipole which will experience an attractive force with the polarizing, polar dipole. P. Debye showed that in a molecule with a "polarizability" of (α) the attractive potential arising from dipole-induced dipole interaction is given as:

$$E_{Dipole-Induceddipole} = -\frac{2\alpha\mu^2}{Dr^6}$$



Gig. Dipole-Induced Dipole Interaction.

Induced dipole interaction is important in aqueous solutions and very effective during adsorption of inert molecules on active solid substrates.

London Dispersion Forces

It is a well-known fact that all substances, including rare gases and hydrogen, assume liquid state at finite temperature, an indication of the existence of attractive interatomic and intermolecular forces, even in the absence of permanent dipole systems. The origin of this force has been proposed by F. London in 1930. Accordingly, orbiting electrons will at any instance generate a "temporary dipole", the configuration of which changes as the electrons move.

Since all atoms of a given system similarly experience temporary instantaneous dipole moments, their effect is expected to be cancelled because of the statistically random orientation of dipoles. It is evident that, should the dipoles be synchronized in a given assembly of atoms, then a net attractive force would result.

But since such an attractive force constitutes a lowering of the energy of a given system, synchronization can and will take place because all systems will attempt to assume minimum energy configuration. The London dispersion force can be formulated as:

$$E_{London} = -K\frac{\alpha^2}{r^6}$$

The attractive London forces are small, as manifested by the very low boiling points of the smaller rare gases, of hydrogen and nitrogen.

Hydrogen Bonding

The short and long range dipole interactions calculated from molecular dipole moments are inadequate in explaining a multitude of phenomena in organic as well as some inorganic systems. L. Pauling studied such London Dispersion (Fluctuating Dipole Interaction) Electron motion in atoms generates fluctuating dipoles. Since the polarization is random attractions are cancelled by repulsions.

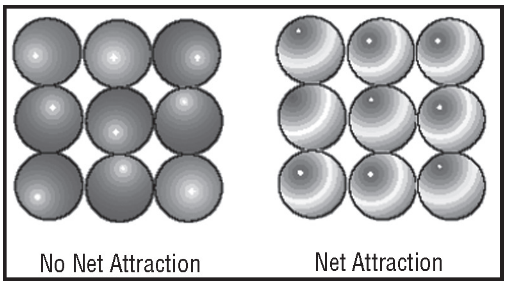


Fig. Fluctuating Dipole Interaction.

London

Upon synchronization of electron motion inter atomic attraction will be established in an assembly of atoms. Since this attraction constitutes a lowering of the energy of the system - attraction by synchronization will take place - as all systems attempt to assume lowest energy configuration phenomena and concluded the existence of highly specific attractive interaction between hydrogen that is acidic (carries a fractional positive charge) and the elements O, F, N and, to a lesser extent, S in both organic and inorganic molecules.

This interaction, which can as yet not be formulated, is referred to as hydrogen bonding; its magnitude, ranging up to 40 kJ/mole, is significantly larger than that of any other secondary bonding type. Hydrogen bonding is considered instrumental in controlling most properties of water, is a key element in the structure of nucleic acid and thought to be an essential component in memory functions of the human brain.

5

Nomenclature of Coordination Compounds

Coordination compounds are named according to the recommendations of IUPAC. The basic rules are as follows.

1. A coordination entity has a one-word name, formed from the name of the central atom and the names of the ligands.
2. If the entity is a cation or neutral, the usual name of the central atom is used (cobalt). If the entity is an anion, the name of the central atom is changed to end in -ate (cobaltate). For a few elements, Latin forms are used for anions (ferrate, cuprate).
3. Most neutral ligands have their usual names. A few have special names, e.g.

NH_3	ammine
H_2O	aqua

4. Anionic ligands have their usual names, modified to end in –o, e.g.

Cl^-	chloro
$CH_3CO_2^-$	acetato

A few have special names, e.g.

O^{2-}	oxo
OH^-	hydroxo
NO_2^- (coordinated through N)	nitro

5. The numbers of ligands are indicated by Greek numerical prefixes (di, tri, tetra, penta, hexa, etc.). Where these would create ambiguity, multiplicative prefixes (bis, tris, tetrakis, pentakis, hexakis, etc.) and brackets are used, e.g. bis(methylamine).
6. Ligands are listed first, in alphabetical order (triamminedibromochloro), followed by the central atom.
7. There are alternative ways of indicating the overall stoicheiometry, as illustrated below for the compound $[CoCl(NH_3)_5]Cl_2$.

i. By specifying the oxidation number of the central atom,e.g. pentaamminechlorocobalt(III) chloride

ii. By specifying the charge on the coordination entity,e.g. pentaamminechlorocobalt(2+) chloride

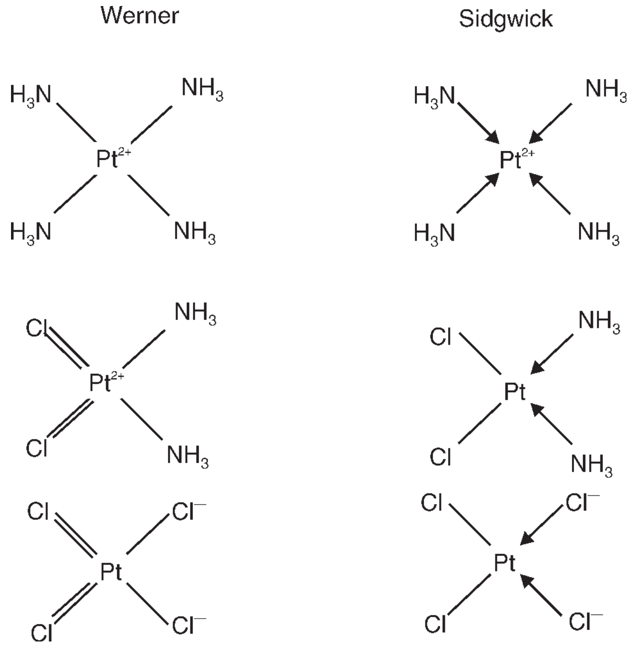
iii. By specifying the proportions of the constituent ions,e.g. pentaamminechlorocobalt dichloride

8. Bridging ligands are indicated by m and separated by hyphens,

e.g. –μ-chloro–, –di-μ-hydroxo–

Bonding in coordination compounds

The bonding in coordination compounds is most easily described in the manner first proposed by the Oxford chemist. Sidgwick suggested that



This is illustrated above.

1. The bonds indicated by a double line (——) in the above formulae are ordinary covalent bonds, and

(ii) the bonds indicated by a green line (.....) are donor bonds, the ligand acting as the donor and the central atom as the acceptor.

Sidgwick based his hypothesis on the following observations:

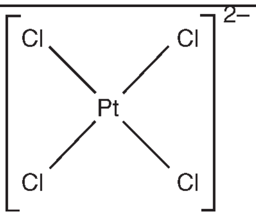
1. All ligands thought to be bound by a dative bond possess at least one unshared pair of electrons, and no ligand is ever required to form more dative bonds than the number of lone pairs it has available.

2. For many of the more stable coordination compounds (stable, that is, with respect to dissociation), the number of electrons calculated to be round the central atom on the above model is the same as the number of electrons round the atom of the next inert gas. For example:

$[Co(NH_3)_6]^{3+}$	Co^{3+} has	24 electrons
	$6NH_3$ donate	12 electrons
	Total	**36 cf. Kr**

This he called the "effective atomic number rule". It is now called the "inert/rare gas rule", or the "18 electron rule". The latter is based on the number of outer electrons (i.e. electrons outside an [Ar], [Kr], or $[Xe4f^{14}]$ core):

$[Co(NH_3)_6]^{3+}$	Co^{3+} has	6 outer electrons
	$6NH_3$ add	12 electrons
	Total	**18**

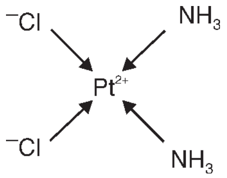


Sidgwick recognized that, when the above formula for $[PtCl_4]^{2-}$ is drawn as a Lewis structure with only dots, all the Pt–Cl bonds are the same (Pt:Cl), as observed experimentally. He accordingly also wrote the formula This effectively places the negative charge on the platinum atom.

Sidgwick's understanding of the bonding in coordination compounds is accepted today in a slightly modified form. This is as follows:

i. The bonds thought by Sidgwick as covalent bonds are now regarded as having some ionic character, in common with other electron-pair bonds between unlike atoms.

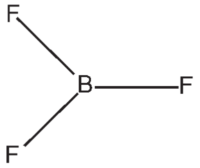
ii. These bonds are replaced by their ionic-cum-dative equivalent, i.e. A–B is replaced by $A^+ \leftarrow B^-$. This gives for $[PtCl_2(NH_3)_2]$



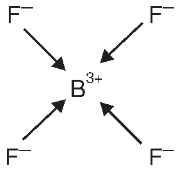
This is equivalent to taking all of the black lines in the earlier formulae as ionic bonds and all of the green lines as dative bonds.

The merit of the modern formulation is that it represents all the coordinate bonds in the same way. Its disadvantage, however, is that it exaggerates the extent to which it is necessary to go beyond a simple formulation, and creates inconsistencies of the type illustrated below:

Formula of BF^3



Formula of BF_4^-



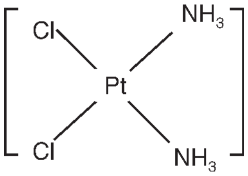
For many purposes, it is better to use Sidgwick's formulae, with A—B replaced by A—B.

Notes:

i. The extent to which a ligand donates its electrons varies widely. Quantum-mechanical calculations indicate that in some complex ions the degree of donation is small. In these cases, most of the coordinate bonding comes from the attraction between the positive charge on the central atom and the negative charge on the coordinating atoms. (Neutral ligands are polar with a negative charge on the coordinating atom. For example, the charge on the N atom of NH_3 is about –0.8.)

ii. The 18 electron rule is of limited applicability among classical coordination compounds. It holds for octahedral cobalt(III) and platinum(IV) complexes, but not chromium(III) (15 electrons) or square-planar platinum(II) (16 electrons). Classical compounds of transition elements are best treated as containing variable cores. Complexes containing >18 outer electrons, e.g. octahedral nickel(II) (20), can be understood in the same way as main-group compounds with >8 outer electrons: i.e. polarity of the coordinate bonds reduces the number of electrons round the central atom.

iii. Modern chemists often represent coordination entities by simple single-stroke formulae,

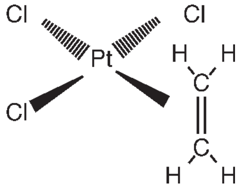


Nonclassical coordination compounds

Transition elements form coordination compounds with some ligands that bind weakly, if at all, to main-group electron-pair acceptors (BF_3). The principal ligands of this type are carbon monoxide and unsaturated hydrocarbons. Some examples of compounds are:

Nickel carbonyl, $Ni(CO)_4$. This is made by passing carbon monoxide over nickel powder. It is a colourless liquid, boiling at 43 °C. The $Ni(CO)_4$ molecule is tetrahedral. The C-O bond length is 1.15 Å, which is similar to that in CO (1.13 Å), and shorter than that in aldehydes and ketones (typically 1.22 Å). This suggests that the molecule should be formulated $[Ni(\leftarrow CO)_4]$, with zero-valent nickel, rather than $Ni(=C=O)_4$, with octovalent. However, the strength of the bonds compared with the weakness of bonds between CO and main-group acceptors indicates some enhancement of the bonding.

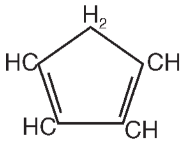
Iron pentacarbonyl, $Fe(CO)_5$. This is made by heating iron powder with carbon monoxide in an autoclave (at 200 °C and 200 atm). It is a yellow liquid, boiling at 103 °C. The molecule is trigonal bipyramidal, with a C-O distance of 1.15 Å, as in $Ni(CO)_4$.

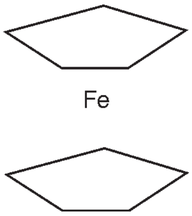


Ziese's salt. This can be made by shaking a solution of $K_2[PtCl_4]$ in aqueous hydrochloric acid with ethylene. It forms yellow crystals, which X-rays show contain square-planar $[PtCl_3(C_2H_4)]^-$ ions with the C_2H_4 bound sideways on:

Since C_2H_6 does not form a similar compound, the presumption is that the C_2H_4 molecule is bound to the platinum atom by one of the electron pairs from the double bond. This may be indicated: Pt← | |, where | | represents the double bond. There may again be some enhancement of the bonding.

