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Basic Chemical Principles and Facts for Safety, Health and Environmental Management (SHEM) Managers and Others

Part One: Inorganic chemistry *and* nomenclature

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Safety, Health and Environmental Management (SHEM) Managers And Others

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SHEM Managers and other safety and environmental protection specialists frequently review technical documents and reports which are replete with chemical information and data. To aid them in this work Part One is offered together with two other parts now in progress. A knowledge of relevant chemical principles, facts and laws, and pertinent industrial hygiene and toxicology, greatly helps in understanding the technical language of the NIOSH Criteria and Profile Documents and similar environmental reports, and in supporting EPA's programs and staff.

The three part together cover applicable basic inorganic, organic, and physical chemistry and explain the chemistries of selected elements and compounds, according to their environmental and/or occupational importance. Certain sections address energy changes associated with changes of state, and other matters and provide data which support the points being made. These data are approximate. Asbestiform silicates, radon and other common, well-publicized substances are not discussed.

This material collectively is intended for use in a classroom setting, with appropriate detailed explanations and "visuals," and for individual reading. Environmental protection program professionals and managers, as well as the SHEM Managers, may find it useful as a basic chemistry "refresher" in their work.

***Part 1. Aspects of inorganic chemistry.** This part covers: definitions; principles and rules; atomic electron configuration and molecular structures; environmentally or occupationally important elements and their oxidation states; chemical bonds; reduction and oxidation reactions; oxidation state and number; electrode potential; electronegativity and electron affinity; acids, bases, and chemical buffers; the Periodic Table (PT); properties of the PT Groups and elements; radiometric dating; the main chemistries of key entities such interest: H^+, NOx, NO_3^-, O_3, SO_2, PO_4^{3-}, Fe, Al, Pb, Hg, Cr; and nomenclature.*

***Part 2. Aspects of organic chemistry.** The plan of this part covers common environmental organic products, pollutants, and situations; key properties, including comments on solubility, transport, and fate; hydrolysis and pH; important aliphatic and aromatic compounds; electrophillic properties and reactions; enantiomorphs; functional groups, e.g. amines, acids, and esters; alkyl and aryl compounds; halogenated compounds, including dioxins and their precursors, brominated diphenyls and diphenyl ethers (ubiquitous flame retardants used in plastic and cloth materials); and organo-sulphur and organo-phosphorus compounds (mostly of the cholinesterase-inhibitor type).*

***Part 3. Some chemical laws.** This part addresses solids, gases and mixtures; vapor pressure; solubility; the ideal gas law; and Henry's and Dalton's laws, and includes worked examples.*

***Acknowledgment.** Much of the data are from the Handbook of Chemistry and Physics, 1992. Inorganic Chemistry by Huheey, Keiter and Keiter, Harper Collins College Publications (1973), Advanced Inorganic Chemistry by Cotton and Wilkinson, numerous journals, papers presented on internet chemistry sites, and personal chemical notes. The reviews and suggestions of the following are acknowledged with pleasure Brian Morris, MD, MPH, Dwight Peavey, PhD, and Stephen Perkins.*

***Disclaimer.** This material is not presented as any official policy or position of any agency or group. Also, no warrantee is made as to its correctness.*

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Part One — Basic chemical principles and information. The Periodic Table. Selected chemistries. Naming Inorganic Compounds

Introduction

Some general chemical principles as short summaries, together with a few examples, are provided first. This will help in understanding the information given in the subsequent sections. The discussion on the Periodic Table (PT) centers on some of the more environmentally or occupationally important Groups, elements and compounds. The section on naming inorganic compounds is not a "rules" statement, rather it stresses that while many common chemical names (e.g. ammonia) are perfectly satisfactory, some others are confounding (e.g. hyper-, hypo-, -ic, -ous pre-fixed names in sulphur, nitrogen, and phosphorus chemistries). Systematic names, endorsed by the *International Union of Pure and applied Chemistry, IUPAC,* can be more informative, even though the nomenclature may be awkward-sounding or difficult to apply. Organic chemistry has its own, often difficult nomenclature, which is replete with trivial and trade names.