Ferrocene, $Fe(C_5H_5)_2$. This can be made by several methods, starting from cyclopentadiene, C_5H_6 (below left). It forms brown crystals, melting at 173 °C. X-rays show that, instead of each C_5H_5 radical being bound to the iron atom through one carbon atom (>CH—Fe—CH<), the rings are bound face on, producing a "sandwich" structure (below right). The rings display aromatic reactivity, undergoing substitution rather than addition.





The molecule is most easily formulated with integral bonds in the rings (as above left with -CH_2- replaced by -CH<). There is then one Fe—C bond to each ring and two Fe← | | bonds. However, the Fe–C and C-C bond lengths are all the same. Therefore a better formulation is with equal ring bonds, of value 1.4 [the average of three single bonds and two double]. There are then five Fe—$_{0.2}$—C bonds to each ring [a single bond shared between five linkages] and five Fe←$_{0.4}$—¦ | bonds.

Compounds of this type conform to the 18 electron rule better than classical coordination compounds. Thus:

$Ni(CO)_4$: a nickel atom has 10 outer electrons; each CO molecule donates 2 electrons; the total number of electrons is therefore 10 + 4 × 2 = 18.

$Fe(CO)_5$: an iron atom has 8 outer electrons; the total number of electrons is therefore 8 + 5 × 2 = 18.

$Fe(C_5H_5)_2$: Fe has 8 outer electrons; each C_5H_5 radical shares its unpaired electron to form one Fe¾C bond or five Fe—$_{0.2}$—C bonds, and donates four electrons to form two Fe¬| | or five Fe<—$_{0.4}$—¦ | bonds; the total number of electrons in the molecule is therefore 8 + 2 × (1 + 4) = 18.

The platinum atom in $[PtCl_3(C_2H_4)]^-$ has only 16 electrons, but this number is characteristic of square-planar complexes (the "16 electron rule").

Nomenclature of pseudo-binary compounds

Pseudo-binary compounds are named in a similar way to binary compounds. In general, the name of the electropositive constituent is cited first, and that of the electronegative constituent second. Strictly speaking, this requires the incorporation of radicals in the electrochemical series, but in practice this is only done very roughly. Thus NO_3 and SO_4 are always regarded as being the electronegative constituent of a compound, even though in a few cases this is disputable, e.g. in FNO_3.

Examples of nomenclature:

CH_3Cl	Methyl chloride
$NaCH_3$	Sodium methyl
$(CH_3)_2SO_4$	Dimethyl sulfate
FNO_3	Fluorine nitrate

Involatile Nonmetallic Compounds

Some nonmetallic compounds are involatile because their molecules are very large (e.g. higher paraffins). Although the van der Waals interactions between atoms in different molecules are small (they are the same as the interactions between atoms of small molecules), there are so many atoms that the total interaction between molecules is large.

Compounds of this type nevertheless dissolve in volatile solvents (e.g. higher paraffins in lower ones), because each molecule can interact with as many solvent molecules as it can get round it.

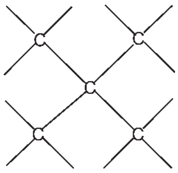
These interactions add up to overcome the large interaction between molecules of the compound. Very large molecules are called “macromolecules”.

Other involatile nonmetallic compounds are different in being insoluble in volatile solvents (e.g. diamond, silicon carbide, and silica).

The nature of these compounds can be inferred as follows:

- From the above discussion of volatile compounds, the molecules of these compounds in the vapour phase must interact very strongly in the liquid and solid phases.
- In many volatile compounds, carbon atoms are known to bond to four other atoms in directions defined by a tetrahedron. Now if carbon atoms were to bond to each other in this kind of way, instead of a small molecule being produced, a continuous three-dimensional network would be\ formed, each atom being held in the network by very strong bonds - the same kind of bonds that hold the atoms of each molecule together in volatile compounds.

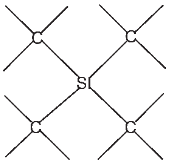
  In two dimensions this may be drawn:



Such a structure would satisfy:

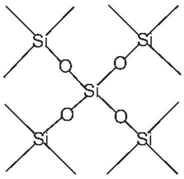
- And suggests itself for diamond.
- A determination of the structure of diamond by X-ray crystallography shows that it indeed has this structure, with carbon-carbon bond lengths of 1.54 Å, as compared with 1.53 Å in C_2H_6.
- In a similar way we can “guess” the structures of silicon carbide and silica. Silicon also forms volatile

compounds in which the silicon atom is surrounded by a tetrahedron of other atoms (e.g. simple molecules like SiH_4 and $SiCl_4$, and resolvable ones of the type SiWXYZ). Silicon carbide could thus have a similar structure to that of diamond:



Further, since oxygen forms compounds in which its atom has two neighbours, silica could have a structure of the diamond type, only with an oxygen atom between every pair of silicon atoms.

That silicon carbide and silica indeed have structures of this kind has been shown by X-ray crystallography. (Both compounds are polymorphic, but in each case the different forms have the same arrangement of nearest neighbours, and differ only in the relative orientation of more distant neighbours.)



Compounds of this type thus consist of giant assemblies of atoms tightly held together. Such assemblies of atoms are called “frameworks” and such compounds “nonmolecular”. Liquefaction of compounds of this type involves the breaking of some of the bonds, for only in this way can atoms move positions.

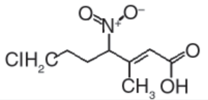
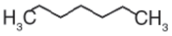
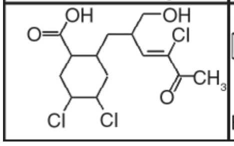
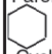
Clearly, however, the system will resist whole-scale breaking of bonds, and fluidity will rely on a process whereby the breaking of one bond is compensated for by the remaking of another bond somewhere else. Consequently the fluidity of such compounds in the liquid state is low: that is, their viscosity is high.

Nomenclature Operations

The operations described in this section all involve structural modification, and are classified first according to the type of modification, for example, “replacement”; and then according to the way in which the modification is expressed, for example, “by use of replacement infixes”.

The structures to which the various modifications are applied can be regarded as parent structures, and the modifications are expressed by affixes, i.e., infixes, prefixes, and suffixes.

Examples:

	Parent:  Heptane
	Parent:  Cyclohexane (Cyclohexane is Chosen as Parent Because it Bears the Principal Characteristic Group -COOH).

Indicated Hydrogen

Under certain circumstances it is necessary to indicate in the name of a ring, or ring system, containing the maximum number of noncumulative double bonds, one or more positions where no multiple bond is attached.

This is done by specifying the presence of an “extra” hydrogen atom at such positions by citation of the appropriate numerical locant followed by an italicized capital

H.

Example:

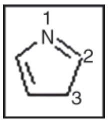


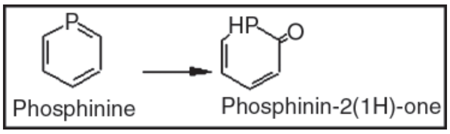
Fig. 3H–Pyrrole

In the above example, the "indicated hydrogen" locates two hydrogen atoms at position 3 (an "extra" hydrogen over the number present if there were a double bond in the ring at that position), thus specifying a particular pyrrole tautomer, as illustrated. Indicated hydrogen of this type normally precedes the name of a parent hydride.

A second type of indicated hydrogen (sometimes referred to as "added hydrogen") describes hydrogen atoms added to a specified structure as a consequence of the addition of a suffix or a prefix describing a structural modification.

This type of indicated hydrogen is normally cited in parentheses after the locant of the additional structural feature.

Example:



The detailed procedures for using indicated hydrogen, including differences in approach used in index nomenclature by Chemical Abstracts Service and in *Beilstein*, will be described in a separate publication.

Parent Hydrides and their Derived Substituent Groups

A "parent hydride" is the structure which is named before the addition of affixes denoting substituents to yield the name of a specific compound. Its name is understood to signify a definite population of hydrogen atoms attached to a skeletal structure. Acyclic parent hydrides are always unbranched, for example pentane and trisilane; although a few trivial names for branched acyclic hydrocarbons are retained, their use for naming substitutive derivatives is not recommended.

Cyclic parent hydrides are usually either fully saturated, for example, cyclopentane, cyclotrisiloxane, azepane, bicyclo octane, and spiro[4.5]decane, or fully unsaturated, i.e., they contain the maximum number of noncumulative double bonds.

For example, pyridine, 1,3–oxazole, 1*H*–phenalene, phenanthroline, and benzo[*a*]anthracene.

Also, there are parent hydrides that are partially saturated, for example, 1,4–dihydro–1,4–ethanoanthracene and spiro[1,3–dioxane–2,1'–[1*H*]indene], and that are combinations of cyclic and saturated acyclic structures having retained trivial names.

Mononuclear Hydrides

The names of mononuclear hydrides of the elements for use as parents in substitutive nomenclature are given in Table. Many are formed systematically by combining the ‘a’ term of the element (with elision of the terminal “a”) with the ending “-ane”, for example, borane for BH_3, silane for SiH_4, etc. There are important exceptions: methane for CH_4, oxidane for OH_2, sulfane for SH_2, selane for SeH_2, etc.,

Table. Mononuclear Hydrides.

BH_3	***Borane***	OH_2
	Oxidane	

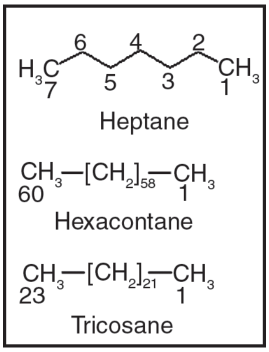
CH_4	*Methane (Carbane)*	SH_2		*Sulfane*
SiH_4	*Silane*	SH_4	λ^{3}'–	*Sulfane*
GeH_4	*Germane*	SH_6	λ^{5}'–	*Sulfane*
SnH_4	*Stannane*	SeH_2		*Selane*
PbH_4	*Plumbane*	TeH_2		*Tellane*
NH_3	*Azane*	PoH_2		*Polane*
PH_3	*Phosphane (Phosphine)*	FH		*Fluorane*
PH_5	*λ^5–Phosphane* *(Phosphorane)*	ClH		*Chlorane*
AsH_3	*Arsane (Arsine)*	BrH		*Bromane*
AsH_5	*λ^5– Arsane (Arsorane)*	IH		*Iodane*
SbH_3	*Stibane (Stibine)*	IH_3	λ^3–	*lodane*
SbH_5	*λ^5– Stibane (Stiborane)*	IH_5	λ^3–	*lodane*
BiH_3	*Bismuthane(Bismuthine)*	AtH		*Astatane*

The systematic alternatives to well established common names, e.g., azane for ammonia, oxidane for water, and chlorane, bromane, etc., for hydrogen chloride, bromide, etc., are necessary for naming some derivatives and for generating names of polynuclear homologues. If the bonding number of the element differs from the normal one, the name of the hydrides is modified by affixing a λ^n symbol.

HydroCarbons

The saturated unbranched acyclic hydrocarbons from C_2 to C_4 are named ethane, propane, and butane. Systematic names of the higher members of this series consist of a numerical term, followed by "-ane" with elision of a terminal 'a' from the basic numerical term. The generic name for saturated acyclic hydrocarbons (branched or unbranched) is "alkane". The chain is numbered from one end to the other with arabic numerals.

Examples:



Heptane

$CH_3-[CH_2]_{58}-CH_3$

Hexacontane

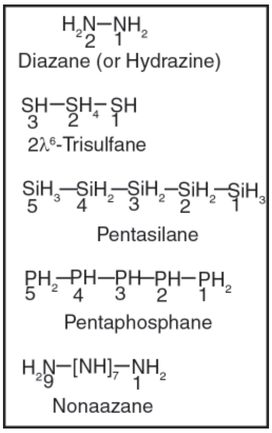
$CH_3-[CH_2]_{21}-CH_3$

Tricosane

Homogeneous Hydrides other than Hydrocarbons or Boron Hydrides

A compounds consisting of a unbranched chain containing several identical heteroatoms saturated with hydrogen atoms, may be names by citing the appropriate multiplying prefix (with *no elision* of the terminal vowel of the multiplying prefix) followed by the appropriate name of the hydride. If necessary, a.λ symbol is used.

Example:



Diazane (or Hydrazine)

2λ⁶-Trisulfane

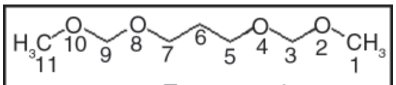
Pentasilane

Pentaphosphane

Nonaazane

Heterogeneous Hydrides

- Heterogeneous hydrides consisting of chains containing carbon atom and several heteroatoms, alike or different, and terminating with carbon may be named by replacement nomenclature. *Example:*



2,4,8,10-Tetraoxaundecane

- Compounds containing an unbranched chain of alternating atom terminated by two identical atoms of the element coming later in Table may be named by citing successively a multiplying prefix denoting the number of atoms of the terminating element followed by the "a" term of that element, then the "a" term of the other element of the chain and the ending "-ane". The terminal letter "a" of an "a" term is elided when followed by a vowel; the terminal vowel of a numerical prefix is not elided even when the "a" term begins with the same vowel.

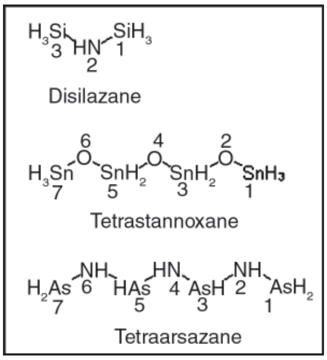
Hantzsch-Widman System Prefixes

Table. In Decreasing Order of Priority

Element	*Bonding number (valence)*	*Prefix*

Fluorine	*1 (I)*	*Fluora*
Chlorine	*1 (I)*	*Chlora*
Bromine	*1 (I)*	*Broma*
Iodine	*1 (I)*	*Ioda*
Oxygen	*2 (II)*	*Oxa*
Sulfur	*2 (II)*	*Thia*
Selenium	*2 (II)*	*Selena*
Tellurium	*2 (II)*	*Tellura*
Nitrogen	*3 (III)*	*Aza*
Phosphorus	*3 (III)*	*Phospha*
Arsenic	*3 (III)*	*Arsa*
Antimony	*3 (III)*	*Stiba*
Bismuth	*3 (III)*	*Bisma*
Silicon	*4 (IV)*	*Sila*
Germanium	*4 (IV)*	*Germa*
Tin	*4 (IV)*	*Stanna*
Lead	*4 (IV)*	*Plumba*
Boron	*3 (III)*	*Bora*
Mercury	*2 (II)*	*Mercura*

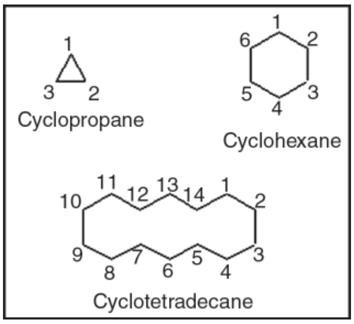
Examples:



Hydrocarbons

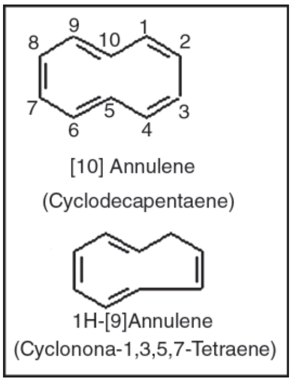
- The names of saturated monocyclic hydrocarbons are formed by attaching the prefix “cyclo-” to the name of the acyclic saturated unbranched hydrocarbon with same number of carbon atoms. The generic name of monocyclic hydrocarbons is "cycloalkane". Numbering proceeds sequentially round the ring.

Examples:



- Unsubstituted monocyclic hydrocarbon polyenes having the maximum number of noncumulative double bonds and with a general formula of C*n*H*n* or C_nH_{2n+1} (with *n* greater than 6) are called annulenes generically. A specific annulene may be named as an [*n*]annulene, where *n* is the number of carbon atoms of the ring. When *n* is an odd number, i.e., when the annulene has the general formula C*n*H*n*+1 the extra hydrogen atom is denoted as "indicated hydrogen".

  Examples:



6

Complex Metal Ions

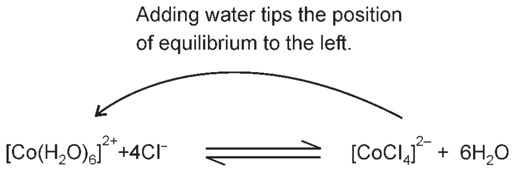
Some common ligand exchange (substitution) reactions involving complex metal ions. It assumes that you are familiar with basic ideas about complex ions.A ligand exchange reaction is exactly what it says - a reaction in which one ligand in a complex ion is replaced by a different one.

Replacing the water in the hexaaquacobalt(II) ion: If you add concentrated hydrochloric acid to a solution containing hexaaquacobalt(II) ions (cobalt(II) chloride solution), the solution turns from its original pink colour to a dark rich blue. The six water molecules are replaced by four chloride ions.

The reaction taking place is reversible.

$$[\mathrm{Co(H_2O)_6}]^{2+} + 4\mathrm{Cl} \square \quad [\mathrm{CoCl_4}]2^{-} + 6\mathrm{H_2O}$$

Concentrated hydrochloric acid is used as the source of chloride ions because it provides a very high concentration compared to what is possible with, say, sodium chloride solution. Concentrated hydrochloric acid has a chloride ion concentration of approximately 10 mol dm^{-3}. The high chloride ion concentration pushes the position of the equilibrium to the right according to Le Chatelier's Principle.



Notice the change in the co-ordination of the cobalt. Chloride ions are bigger than water molecules, and there isn't room to fit six of them around the central cobalt ion.This reaction can be easily reversed by adding water to the solution. Adding water to the right-hand side of the equilibrium has the effect of moving the position of equilibrium to the left. The pink colour of the hexaaquacobalt(II) ion is produced again (only paler, of course, because it is more dilute).

Replacing the Water in the Hexaaquacopper(II) Ion

The colour of the tetrachlorocuprate(II) ion is almost always seen mixed with that of the original hexaaqua ion.The reaction taking place is reversible, and you get a mixture of colours due to both of the complex ions.

$$[Cu(H_2O)_6]^{2+} + 4Cl\square\quad [CoCl_4]^{2-} + 6H_2O$$

You may find the colour of the tetrachlorocuprate(II) ion variously described as olive-green or yellow.Adding water to the green solution, replaces the chloride ions as ligands by water molecules again, and the solution returns to blue.

Replacing Water Molecules by Ammonia

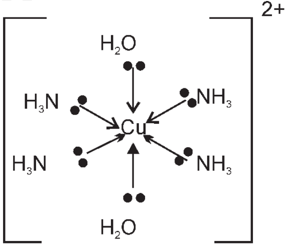
Water molecules and ammonia molecules are very similar in size, and so there is no change in co-ordination this time.

Unfortunately, the reactions aren't quite so straightforward to describe.Ammonia solution can react with hexaaqua metal ions in two quite distinct ways, because it can act as a base as well as a ligand.If you add a small amount of ammonia solution you get precipitates of the metal hydroxide - the ammonia is acting as a base.

In some cases, these precipitates redissolve when you add more ammonia to give solutions in which a ligand exchange reaction has occurred.In the diagrams below, both steps are shown, but we are only going to consider the chemistry of the overall ligand exchange reaction. The precipitates dissolve because of a complicated series of equilibrium shifts, and we shan't worry about that for the moment.

Replacing the water in the hexaaquacopper(II) Ion

This is a slightly untypical case, because only four of the six water molecules get replaced to give the tetraamminediaquacopper(II) ion, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.



the tetraamminediaquacopper(II) ion

Notice that the four ammonias all lie in one plane, with the water molecules above and below.The main equilibrium involved in the ligand exchange reaction is:

$$[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2^{\ 2+} + 4H_2O$$

The colour of the deep blue complex is so strong that this reaction is used as a sensitve test for copper(II) ions in solution. Even if you try to reverse the change by adding large amounts of water to the equilibrium, the strength of the deep blue (even highly diluted) always masks the pale blue of the aqua ion.

Replacing the water in the hexaaquacobalt(II) Ion

This time, all the water molecules get replaced.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O$$

The straw coloured solution formed changes colour very rapidly on standing to a deep reddish brown. The hexaamminecobalt(II) ions are oxidised by the air to hexaamminecobalt(III) ions. However, that is a quite separate reaction, and isn't a part of the ligand exchange reaction.

Replacing the Water in the Hexaaquachromium(III) Ion

Again, all the water molecules get replaced by ammonias. The difference this time is that the reaction isn't so complete. The precipitate has to be left to stand in the presence of excess concentrated ammonia solution for some time in order to get the ammine complex.Even so, you still get left with some unreacted precipitate.

$$[Co(H_2O)_6]^{3+} + 6NH_3 \rightleftharpoons [Cr(NH_3)_6]^{3+} + 6H_2O$$

Two More Replacements of the Water in the Hexaaquachro-mium(III) Ion

The colour of the hexaaquachromium(III) ion has been shown as a "difficult to describe" violet-blue-grey in all the diagrams above. In practice, when it is produced during a reaction in a test tube, it is often green.A typical example of this is the use of acidified potassium dichromate(VI) as an oxidising agent. Whenever this is used, the orange solution turns green and we nearly always describe the green ion as being $Cr^{3+}_{(aq)}$ - implying the hexaaquachromium(III) ion. That's actually an over-simplification.

What happens is that one or more of the ligand water molecules get replaced by a negative ion in the solution - typically sulphate or chloride.

Replacement of the Water by Sulphate Ion

You can do this simply by warming some chromium(III) sulphate solution.One of the water molecules is replaced by a sulphate ion. Notice the change in the charge on the ion. Two of the positive charges are cancelled by the presence of the two negative charges on the sulphate ion.

Replacement of the Water by Chloride Ions

In the presence of chloride ions (chromium(III) chloride), the most commonly observed colour is green.

This happens when two of the water molecules are replaced by chloride ions to give the tetraaquadi-chlorochromium(III) ion - $[Cr(H_2O)_4Cl_2]^+$.

Once again, notice that replacing water molecules by chloride ions changes the charge on the ion.

A Ligand Exchange Reaction in the Test for Iron(III) Ions

This provides an extremely sensitive test for iron(III) ions in solution.If you add thiocyanate ions, SCN^-, (from, say, sodium or potassium or ammonium thiocyanate solution) to a solution containing iron(III) ions, you get an intense blood red solution containing the ion $[Fe(SCN)(H_2O)_5]^{2+}$.

COMPLEX METAL IONS - STABILITY CONSTANTS

The stability constant for a complex ion, and goes on to look at how its size is governed in part by the entropy change during a ligand exchange reaction.

Stability Constant

If you add ammonia solution to a solution containing hexaaquacopper(II) ions, $[Cu(H_2O)_6]^{2+}$, four of the water molecules are eventually replaced by ammonia molecules to give $[Cu(NH_3)_4(H_2O)_2]^{2+}$. This can be written as an equilibrium reaction to show the overall effect:

$$[Co(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$$

In fact, the water molecules get replaced one at a time, and so this is made up of a series of part-reactions:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + 4H_2O$$

$$[Cu(NH_3H_2O)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O$$

$$[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O$$

$$[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O$$

Although this can look a bit daunting at first sight, all that is happening is that first you have one, then two, then three, then four water molecules in total replaced by ammonias.

Individual Stability Constants

Let's take a closer look at the first of these equilibria:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O$$

Like any other equilibrium, this one has an equilibrium constant, K_c - except that in this case, we call it a *stability constant*. Because this is the first water molecule to be replaced, we call it K_1.

Here is the equation again:

$$[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O$$

K_1 is given by this expression:

$$K_1 = \frac{[Cu(NH_3)(H_2O)_5{}^{2+}]}{[Cu(H_2O)_6{}^{2+}][NH_3]}$$

There are two points of possible confusion here - one minor, one more important!

- First, the square brackets have changed their meaning! Square brackets are often used to keep everything in a complex ion together and tidy. Here, they have reverted to their other use, which implies concentrations in mol dm^{-3}.

In order to avoid complete confusion, the square brackets keeping the complexes together have been removed entirely.

- More importantly, if you compare the equilibrium constant expression with the equation, you will see that the water on the right-hand side hasn't been included. That is normal practice with these expressions.

Because everything is dissolved in water, the water is present as a huge excess. Generating a little bit more during the reaction is going to make no effective difference to the total concentration of the water in terms of moles of water per dm^3.