Carbon compounds of every-day environmental importance[1] include carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), benzene (C_6H_6), carbon disulphide (CS_2), the "carbon chlorides," such as carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$), compounds containing C-F bonds (freons), and organic compounds with common functional groups, including esters and types of compounds. Some of the common functional groups are aldehydes, e.g. formaldehyde used in disinfectants and paper products; ketones, e.g. acetone used in paints and polish removers; aliphatic hydrocarbons, e.g. propane used in aerosols); aromatic hydrocarbons, e.g. ortho-, meta-, para- xylenes, used in alkyd paints); halogenated hydrocarbons; and other organic classes, such as the carbamates, e.g. carbaryl pesticide; and the organo-phosphorus compounds (e.g. Diazinon pesticide).

These substances, which are used widely in general industry or agriculture, pose significant occupational and environmental hazards, including human hazards to the central nervous system, the cardiovascular system, the kidneys, or the liver, and possible interference with endocrinal or enzymatic functions. Even a relatively low-level, chronic exposure to these substances may aggravate a pre-existing condition, such as high chemical sensitivity, asthma, contact dermatitis, or a diseased lung, liver or kidney condition.

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1. Environmental importance includes occupational and public health importance. Occupational health relates to healthy workers aged 18-65 years, who work for about 2000 hours a year for about 40 years in an industrial or some other kind of workplace. Public health relates to everyone for a full lifetime. Occupational and public exposures to noxious chemicals has declined drastically since the late '60's, due in large part to OSHA and EPA enforcing their controlling rules and standards. These agencies limit emissions, exposures, and, in some cases, specify engineering and administrative controls. While all of the pre-1970's public and environmental safety, and occupational safety and health standards' limits have undergone major reductions, a good case can be made for making further *large-scale, more stringent* revisions on both these fronts. On another point, an on-going issue is that of "thresholds of chemical safety." While it is reasonable to apply a threshold of some kinds of exposures, this does not extend to every exposure situation. The absence of an observable response to a chronic exposure is not a guarantee of safety, and on biological grounds, one may reasonably believe in the absence of a threshold (for some cancer-causing agents for instance). This all leads to a healthy skepticism about claimed safety, especially when it involves chronic exposures, and the need to keep all chemical exposures to the feasible minimum. In some "threshold" exposure situations, the concentration of a substance, rather than the exposure time at some concentration is the dominant risk factor. Also, many elements and compounds/ions (e.g. chromium, cobalt, cyanide, etc., in trace amounts, are essential to life, but when they occur at above-trace concentrations, in human tissues, animal tissues, or in air, water or soil, they may constitute serious occupational or environmental hazards. In the latter regard, compounds and ions which are significant water pollutants or contaminants are: H_3O^+, $CaCO_3$, CO_2, CS_2, Fe^{3+}, Mn^{2+}, SO_4^{2-}, HS^-, Hg and Hg^{2+} (including lipophilic alkyl mercury compounds). Several of these listed entities react with one another. See 'Redox reaction' at page 13.