The concentration of the water is approximately constant. The equilibrium constant is defined so that you avoid having an extra unnecessary constant in the expression. With that out of the way, let's go back to where we were - but introduce a value for K_1:

$$[M(H_2O)_5(OH)]^{+}{}_{(aq)} \rightleftharpoons [M(H_2O)_4(OH)_2]_{(3)} + H^{+}{}_{(aq)}$$

$$K_1 = \frac{[\mathrm{Cu(NH_3)(H_2O)_5}^{2+}]}{[\mathrm{Cu(H_2O)_6}^{2+}][\mathrm{NH_3}]}$$

$$= 1.78 \times 10^4\,\mathrm{mol^{-1}\ dm^3}$$

The value of the equilibrium constant is fairly large, suggesting that there is a strong tendency to form the ion containing an ammonia molecule.A high value of a stability constant shows that the ion is easily formed.Each of the other equilibria above also has its own stability constant, K_2, K_3 and K_4. For example, K_2 is given by:

$$[\mathrm{Cu(NH_3H_2O)_5}]^{2+} + \mathrm{NH_3} \rightleftharpoons \left[\mathrm{Cu(NH_3)(H_2O)_4}]^{2+} + \mathrm{H_2O}\right]$$

$$K_2 = \frac{\left[\mathrm{Cu(NH_3)_2(H_2O)_4}^{2+}\right]}{\left[\mathrm{Cu(NH_3)(H_2O)5^{2+}}\right][\mathrm{NH_3}]}$$

$$= 4.07 \times 10^3\,\mathrm{mol^{-1}\,dm^3}$$

The ion with two ammonias is even more stable than the ion with one ammonia.You could keep plugging away at this and come up with the following table of stability constants:

ion	**K_n**	**value ($\mathrm{mol^{-1}\ dm^3}$)**	**log K_n**
$[\mathrm{Cu(NH_3)(H_2O)_5}]^{2+}$	K_1	1.78 x 10^4	4.25
$[\mathrm{Cu(NH_3)_2(H_2O)_4}]^{2+}$	K_2	4.07 x 10^3	3.61
$[\mathrm{Cu(NH_3)_3(H_2O)_3}]^{2+}$	K_3	9.55 x 10^2	2.98
$[\mathrm{Cu(NH_3)_4(H_2O)_2}]^{2+}$	K_4	1.74 x 10^2	2.24

You will often find these values quoted as log K_1 or whatever. The ions keep on getting more stable as you replace up to 4 water molecules, but notice that the equilibrium constants are gradually getting less big as you replace more and more waters. This is common with individual stability constants.

Overall Stability Constants

The overall stability constant is simply the equilibrium constant for the total reaction:

$$\left[Cu(H_2O)_6\right]^{2+} + 4NH_3 \rightleftharpoons \left[Cu(NH_3)_4(H_2O)_2\right]^{2+} + 4H_2O$$

It is given by this expression:

$$\text{overall } K_{stab} = \frac{[Cu(NH_3)_4(H_2O)_2{}^{2+}]}{[Cu(H_2O)_6{}^{2+}]\,[NH_3]^4}$$

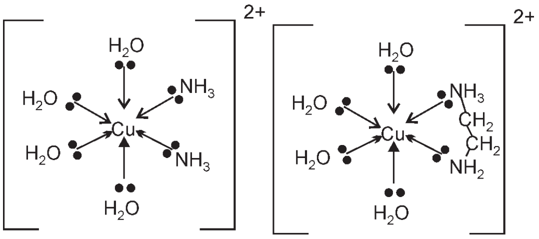
$$= 1.20 \times 10^{13} \ \ mol^{-4} \ dm^{12}$$

Overall this is a very large equilibrium constant, implying a high tendency for the ammonias to replace the waters. The "log" value is 13.1.This overall value is found by multiplying together all the individual values of K_1, K_2 and so on. Write down expressions for all the individual values (the first two are done for you above), and then multiply those expressions together. You will find that all the terms for the intermediate ions cancel out to leave you with the expression for the overall stability constant.Whether you are looking at the replacement of individual water molecules or an overall reaction producing the final complex ion, a stability constant is simply the equilibrium constant for the reaction you are looking at.The larger the value of the stability constant, the further the reaction lies to the right. That implies that complex ions with large stability constants are more stable than ones with smaller ones.

Stability constants tend to be very large numbers. In order to simplify the numbers a "log" scale is often used. Because of the way this works, a difference of 1 in the log value comes from a 10 times difference in the stability constant. A difference of 2 comes from a 100 (in other words, 10^2) times difference in stability constant - and so on.

Stability constants and entropy

This is an effect which happens when you replace water (or other simple ligands) around the central metal ion by multidentate ligands like 1,2-diaminoethane (often abbreviated to "en") or EDTA.Compare what happens if you replace two water molecules around a $[Cu(H_2O)_6]^{2+}$ ion with either 2 ammonia molecules or one molecule of 1,2-diaminoethane.

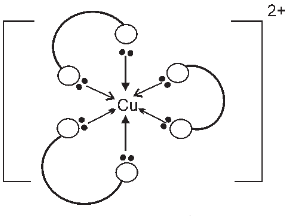


This second structure is known as a *chelate* from a Greek word meaning a crab's claw.

You can picture the copper ion as being nipped by the claw of the 1,2-diaminoethane molecule.Chelates are much more stable than complex ions formed from simple monodentate ligands. The overall stability constants for the two ions are:

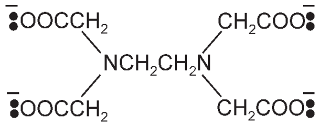
ion	**log K**
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	7.86
$[Cu(H_2O)_4(en)]^{2+}$	10.6

The reaction with the 1,2-diaminoethane could eventually go on to produce a complex ion $[Cu(en)_3]^{2+}$. Simplifying the structure of this:

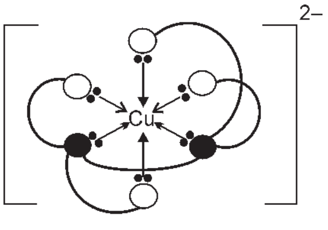


The overall stability constant for this (as log K) is 18.7.

Another copper-based chelate comes from the reaction with EDTA.



the EDTA^{4-} ion



the [Cu(EDTA)]$^{2-}$ ion

This also has a high stability constant - log K is 18.8.

However many examples you take, you always find that a chelate (a complex ion involving multidentate ligands) is more stable than ions with only unidentate ligands. This is known as the *chelate effect*.

The Reason for the Chelate Effect

If you compare the two equilibria below, the one with the 1,2-diaminoethane ("en") has the higher equilibrium (stability) constant.

$$[Cu(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_4]^{2+} + 2H_2O]$$

$$[Cu(H_2O)_6]^{2+} + en \rightleftharpoons [Cu(H_2O)_4(en)]^{2+} + 2H_2O]$$

The enthalpy changes of the two reactions are fairly similar. You might expect this because in each case you are breaking two bonds between copper and oxygen atoms and replacing them by two bonds between copper and nitrogen atoms.If the enthalpy changes are similar, what causes the difference in the extent to which the two reactions happen.You need to think about the *entropy change* during each reaction. Entropy is most easily thought of as a measure of disorder. Any change which increases the amount of disorder increases the tendency of a reaction to happen. If you look again at the two equiilbria, you might notice that the 1,2-diaminoethane equilibrium does lead to an increase in the disorder of the system (an increase in its entropy). There are only two species on the left-hand side of the equation, but three on the right.

$$[\mathrm{Cu}(\mathrm{H_2O})_6]^{2+} + \mathrm{en} \rightleftharpoons [\mathrm{Cu}(\mathrm{H_2O})_4(\mathrm{en})]^{2+} + 2\mathrm{H_2O}]$$

You can obviously get more disorder out of three species than out of only two.Compare that with the other equilibrium. In this case, there is no change in the total number of species before and after reaction, and so no useful contribution to an increase in entropy.

$$[\mathrm{Cu}(\mathrm{H_2O})_6]^{2+} + 2\mathrm{NH_3} \rightleftharpoons [\mathrm{Cu}(\mathrm{NH_3})_2\mathrm{H_2O})_4]^{2+} + 2\mathrm{H_2O}]$$

In the case of the complex with EDTA, the increase in entropy is very pronounced.

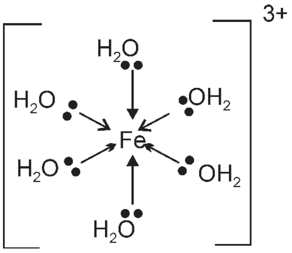
$$[\mathrm{Cu}(\mathrm{H_2O})_6]^{2+} + \mathrm{EDTA}^{4-} \rightleftharpoons \mathrm{Cu(EDTA)}\ ]^{2-} + 6\mathrm{H_2O}$$

Here, we are increasing the number of species present from two on the left-hand side to seven on the right. You can get a major amount of increase in disorder by making this change.Reversing this last change is going to be far more difficult in entropy terms. You would have to move from a highly disordered state to a much more ordered one. That isn't so likely to happen, and so the copper-EDTA complex is very stable.

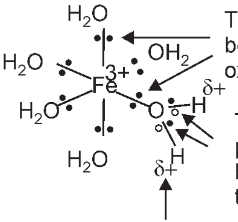
Complexes involving multidentate ligands are more stable than those with only unidentate ligands in them.The underlying reason for this is that each multidentate ligand displaces more than one water molecule. This leads to an increase in the number of species present in the system, and therefore an increase in entropy.An increase in entropy makes the formation of the chelated complex more favourable.

COMPLEX METAL IONS

The pH's of solutions containing hexaaqua ions vary a lot from one metal to another (assuming you are comparing solutions of equal concentrations). However, the underlying explanation is the same for all of them.We'll take the hexaaquairon(III) ion, $[Fe(H_2O)_6]^{3+}$ as typical. The structure of the ion is:



Each of the six water molecules are attached to the central iron(III) ion via a co-ordinate bond using one of the lone pairs on the oxygen.We'll choose one of these water molecules at random (it doesn't make any difference which one!), and look at the bonding in a bit more detail - showing all the bonds around the oxygen.Imagine for the moment that the 3+ charge is located entirely on the iron.



These electron pairs are all being pulled away from the oxygens towards the 3+ ion.

That causes the electron pairs in the O-H bonds to be pulled even doser to the oxygen than normal.

That makes the hydrogen atoms even more positive than they normally are when they are attached to oxygen.

Note: Each oxygen has another lone pair which is left out to avoid even more dutter!

When the lone pairs on the oxygens form co-ordinate bonds with the iron, there is obviously a movement of electrons towards the iron.That has an effect on the electrons in the O-H bonds. These electrons, in turn, get pulled towards the oxygen even more than usual. That leaves the hydrogen nuclei more exposed than normal.The overall effect is that each of the hydrogen atoms is more positive than it is in ordinary water molecules. The 3+ charge is no longer located entirely on the iron but spread out over the whole ion - much of it on the hydrogen atoms.

The hydrogen atoms attached to the water ligands are sufficiently positive that they can be pulled off in a reaction involving water molecules in the solution.The first stage of this process is:

$$[\mathrm{Fe(H_2O)_6}]^{3+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Fe(H_2O)_5(OH)}]^{2-} + \mathrm{H_3O^+}$$

The complex ion is acting as an acid by donating a hydrogen ion to water molecules in the solution.

The water is, of course, acting as a base by accepting the hydrogen ion.Because of the confusing presence of water from two different sources (the ligands and the solution), it is easier to simplify this:

$$[\mathrm{Fe(H_2O)_6}]^{3+}{}_{(aq)} \rightleftharpoons [\mathrm{Fe(H_2O)_5(OH)}]^{2+}{}_{(aq)} + \mathrm{H^+}{}_{(aq)}$$

However, if you write it like this, remember that the hydrogen ion isn't just falling off the complex ion. It is being pulled off by a water molecule in the solution. Whenever you write "$H^+_{(aq)}$" what you really mean is a hydroxonium ion, H_3O^+.The hexaaquairon(III) ion is quite strongly acidic giving solutions with pH's around 1.5, depending on concentration. You can get further loss of hydrogen ions as well, from a second and a third water molecule.