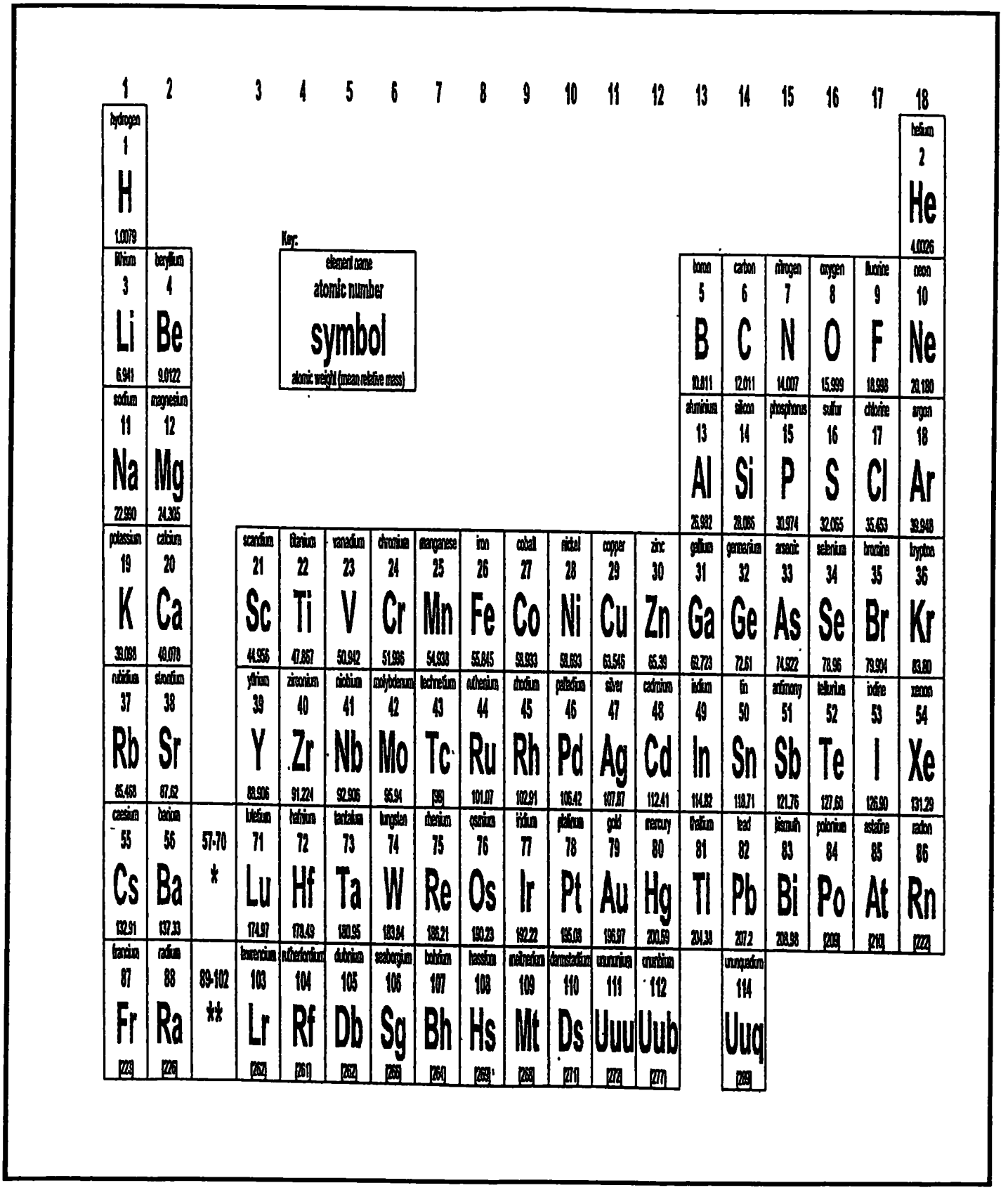

Fig. 1. The IUPAC Format Periodic Table, less the Actinides (Z, 57-70) & the Lanthanides (Z, 89-102). (Re: pages 29-31)

Other elements of everyday environmental importance include: hydrogen (as H_3O^+); metals[2], such as beryllium, (radioactive) strontium, barium, chromium, cobalt, copper, cadmium, aluminum, mercury and lead; and nitrogen and sulphur (especially as their acidic oxides); oxygen (as ozone); phosphorus; arsenic; fluorine and chlorine, and radon. [Radon is radioactive. Its chemistry, toxicology, permissible exposure and remedial action standards, and mitigation are extensively covered in numerous U.S. EPA technical publications].These and other elements, as various compounds, are found in hazardous household wastes and in public incinerator emissions (incineration does not destroy metals, they need to be trapped). They are major pollutants of surface waters and soils, as well as air pollutants. Many of them underlie today's challenges to protecting the environment and the public health. Acidic oxides of nitrogen and sulphur and mercury, from incinerators and power generation stations, have caused and continue to cause serious local and regional environmental and health problems. Airborne pollutant transport[3] has devastated large tracts of forest and seriously contaminated great bodies of water, rivers, streams and ponds Soil and water, at pH levels of 4.5 or lower, are hostile to plant and animal growth. Germinating seeds and fish eggs and do not survive long under this kind of stress. Acidic particles in air ultimately settle on soil and live leaves and slowly kill trees and other plants. In water, mercury is biochemically methylated to highly toxic methyl mercury, which bio-accumulates up through the aquatic food chain to humans.