Losing a second hydrogen ion:

$$[\mathrm{Fe(H_2O)_5(OH)}]^{2+}{}_{(aq)} \rightleftharpoons [\mathrm{Fe(H_2O)_4(OH)_2}]^{+}{}_{(aq)} + \mathrm{H^+}{}_{(aq)}$$

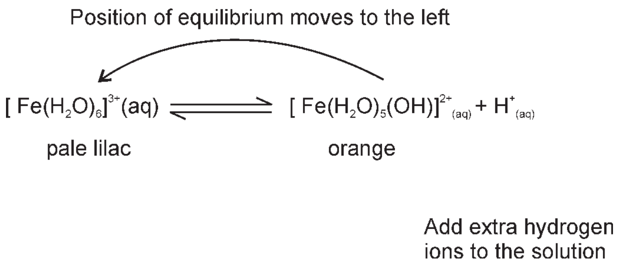
... and a third one:

$$[\mathrm{Fe(H_2O)_4(OH)_2}]^{+}{}_{(aq)} \rightleftharpoons [\mathrm{Fe(H_2O)_3(OH)_3}]_{(3)} + \mathrm{H^+}{}_{(aq)}$$

This time you end up with a complex with no charge on it. This is described as a *neutral complex*. Because it has no charge, it doesn't dissolve in water to any extent, and a precipitate is formed.What do you actually get in solution if you dissolve an iron(III) salt in water?

In fact you get a mixture of all the complexes that you have seen in the equations above. These reactions are all equilibria, so everything will be present. The proportions depend on how concentrated the solution is.The colour of the solution is very variable and depends in part on the concentration of the solution. Dilute solutions containing iron(III) ions can be pale yellow. More concentrated ones are much more orange, and may even produce some orange precipitate.None of these colours represents the true colour of the $[Fe(H_2O)_6]^{3+}$ ion - which is a very pale lilac colour! That colour is only really easy to see in solids containing the ion.The colour of the new complex ion on the right-hand side is so strong that it completely masks the colour of the hexaaqua ion.In concentrated solutions, the equilibrium position will be even further to the right-hand side (Le Chatelier's Principle), and so the colour darkens.

You will also get significant loss of other hydrogen ions leading to some formation of the neutral complex - and so you get some precipitate.You can move the position of this equilibrium by adding extra hydrogen ions from a concentrated acid - for example, by adding concentrated nitric acid to a solution of iron(III) nitrate.The new hydrogen ions push the position of the equilibrium to the left.The colour of the hexaaqua ion. This is slightly easier to follow if you write the simplified version of the equilibrium.



The Effect of Charge on the Acidity of the Hexaaqua Ions

Solutions containing 3+ hexaaqua ions tend to have pH's in the range from 1 to 3. Solutions containing 2+ ions have higher pH's - typically around 5 - 6, although they can go down to about 3.Remember that the reason that these ions are acidic is because of the pull of the electrons towards the positive central ion.

An ion with 3+ charges on it is going to pull the electrons more strongly than one with only 2+ charges.In 3+ ions, the electrons in the O-H bonds will be pulled further away from the hydrogens than in 2+ ions.That means that the hydrogen atoms in the ligand water molecules will have a greater positive charge in a 3+ ion, and so will be more attracted to water molecules in the solution.If they are more attracted, they will be more readily lost - and so the 3+ ions are more acidic.

The Effect of Ionic Radius on Acidity

If you have ions of the same charge, it seems reasonable that the smaller the volume this charge is packed into, the greater the distorting effect on the electrons in the O-H bonds.Ions with the same charge but in a smaller volume (a higher charge density) would be expected to be more acidic.You would therefore expect to find that the smaller the radius of the metal ion, the stronger the acid. Unfortunately, it's not that simple!

pK_a

pK_a is a scale for comparing the strengths of weak acids. All you really need to know for the present topic is that the lower the value of pK_a, the stronger the acid. As a reasonable approximation, if you divide the pK_a value of a weak acid by 2, that will give you the pH of a 1 mol dm^{-3} solution of the acid.

Ionic Radius

A real problem arises here! Almost every data source that you refer to quotes different values for ionic radii. This is because the radius of a metal ion varies depending on what negative ion it is associated with.

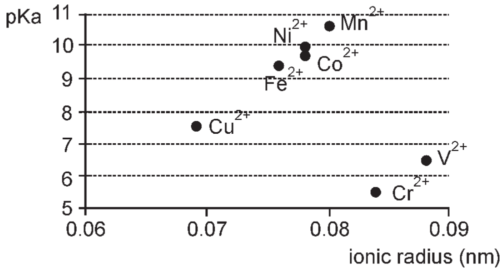
We are interested in what happens when the metal ion is bonded to water molecules, so haven't got simple ions at all! Whatever values we take are unlikely to represent the real situation.In the graphs which follow values for ionic radii.

The Graphs

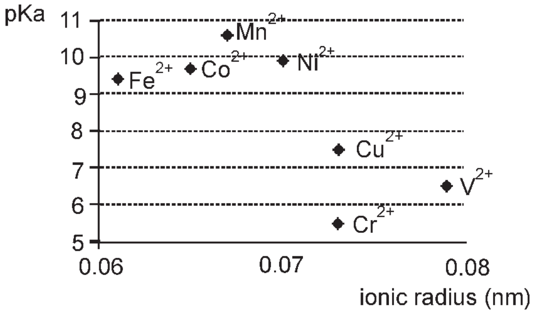
If it is true that the smaller the ionic radius, the stronger the acidity of the hexaaqua ion, you would expect some sort of regular increase in pK_a (showing weaker acids) as ionic radius increases.

The following graphs plot pK_a against ionic radii for the 2+ ions of the elements in the first transition series from vanadium to copper.

The first graph plots pK_a against ionic radii.



There is a trend for several of the ions, but it is completely broken by vanadium and chromium.The second graph uses ionic radii.



A Final Comment

During the couple of weeks I spent trying to understand this, I failed completely. The only conclusion I came to is that there probably is a relationship between ionic radius and acid strength. The problem is that there are other more important effects operating as well (quite apart from differences in charge) and these can completely swamp the effect of the changes in ionic radius. You have to look in far more detail at the bonding in the hexaaqua ions and the product ions. This is all just too difficult to understand at this level. In fact, to be honest, I did wonder while I was researching this whether *anyone* really understood all of this! There is, of course, no reason why they should - it is nonsense to think that we can explain everything in chemistry at the present moment.

7

The Separation of Isotopes

Early attempts towards the separation of isotopes were motivated by theoretical interests and met with indifferent success. The examination of nonradioactive elements, notably neon, by Thomson's parabola method demonstrated that isotopic species were separable. It will be recalled that, in connection with this same method, Aston partly separated neon into two fractions of different atomic weights by repeated diffusion. Historically this was the first successful attempt at isotopic concentration. These and other experiments which followed demonstrated the feasibility of utilizing variation in mass as a means of isotopic separation. However, the early methods, involving inadequate equipment, laborious effort, and small amounts of materials, resulted, at best, in only a slight enrichment of isotopic species. It was not until the discovery, in 1939, that U^{235} was a fissionable material and, as later revealed, capable of a chain reaction, that sufficient impetus was attained to develop and to explore the possibilities of isotopic separation with improved macromethods.

Beginning with 1939, and in succeeding years, scientists were early in recognizing that the scarce isotope, uranium-135, is the key material for the production of destructive atomic weapons and for the utilization of nuclear power. Therefore the stimulus of war-nurtured research produced greater strides in the development of effective methods for isotopic separation than might normally have been expected. Despite the fact that the incentive for developing efficient macromethods for isotopic separation was provided by military exigencies, it is quite likely that the contributions to human welfare resulting from the use of isotopes will outweigh their use in preparing destructive weapons.

The most important applications of isotopes are as tracers in investigating some of the fundamental problems in the various sciences. The characteristic property of a particular isotope is its mass or, for a radioactive isotope, its radioactivity. Either of these properties may serve as a "label" or a "tag" permitting the isotopic species to be followed through a series of chemical or physical changes. Not only is tracer research important to the chemist in following the course of a chemical reaction or in establishing the chemical constitution of a compound, but it is of even greater importance to the biologist and physiologist in their investigations of metabolic processes. The possibilities of use for isotopes as tracer elements are too numerous to mention here, but a partial survey of these uses is to be found in.

Factors Affecting the Separation of Isotopes

By definition the isotopes of an element vary in mass but not in chemical properties. It would appear, therefore, that the only methods which might be applied to isotopic separation would be physical methods depending entirely on properties related to mass. We shall find later that this interpretation is not entirely true, inasmuch as isotopes can also be separated by chemical means. This does not imply that isotopes of the same element can differ chemically, but rather that there are slight differences in their reaction rates.

The theoretical principles which can be put into practice to produce separation among particles upon the basis of mass alone are few in number. Obviously they must be related to the physical properties of the particles themselves. One such property is that of motion, which is related to mass in terms of kinetic energy. In this relationship kinetic energy is defined as $\frac{1}{2}mv^2$, where m is the mass and v is the speed of the particle. Thus in a gas composed of a mixture of two isotopes the average kinetic energy of the light molecules and of the heavy ones is the same. Accordingly, if the average kinetic energies are the same, the average speeds of the lighter molecules must be greater than those of the heavier molecules. Consequently any process depending upon the average speed of molecules should produce separation in particles varying in mass. The separation factor in such a process will always be small because the average speed is inversely proportional to the square root of the mass and mass differences between isotopes, except for the very light elements, are always slight.

Atoms and molecules are subject to gravitational fields, and the gravitational force acting upon a particle is proportional to its mass. We know that the heavier molecules of the atmosphere are, in proportion, more highly concentrated at lower levels than the lighter molecules, but the earth's gravity alone is quite ineffectual in producing any appreciable separation. Pseudogravitational forces of large magnitude may be secured by means of a high-speed centrifuge, and, in theory, this method of separation should be quite effective.

Particles existing in a gaseous form may be ionized by subjecting them to an electric discharge, and the movement of the resulting ions can be influenced by electric and magnetic fields. This principle is employed in the mass spectrograph, and when the process is converted from a microgram to a kilogram basis, it becomes an effective method for separating isotopes.

Isotopes of the same element may differ appreciably in their chemical reactivities. The difference is more pronounced among isotopes of the lighter elements, as, for example, hydrogen and deuterium. Furthermore the slight variation in chemical reactivity affects the reaction rates of isotopic molecules. If two isotopic forms of an element were equally reactive, the equilibrium constant of a reaction involving both isotopes would be unity. However, the fact that the reactivities are different results in equilibrium constants which are not unity.

Thus it is possible, in certain cases, for an isotope of a light element in chemical combination to exchange with another isotope of the same element in another chemical compound. If the equilibrium constant of the reaction is not unity, the reaction may be utilized for the concentration or separation of isotopes. Such reactions are designated as *chemical-exchange reactions,* and they form the basis for the most widely used method of concentrating isotopes. Although a number of methods for the separation of isotopes are described in this chapter, there are only four factors to be considered in devising a separation process.

These factors, which have been discussed in the preceding paragraphs, are enumerated again as follows:

1. At a given temperature, gaseous molecules, regardless of mass, have the same average kinetic energy;
2. The gravitational or centrifugal forces acting upon a particle of matter are directly proportional to its mass;
3. The electric or magnetic forces affecting ionized atoms or molecules follow Coulomb's laws for these forces
4. Among the lighter elements isotopic species may vary slightly in their chemical reactivities.

The Separation Factor

The extent to which a mixture of two isotopes may be separated in one stage of a particular process is called the *separation factor.* It is a ratio of the relative concentration of the desired isotope after processing to its relative concentration before processing. The factor, therefore, is a quantitative value for a one-stage process indicating the efficiency of the separation. In mathematical notation, if n_1 and n_2 are the numbers (or moles) of light and heavy species in a mixture before processing and N_1 and N_2 are the corresponding quantities after processing, in a one-stage process, the separation factor s may be indicated as,

$$s = \frac{N_1 / N_2}{n_1 / n_2}.$$

The size of the separation factor indicates the effectiveness of the separation. Usually this factor is only slightly greater than unity, and consequently a useful separation process is a composite of many single separation stages. In such a case the separation factor is s for each stage, and if the entire process consists of x stages, then the over-all separation factor is expressed as s^x. Several thousand stages are sometimes necessary for effective separation of isotopic species.

The Gaseous-diffusion Method

It was pointed out that the average kinetic energy of all molecules is $\frac{1}{2}mv^2$ at a given temperature; therefore two different molecules with masses m_1 and m_2 will have velocities v_1 and v_2, and the kinetic energy of one molecule is equal to that of the other, as indicated by the equation

$$\frac{1}{2}m_1 v_1^2 = \frac{1}{2}m_2 v_2^2.$$

The Equation may be Rearranged as Follows

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}.$$

This is a mathematical statement of Graham's law of diffusion, discovered in 1892, which states that the rates at which different gases diffuse at the same temperature are inversely proportional to the square roots of their densities. In the above equation mass is substituted for density, since the two terms are directly proportional to each other.

The word *diffusion* may be used to describe the passage of gases through a porous barrier. Accordingly, from Graham's law of diffusion, it may be deduced that a light gas will diffuse, or pass through a porous barrier, more rapidly than a heavy one. This principle was the basis for Aston's partial separation of the isotopes of neon in 1913.

Later, between 1916 and 1921, W. D. Harkins at the University of Chicago applied the same principle of gaseous diffusion in an attempt to separate gaseous HCl into two fractions containing enriched proportions of the two isotopes of chlorine, Cl^{35} and Cl^{37}. Five years after attacking the problem, he reported the separation of a heavy fraction with an atomic weight 0.055 greater than that of ordinary chlorine.

Theoretically the rate of diffusion of an ideal gas through an ideal porous barrier is inversely proportional to the square root of its mass. If a gas consisting of two isotopes passes through a barrier into an evacuated container, the lighter isotope diffuses more rapidly than the heavier and, for a very short period of time, the relative concentration of the lighter isotope in the container is greater than on the other side of the barrier. For example, if hydrogen gas containing a mixture of protium and deuterium, H_2 and D_2, is passed through a barrier, the separation factor is,

$$s = \sqrt{4/2} = 1.414 .$$

However, if the process is allowed to continue indefinitely, equilibrium will be established, and the composition of the gas will be the same on both sides of the barrier. Even though the diffusate (the gas passing through the barrier) is removed from the container by means of a pump, the relative amount of the heavier isotope passing through the barrier will increase, since the gas is progressively being impoverished of the lighter isotope. Successful separations have been accomplished by using.

A cascade (many successive diffusion stages) in which only one half of the gas passing through the barrier of any given stage is passed along to the next higher stage, the other half being returned to the earlier stage. This removal of one-half of the diffusate for recycling represents a compromise for those factors involving the quantity of gas permitted to diffuse, the time required to reach equilibrium, the extent of impoverishment of the gas by removal of the lighter isotope, and the over-all enrichment factor per stage for the entire process.

The efficiency of the diffusion process was greatly increased by G. Hertz in 1932. By incorporating the porous barriers in series with a large number of mercury-diffusion pumps he employed a recycling process which avoided some of the difficulties inherent in the Harkins procedures. The pumping and diffusing units, operating under reduced pressures, were so arranged that the heavier and lighter constituents accumulated at opposite ends of the system.

The first Hertz system, utilizing 24 pumps, separated neon into two fractions which differed by 1.4 units of atomic weight. Later, a 50-pump system produced two fractions of neon, Ne^{20} and Ne^{22}, which were spectroscopically pure, and accomplished a complete separation of protium and deuterium. Diagrammatic representation of the Hertz system, showing four diffusion units within the multiunit process. If we consider these four units as a process for separation, then the original gas enters at the lower right and the pumping system is so designed that only one half of the gas passes through barrier No. 1. The other half returns to mix with the entering gas. The diffusate, slightly enriched with the lighter isotope, passes on to barrier No. 2.

Again, only one half of the gas is permitted to pass through the diffusion barrier, the other half being recycled back to the gas entering barrier No. 2. The diffusate from barrier No. 2 is passed on to diffusion barrier No. 3, where the pumping system again divides the gas into halves, one half being diffused through the barrier and the other half being recycled.

This process is continued through all the diffusion stages, each diffusate being slightly enriched with the lighter isotope. The Hertz process used a closed system, so that after a period of operation an equilibrium condition was reached with the gas enriched in the lighter isotope collected at one end of the system and the gas enriched in the heavier isotope accumulated at the other end. In this process the total separation factor increases exponentially with the number of units, so that, theoretically, any degree of separation can be obtained by adding sufficient units.

As has been mentioned before, the key material for the production of atomic weapons and the development of nuclear power is the fissionable isotope of uranium, U^{235}. Uranium, as it occurs in nature, contains three isotopes, U^{238}, U^{235}, and U^{234}, and the values of their abundance are 99.3, 0.7, and 0.006 per cent, respectively. The amount of the 234 isotope is so small that it can be ignored, but most uses of uranium require that it be considerably enriched in the 235 isotope. For the preparation of nuclear weapons the fissionable material must be practically pure. Consequently one of the major engineering problems has been the development of a system, or systems, for isolating U^{235} from natural uranium.

Since uranium combines with fluorine to form uranium hexafluoride, UF_6, which, although a solid at room temperature, is vapourized at atmospheric pressure above 56°C, it is obvious that one of the first methods to be used for the enrichment of U^{235} is that of fractional diffusion. Moreover, the fact that fluorine has only a single isotope, F^{19}, reduces the separation process of the uranium hexafluoride gas to the isotopes of uranium. The molecular weights of the two isotopic forms of uranium hexafluoride are 352 and 349; therefore, the maximum separation factor for a diffusion stage is,

$$s = \sqrt{352/349} = 1.0043\,.$$

As has been explained earlier in this section, the maximum diffusion factor can never be realised, and, in practice, it has been found that maximum efficiency is obtained by using a cascade system and recycling one-half of the gas from each stage back to the previous stage. The first experimental separation of uranium hexafluorides by E. T. Booth, H. C. Paxton, and C. B. Slade, at Columbia University, indicated that the actual separation factor was approximately 1.0014. Upon a basis of this revised value it would require approximately 4,000 diffusion stages to produce 99 per cent pure $U^{235}F_6$ from uranium hexafluoride derived from natural uranium.

A gaseous-diffusion plant with this many stages must of necessity be a huge, sprawling structure. The one built by the government at Oak Ridge, Tenn., during World War II covers an area of over 100 acres and is approximately four stories high. It requires a power plant supplying nearly ¼ million kw of power and steam.

The cost of the entire installation was about 500 million dollars. In spite of the enormous size of this plant its output, in terms of weight, is comparatively small. The handling of large volumes of gases at low pressures necessitates a largevolume process, but when the gaseous product is converted into terms of weight, the value must necessarily be small.

In addition to the disadvantage of the large-volume process with a small weight yield the engineering problems of handling a highly reactive, poisonous, and corrosive gas made necessary the development of special pumps, nonreactive lubricants, and noncorrosive diffusion barriers. It might be added that the barriers not only had to be corrosion-resistant but also had to be mechanically strong, and uniform as to their pore structure. To ensure true diffusion, the diameter of the holes in the barriers had to be less than one-tenth the mean free path of the molecules. Or, in other words, the pores could not be larger than one-tenth of the average distance that a gas molecule travels before it collides with another molecule. The maximum size permitted for these holes was calculated as being approximately one-millionth of a centimeter in diameter.

The huge diffusion plant at Oak Ridge, Tenn., was put into successful operation before the summer of 1945. It represents one of the greatest technical achievements in the history of mankind. This particular plant was designed and built for the purpose of separating the isotopes of uranium; yet, if the necessity should arise, there is no reason why the same general process could not be utilized for the separation of the isotopes of other elements.

The Electromagnetic Method

In fact the electromagnetic method is simply the utilization of a giant mass spectrograph for the separation of appreciable quantities of isotopes. An oversimplification of the method would be to describe it as a macroseparation of isotopes, using essentially the principle of the early Dempster mass spectrograph. The electromagnetic method was the first to yield appreciable amounts of U^{235} for experimental purposes in the early stages of the wartime atomic-energy project.

In the electromagnetic method of separating U^{235} and U^{238} a salt of uranium containing the two isotopes is vapourized and passed through an electric are which produces positively charged uranium ions. The ions are accelerated by an electric field and converted, by means of slits, into a beam. The beam of ions is directed into a magnetic field produced by the poles of a powerful electromagnet.

The ions have practically the same kinetic energy, but since the two isotopes differ in mass, their resulting ions also differ in this respect. As a result of mass differences the ions of the lighter isotope move faster than those of the heavier one. Within the magnetic field all ions are forced into curved paths, but the curved paths are of different radii, depending, again, upon mass. The lighter ions are affected less by the magnetic field than the heavier ones and therefore follow paths of least curvature. Suitable containers are placed at the proper locations to collect the separated isotopes. The entire process is carried out in a high vacuum. The electromagnetic method has a high separation factor, but the operation is not so simple as the description and the sketch might lead one to believe. In developing this process three limitations as to the amount of material that could be handled were encountered: First it is difficult to produce a large quantity of gaseous ions, and if they are produced, the actual weight of material in the total volume of the gaseous ions will be small. Second, in producing the narrow beam by means of a slit system, only a small fraction of the total ions can be utilized. Third, as the quantity of material in the beam is increased, there is a corresponding increase in space-charge effects which interfere with the separating action.

The first large-scale research attempt to improve the design of this method in such a manner as to minimize the foregoing limitations was performed by E. O. Lawrence and his coworkers at the University of California. His first apparatus was built around a 37-in. electromagnet removed from a cyclotron, and was called a *calutron,* a contraction of *California University cyclotron.* It is interesting to note that the huge electromagnetic separators now in use at Oak Ridge, Tenn., are still referred to as calutrons. With his experimental apparatus Lawrence was able to overcome the early limitations of the method and also to prove that this method was entirely feasible for efficient separation of isotopes. Construction of the first large-scale electromagnetic units at Oak Ridge began in March, 1943, and they were ready for operation in November, 1943.

It was soon realised that the efficiency of the method could be greatly increased if an enriched material were fed into the units. Thus, in the summer of 1944, a thermal-diffusion separation plant was built to furnish enriched feed material for the electromagnetic process and thereby increase the over-all rate of production of pure uranium-235.

On a commercial scale this process requires enormous amounts of electric power, and complex electrical and mechanical equipment are necessary for its control. The electromagnetic plant at Oak Ridge consists of 175 buildings, which cost more than 300 million dollars. In addition the electromagnets were wound with more than 14,000 tons of pure silver, valued at approximately 400 million dollars. Therefore this plant actually cost more than the gaseous-diffusion plant. The large electromagnetic separators are no longer used for separating isotopes of uranium but are now utilized for the separation of isotopes of a large number of elements throughout the periodic table. Since many elements contain several isotopes, it is often necessary to use more than the two collecting containers indicated in figure.

A large number of isotopes are now available for research purposes, and it is possible, as was stated in the introduction to this subtopic, that the results from the use of these tracer isotopes, in solving problems bearing on life processes, may more than repay the cost of building the electromagnetic separation units.

The Thermal-diffusion Method

The kinetic theory of gases has unduly occupied the attention of theoretical chemists and physicists over an extensive period in the development of the modern concepts of science. It is perhaps for this reason that the mathematical theory underlying the thermal-diffusion method was worked out by D. Enskog of Sweden and S. Chapman of England prior to 1920. Upon theoretical principles Enskog predicted that the application of a temperature gradient to a gaseous mixture of molecules of different masses should cause a small gradient in the relative concentrations of the components.

According to this theory the heavier molecules should tend to diffuse towards the region of lower temperature and the lighter molecules to the region of heavier temperature. These two movements should continue until the thermal-diffusion process is counterbalanced by the effect of ordinary diffusion. Chapman had suggested that thermal diffusion might be used to separate isotopes.

He even went so far as to work out, on a theoretical basis, the separation factor for the two isotopes of neon if this gas were placed in a vessel consisting of two bulbs connected by a tube, the two bulbs being maintained at certain definite, but different, temperatures.

The possibility of isotopic separation by means of thermal diffusion was elevated from mathematical speculation to practical importance in 1938 by the experiments of K. Clusius and G. Dickel in Germany.

Their apparatus consisted of a vertical tube, about 3 m in length and 1 cm in diameter, cooled by water on the outside and with a heated platinum wire along the inner axis. Figure is a schematic representation of a thermal-diffusion column.

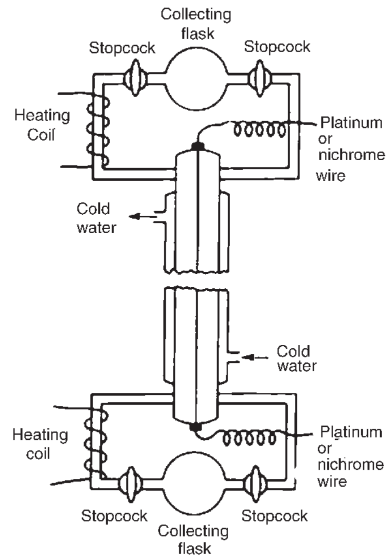


Fig. Sketch of Thermal-diffusion Apparatus for Separation of Isotopes.

By means of this apparatus they discovered that, not only does thermal diffusion take place as predicted by theory, but convection currents, naturally caused by the temperature gradient, instead of hindering the fractional separation actually assisted it to a remarkable degree. Using a temperature difference of 600°C between the wire and the outer surface of the tube, they were able to report definite separation of both the neon and the chlorine isotopes.

Returning to figure the central wire, made of platinum or nichrome, is heated electrically, whereas the glass tube is cooled by an outside jacket carrying a constant flow of cold water. Thermal diffusion causes a concentration of the light isotope around the hot wire, and ordinary convection currents carry these molecules upward. At the same time a similar process causes the accumulation of the heavy isotope near the cool surface of the tube, the molecules of which are carried by convection currents to the lower portion of the tube. Consequently, after a period of time, the gas in the upper part of the tube is enriched with the lighter isotope and that in the lower with the heavier isotope. It should be noted that the length of the column must be quite large as compared with its width; otherwise, ordinary diffusion will tend to restore the gas to a uniform concentration. Either isotopic fraction may be removed by means of two collecting flasks attached by tubing to either end of the fractionating column. The flasks are filled by heating one of the connecting tubes with a heating coil. This continues the convective circulation from the column into, and through, the flask.

Where a high separation factor is desired, several fractionating columns may be connected in series. In such a series the bottom of each unit is connected to the top of the next one by a closed loop of glass tubing.

The reason underlying the thermal-diffusion effect is the transfer of momentum from one molecule to another; for different gases the effect may vary widely. It is greatest for noble gases, whose molecules behave as hard spheres with short-range repulsive forces decreasing as a very large power of the inverse of the distance between atoms.

The effect disappears for soft molecules, such as hydrogen chloride, with repulsive forces varying as the inverse fifth power of the distance. The method of thermal diffusion may also be applied to pure liquids or solutions, but the separation factors in these cases are usually small. Certainly the analysis of molecular attraction in liquids is extremely complicated and almost unpredictable.

A large-scale thermal-diffusion plant was built at Oak Ridge, Tenn., during the summer of 1944 for the specific purpose of furnishing uranium hexafluoride, enriched with the U^{235} isotope, to the electromagnetic process. Uranium hexafluoride is a liquid at temperatures below 56°C, and the plant at Oak Ridge was designed for the thermal diffusion of this liquid. The thermal-diffusion process lends itself to a continuous process, but a large-capacity output cannot be attained because of the very small spacing allowed in the diffusion columns. As far as separating the isotopes of uranium, the thermal-diffusion process is much less efficient than the gaseous-diffusion method. Consequently the commercial plant at Oak Ridge was operated only for a short time. On the other hand the thermal-diffusion method seems quite ideal for isotopic enrichment on a laboratory scale, inasmuch as the apparatus is readily and cheaply constructed and needs little attention while in operation.

Distillation Methods

Isotopes of the same element vary slightly in their physical properties. This variation results from nuclear mass differences and consequently is more pronounced among isotopes of the lighter elements.

The possibility of separating isotopes by means of the difference in their vapour pressures, *i.e.*, their boiling points, was predicted by F. A. Lindemann, in 1919, upon theoretical grounds. According to this theory the surface of a liquid acts as a porous diaphragm, and the rate of escape for two or more isotopes is inversely proportional to the square root of their masses. Applying this theory to a method of ideal distillation, J. N. Brønsted and G. von Hevesy, in 1922, achieved a slight enrichment of the isotopes of mercury.

One form of their apparatus is sketched in figure Mercury was evaporated in a partial vacuum at 40 to 60°C between the walls of a Dewar flask. The inner vessel was cooled with liquid air, placed about 1 to 2 cm above the mercury. This distance is approximately equal to the mean free path of the mercury leaving the surface. Under these conditions there is an absence of collisions, and all the atoms which evaporate condense on the cold surface.

After about one-fourth of the mercury had evaporated, the condensate and residue were separated. The condensate was allowed to melt and then partially evaporated again. After several fractionations in this manner a slight enrichment of the lighter isotope was to be found in the final condensate, whereas a similar enrichment of the heavy isotope occurred in the residue. The use of improved techniques, employing the same ideal distillation principle, has resulted in partial fractionation of the isotopes of chlorine, zinc, and potassium.

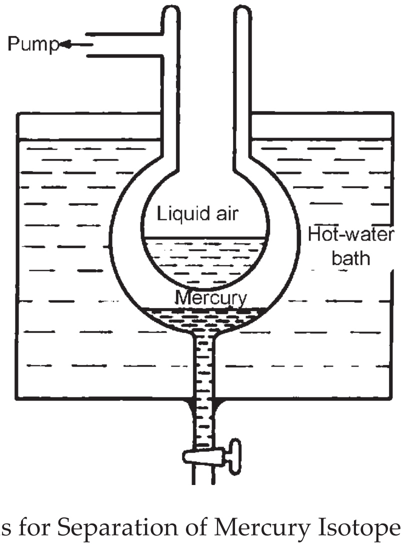


Fig. Apparatus for Separation of Mercury Isotopes.

Enrichment of isotopes for some of the lighter elements and their compounds has been accomplished by means of efficient fractionating columns where there are sufficient differences in vapour pressures (boiling points). H. C. Urey and his collaborators obtained evidence of deuterium through the distillation of liquid hydrogen at its triple point. A slight enrichment in the concentration of O^{18} has been secured by the distillation of liquid oxygen. Heavy water, D_2O, boils at a temperature 1.42°C higher than ordinary water, H_2O. The most efficient process for the enrichment of D_2O by distillation utilizes a fractionating column for a continuous process, in which an upward-directed stream of vapour is kept in contact with a downward-directed stream of liquid, the two streams constantly exchanging molecules. The molecules of H_2O have a relatively greater tendency to get into the vapour stream, and the molecules of D_2O into the liquid.

During the development of the atomic project of World War II it was at first thought that heavy water would be necessary for use as a moderator; consequently a plant for the enrichment of D_2O by distillation of water was built in 1943. However, this plant operated for less than a year, the distillation process being replaced by a more economical method of producing D_2O through a chemical-exchange reaction. Furthermore it was later learned that graphite, being a solid, was more convenient to use as a moderator, and the need for large quantities of heavy water never materialized.

The Centrifugal Method

The gravitational force acting upon atoms and molecules, tending to move them downward, is proportional to their masses. Therefore, if a mixture of two isotopes of the same element in gaseous or liquid state is subjected to a gravitational field, the heavier isotope will tend to concentrate in the direction of the field and, if there is no mixing to counteract this movement, separation will take place.

The extent of separation which may be accomplished by this force is dependent upon the *mass difference* between the two isotopes, and not on their ratio. This differs from diffusion methods, where the separation factor is dependent upon the square root of the ratio of the masses. In theory it has the attractive feature that the separation is fully as effective for isotopes of the heavier elements as for the lighter ones. Accordingly a better separation should be obtained for the isotopes of U^{235} and U^{238}, with a mass difference of three units, that for the isotopes of hydrogen, protium, and deuterium, which have a mass difference of one unit. Moreover the difference between the masses of two isotopes is a constant value, and the efficiency of the separation is not affected by the molecular weight of the compound whose vapour is being subjected to gravitational force.

The centrifuge is essentially a method of applying pseudogravitational forces of large magnitude, and the possibility of separation of isotopes by its use was predicted as early as 1921 by Lindemann and Aston. However, the first experiments with the centrifuge for this purpose, by Joly and Poole, produced no positive results, probably because the speed of their centrifuge was too low. It was not until 1939 that successful enrichment of isotopes by centrifugation was accomplished. Using an air-driven, self-balancing vacuum-type centrifuge, producing a force several hundred thousand times greater than gravity, J. W. Beams and C. Skarstrom [1] obtained an appreciable separation of chlorine isotopes, using carbon tetrachloride as the test liquid.

In the early stages of the atomic-energy project the use of the centrifuge for the separation of the U^{235} and U^{238} isotopes seemed quite promising, especially since these two isotopes have a mass difference of three units. At the suggestion of H. C. Urey tall cylindrical centrifuges with countercurrent flow were developed for this particular separation. In a centrifuge of this description a downward flow of vapour takes place at the periphery of the rotating cylinder and an upward current along its axis. Across the interface region there is a constant diffusion of both types of molecules, containing heavy and light isotopes, between the two currents of gases.

Thus each molecule travels along the periphery for a short distance, then diffuses over to the axis, where it again moves for a short distance in the opposite direction. However, the radial-force field of the centrifuge acts more strongly on the heavy molecules than on the lighter ones, causing an increase in the concentration of the heavier molecules in the peripheral region. A similar concentration of the lighter molecules takes place in the axial region. The lighter isotopic species is withdrawn from the top of the cylinder, near the centre, and the heavier species is removed at the bottom, near the periphery.

A pilot plant for the separation of uranium isotopes by centrifugation was constructed during the war at Bayway, N.J. Although it was operated successfully and gave approximately the degree of separation predicted by theory, no large-scale production was ever attempted. Apparently the magnitude of the engineering problems involved in erecting a large-scale production plant discouraged the development of this process.

The Electrolytic Method

This method is used only for the separation of the two naturally occurring isotopes of hydrogen. The heavier of these isotopes, with a mass number of 2, has been named *deuterium* and given the symbol D. It is the only isotope of any element to be given a special name, and this distinction arises from the fact that its physical properties are somewhat different from those of light hydrogen. The relative abundances of ordinary hydrogen and deuterium in nature are 99.9844 per cent and 0.0156 per cent, respectively. The prediction of the existence of deuterium in nature, queer as it may seem, was the result of an unrecognized and unevaluated error in the estimation of the atomic weight of hydrogen with the mass spectrograph. Aston's value, as determined in 1927 by spectrographic means and based on the standard of O = 16.00000, was 1.00778, which was in excellent agreement with the chemically determined value of 1.00780. However, in 1929, when Giauque and Johnson discovered that oxygen existed as three isotopes, O^{16}, O^{17}, and O^{18} in the relative abundance ratios of 3,150:1:5, respectively, it became apparent that the average atomic weight of the isotopic mixture was 16.0044.

When the chemical atomic weight of hydrogen was changed from the standard of O = 16.0000 to O = 16.0044, a value of 1.00806 was obtained, which is 0.00028 mass unit higher than that obtained by Aston with the mass spectrograph. This discrepancy could be accounted for by assuming that ordinary hydrogen contained a heavier isotope with a mass number of 2 in a concentration of approximately 1 part in 5,000. It was later learned that the error in Aston's method of estimating the atomic weight of hydrogen was greater than this discrepancy. Fortunately, unaware of this possible error, H. C. Urey began his famous and thorough search which resulted in the discovery of heavy hydrogen and for which he received the Nobel prize in 1934. In collaboration with F. G. Brickwedde and G. M. Murphy he subjected liquid hydrogen to continuous fractionation, then, by optical means, demonstrated the presence of an isotope with a mass very close to 2 within the residue.

The suggestion that isotopes might be separable by electrolysis was made as early as 1923 by J. Kendall and E. D. Crittenden, but no positive results were obtained until H. C. Urey and E. W. Washburn obtained an enrichment of deuterium oxide in water by this method in 1932. Their successful experiment led to an examination of many industrial electrolytic processes in which deuterium oxide was found in various degrees of enrichment.

It at once became apparent that in the electrolysis of aqueous solutions, irrespective of whether they are acid or alkaline, the lighter isotope of hydrogen is evolved more readily than the heavier one, resulting in an accumulation of the heavier isotope in the residual solution. In 1933 G. N. Lewis and his collaborators at the University of California succeeded, by the continuous electrolysis of a very large amount of water obtained from an old commercial electrolytic cell, in preparing about 1/10 cc of water which contained practically only deuterium atoms of mass 2. The specific gravity of this water was about 10 per cent greater than that of ordinary water, which was in accordance with the molecular weight of D_2O. The discovery that deuterium oxide can be produced by electrolysis stimulated considerable investigations in this field. The electrolytic production of pure deuterium and deuterium oxide is now carried out commercially in Norway, where electric power is relatively inexpensive.

The current consumption is quite high; about 130,000 amp-hr is required to obtain 1 g of heavy water, which indicates that the process is feasible only where electric power is cheap and plentiful. In practice the electrolysis of an aqueous solution is not a continuous decomposition, from a large volume to that of a small residual solution, because of the loss of deuterium with the gaseous products. Also, the presence of an electrolyte would prevent concentration to a very small volume. Consequently the most successful separations have employed several stages in the electrolytic process.

In the procedure most frequently used a solution of 0.5 M sodium hydroxide is subjected to electrolysis until it is reduced to about onetenth its initial volume. The concentrated alkaline solution resulting from this operation is neutralized with carbon dioxide and then distilled to remove the carbonate. The enriched distillate is carried to the next stage of electrolysis, where the same procedure is repeated.

A succession of electrolytic stages produces an increasing concentration of deuterium in the residual solution. After about three stages the hydrogen which is evolved in the electrolysis contains a sufficient amount of deuterium to justify the latter's recovery. This is accomplished by burning the gases and returning the condensed products to the system at the preceding stage of electrolysis. About seven stages are required to yield fairly pure deuterium oxide. The progress of enrichment which may be expected in a succession of electrolyses is indicated in table.

Table. Concentration of Deuterium by Electrolysis

Stage of deuterium d^{20}_{4}	**Liters of solution in residue**	**electrolysis**	**Density of electrolyzed**	**Per cent of residue,**
1	2,300	0.998	0.03	
2	340	0.999	0.5	
3	52	1.001	2.5	
4	10	1.007	8.0	
5	2	1.031	30.0	
6	0.42	1.098	93.0	
7	0.08	1.104	99.0	

The electrolytic method has not been very successful in the separation of isotopes of elements other than hydrogen. The electrolysis of lithium salts, in successive stages, has resulted in a slight separation of the isotopes of this element. In the enrichment of deuterium oxide in water there should be, at the same time, an enrichment of the O^{18} isotope of oxygen. Such an increase in the O^{18} isotope has been verified experimentally, but the separation factor is extremely small. H. L. Johnson.

Has computed that a volume reduction sufficient to convert ordinary water to a residue 99 per cent in D_2O will enrich the residue with O^{18} to the extent of only 20 ppm in the density of water. Furthermore he concludes that, if the entire ocean were reduced, by electrolysis, to a volume of 1 cc, the concentration of the heavy isotopes of oxygen would be less than doubled.

Chemical-exchange Methods

It was stated that the chemical properties of isotopes of the same element were, as a rule, practically identical but that in some cases there seem to be slight differences in reactivity. These differences appear as differences in reaction rates and are evident in the equilibrium constants of isotopic-exchange reactions.

The differences in the reactivities of isotopic molecules have been ascribed to differences in the energies that, such molecules possess at absolute zero. It is believed that the natural vibration frequency of atoms in a molecule depends to some extent upon the mass of the atoms involved, and this vibration frequency affects the energy of the molecule at absolute zero. This energy is frequently denoted the zero-point energy, and differences in zero-point energies produce differences in activation energies.

It is beyond the scope of our study to explore the theoretical aspects of zero-point energies, but chemical affinity within an isotopic molecule is related to the mass of the isotope present. As might be expected, the greatest difference in chemical reactivity of any isotopes of the same element is exhibited in hydrogen and deuterium. The difference in chemical behaviour of isotopes resulting from a difference in mass is called the isotope effect.

This effect, which is notable in hydrogen and perceptible in the lighter elements, becomes very feeble or disappears in the heavier elements. For those elements in which it does appear the isotope effect maybe utilized as a method for isotopic enrichment. Such a process is known as a chemical-exchange method.

Not only may differences in mass produce differences in chemical reactivity among isotopic atoms, but the mass of such atoms should affect both the velocity and vibrational energy of a molecule. Thus we shall have occasion to use the term *isotopic molecules*, which may be defined as molecules that are identical in chemical and structural formulas but different in their isotopic composition. Inasmuch as there is a difference in chemical reactivity among isotopic atoms, it is not surprising that there is likewise a difference in such activity among isotopic molecules containing the lighter atoms. Furthermore, at the same temperature, heavier isotopic molecules have lower velocities and undergo fewer collisions than lighter ones.

This change in activity is proportional to the square root of the ratio of the masses of the molecules. Heavier molecules also require more energy for dissociation than lighter ones; therefore isotopic molecules may be expected to undergo chemical transformations at different rates. Consequently, if two isotopic molecules with different reaction rates are involved in a chemical reaction, the equilibrium constant for the molecular reaction will not be unity. Therefore it is possible, under certain conditions. for an isotope of a light element in chemical combination to exchange with another isotope of the same element in another chemical compound. The use of chemical-exchange reactions has become the most widely exploited of the various methods for concentrating the isotopes of the lighter elements.

In using the chemical-exchange method to produce an isotopic enrichment it is necessary to exploit an equilibrium reaction involving two isotopes of the same element, in which the isotopic distribution is not the same as would have been the case if the two isotopes had identical reactivities. For example, the equilibrium between gaseous carbon dioxide and the bicarbonate ion in sodium bicarbonate solution,

$$C^{13}O_2 + HC^{12}O_3^- \rightleftharpoons C^{12}O_2 + HC^{13}O_3^-$$

Has been shown to have an equilibrium constant of 1.012 favouring the concentration of C^{13} in the bicarbonate solution. Since the concentrations of $HC^{12}O_3^-$ and $C^{12}O_2$ are large as compared with those containing $C^{13}O_2$, they may be considered as constant; hence the ratio of $HC^{13}O_3^- / C^{13}O_2$ equals 1.012, indicating that the bicarbonate solution contains 1.2 per cent more of the C^{13} isotope than the gaseous carbon dioxide in equilibrium with it. One of the most familiar isotopic equilibrium reactions is the one which is established between hydrogen and water. Since both hydrogen and water contain small amounts of deuterium, the equilibrium may be written as,

$$HD + H_2O \rightleftharpoons H_2 + HDO$$

The equilibrium constant of this reaction at 25°C is 3.703 in the direction of an increase of deuterium in water. The concentrations of H_2O and H_2 are large and can be considered as constant; therefore, the ratio of HDO/HD is 3.703, denoting that the concentration of deuterium in the water is between three and four times as great as in the hydrogen gas in equilibrium with it. The relatively high separation factor of 3.7 for this reaction indicates that it might be utilized as a means for the enrichment of the heavier isotope. One of the original objections to the use of this reaction in a chemical-exchange method for the production of heavy water was its slowness in establishing equilibrium. In the early stages of the wartime atomic-energy project it was thought that large quantities of heavy water would be necessary for use as a moderator. This anticipated need stimulated a search for a suitable catalyst to speed the attainment of equilibrium in the isotopic reaction between hydrogen and water. Such a catalyst was discovered, and a plant for the production of heavy water, utilizing this reaction, was built in British Columbia, Canada.

The chemical-exchange method for producing heavy water turned out to be superior to the electrolytic process in terms of efficiency and power consumption. In this process water flows, from the top of a tower containing a catalyst, downward to meet a mixture of steam and hydrogen moving upward. The catalyst promotes a rapid isotopic exchange reaction between the hydrogen and the water molecules in the steam; and, as indicated by the large separation factor, there is a concentration of deuterium in the steam in the form of D_2O molecules. The flow of water from the top of the tower produces condensation of the steam, and the water emerging from the bottom of the tower is enriched with respect to the heavier isotope. This water is electrolyzed, and the resulting hydrogen, enriched with deuterium, is reprocessed in the system. The actual plant consists of a cascade of towers, with the largest towers at the feed end and the smallest towers at the production end. The repeated operations rapidly furnish a high concentration of D_2O at a reasonable cost.

As a general rule, whenever an isotopic atom in a gaseous substance is in equilibrium with an isotope of the same element in a liquid or a solution, the gas will have a different isotopic composition from that of the liquid. Exchange reactions involving equilibria between gas and liquid phases have been investigated more extensively than other types. Table: lists some of the most common of these reactions. The equilibrium

Table: Isotopic-Exchange Equilibra

Exchange Reaction	K, 25°C
$SO_2{}^{16} + 2H_2O^{18} \rightleftharpoons SO_2{}^{18} + 2H_2O^{16}$	1.028
$CO_2{}^{16} + 2H\ O^{18} \rightleftharpoons CO_2{}^{18} + 2H_2O^{16}$	1.080
$CO^{16} + H_2O^{18} \rightleftharpoons CO18 + H_2O^{16}$	1.028
$O_2{}^{16} + 2H_2O^{18} \rightleftharpoons O_2{}^{18} + 2H_2O^{16}$	1.012
$ClO_2{}^{16} + 2H_2O \rightleftharpoons ClO_2{}^{18} + 2H_2O$	0.993
$Cl_2{}^{35} + 2HCl^{37} \rightleftharpoons C1_2{}^{37} + 2HCl^{35}$	1.006
$Br_2{}^{79} + 2HBr^{81} \rightleftharpoons Br_2{}^{81} + 2HBr^{71}$	1.0008
$HCN^{15} + N^{14}N_4{}^{+} \rightleftharpoons HCN^{14} + N^{15}H_4{}^{+}$	1.038
$HCl + DI \rightleftharpoons DCl + HI$	1.527
$S^{36}O_2 + HS^{32}O_3{}^{-} \rightleftharpoons S^{32}O_2 + HS^{36}O_3{}^{-}$	1.040

Constants for chemical-exchange reactions, except those involving the very light elements, are usually so close to unity that very little concentration can be achieved by a one-stage process. Accordingly multistage processes are usually necessary to produce an appreciable enrichment of an isotopic species. One process, devised by H. G. Thode and H. C. Urey for the enrichment of N^{15}, is claimed to have an efficiency 1,000 times that of the Hertz cascade diffusion method. Their apparatus consisted of several glass-packed colunins filled with efficient packing materials arranged in cascade, such that a smaller second column operates on the product of the first and a third column operates on the product of the second.

The method depends on the isotopic exchange between ammonia gas and ammonium ions in an ammonium nitrate solution, according to the equation,

$$N^{15}H_3 + N^{14}H_4^+ \rightleftharpoons N^{14}H_3 + N^{15}H_4^+$$

for which the equilibrium constant is 1.023. The direction of the reaction favours an increased concentration of N^{15} in the ammonium salt solution at the expense of the ammonia gas in equilibrium with it.

In this method a solution of ammonium nitrate is fed into column E of Unit 1, and 9/10 of the liquid reaching the bottom is passed into a stripper column S, where ammonia gas is liberated by the addition of NaOH and returned through the feed column. Unit 2 operates on the product of Unit 1, which is 1/10 of the solution arriving at the bottom of column E. As in the preceding unit, 9/10 of the liquid reaching the bottom of column E' is passed into stripper S', for regeneration of ammonia, and 1/10 is fed into Unit 3. All the liquid arriving at the bottom of column E" passes to stripper S", from which all the ammonia is liberated and returned through the system. With this cascade system the ratio of the isotopes is changed by a factor of 1,000, and a product containing as much as 72.8 per cent N^{I5} has been obtained.

Exchange reactions are not restricted to gas-liquid equilibria, and although this type seems most promising at present, other types of isotopic exchanges have been investigated. An example of a liquid-solid system is the case where alkali metal ions are exchanged in zeolites. If a solution of lithium chloride is permitted to descend through a column containing sodium zeolite, the isotopes of the lithium replace the sodium ions at a slightly different rate. The Li^6 replaces sodium ions more so that the solution becomes enriched in Li^7. On the other hand, displacement of lithium ions in lithium zeolite by sodium ions removes Li^7 more rapidly, so that the zeolite becomes enriched with Li^6.Exchange reactions involving gas-gas systems have been utilized for the enrichment of isotopes. Conditions for the attainment of an equilibrium between two gases may be secured in gaseous-diffusion columns, and isotopic separation is achieved by arranging such columns in cascade. Two examples of exchange reactions between gaseous isotopic molecules are the carbon dioxide-carbon monoxide system and the nitric oxidenitrogen dioxide system. The isotopic exchanges which take place in these reactions are indicated in the following equations:

$C^{12}O_2 + C^{13}O \rightleftharpoons C^{13}O_2 + C^{12}O$ $N^{15}O + N^{14}O_2 \rightleftharpoons N^{14}O + N^{15}O_2$