§A. Chemical principles and information. The Periodic Table. Selected chemistries

Bonding. The (classic) **Lewis Structure** bond model deals with: bonding by valence electrons in bonding-pairs, non-bonding lone-pairs of outer orbital electrons disposed around an atom; an electron octet arrangement, and electron donation or acceptance, with appropriate adjustment of charge. Three or less "electron pair"arrangements may exist, i.e. single, double and triple bonds. It is the backbone of valence bonding. However, unlike the much more sophisticated molecular bonding theory, this early bond model, which is still very useful, does not adequately explain certain molecular phenomena:, such as paramagnetism (as seen in liquid oxygen), or a partial bond, or the *non-existence* of a molecule like He_2, or the structure of di-hydrogen (for which no 'octet' of electrons exists).

Ionic bonds are bonds formed by electron transfer, rather than by electron pair sharing (covalency). This transference occurs predominantly, between a relatively electropositive element and a relatively electronegative element, when the electronegativity difference is major (i.e. three or more units).

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2. About 20 metals (and numerous other elements) are essential to life, including some which are also major environmental pollutants. Excessive exposure to, or uptake of, these metals, as well as other elements and their compounds, can be seriously hazardous to health and the environment. Conversely, some other metals and elements, which are not biologically essential and which are broadly toxic, may be tolerated by animals and detoxified in the body by various biological mechanisms.
3. Airborne particles of about 10 microns mean diameter or less, quickly settle out in still air; they have a relatively high settling velocity. For particles of a few microns diameter the settling rate in still air (feet per minute) may be approximated by $0.006\ D^2\ SG$, where D=mean aerodynamic diameter and S.G = particle specific gravity. With stack releases and the associated 'thermals' and winds, very small particles emitted from stacks may stay suspended in the atmosphere for days, and travel and disperse accordingly. In respirable air, particles of about 10 microns diameter or more are substantially filtered out by the nose and if the enter the upper respiratory tract they are cleared out via the muco-ciliary ladder. These particles, however, can still be very irritating to the upper respiratory tract, especially when they carry SO_2 and NO_X, or other water soluble contaminants on their surfaces. The water soluble material may rapidly pass from the airways into the blood. Inhaled particles of about one-half to five microns diameter effectively reach the lower airways, and the particles of about 0,1 to 0.5 microns become mostly retained in the lowest branches of the lungs and their gas-exchanging sacs (the alveoli). Particles smaller than about 0.1 micron, however, remain essentially suspended in the inhaled and exhaled air because of their low inertia (low impact) and their low settling velocity. Having said that, however, exceptions are seen (in electromicrography of biopsied lung tissue), with fibers of even 200 microns length having found their way into the gas exchanging parts of the lungs. The American Conference of Government Industrial Hygiene (ACGIH) has established respirable aerodynamic particle and deposition criteria.

Ionic bond

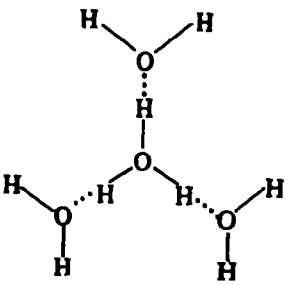
The product of the charge-transfer effected union of atoms of largely different electronegativity, with a resultant non-equidistant charge center between the nuclei, causing a partial charge to the molecule. [δ signifies charge distribution]. For example the primary bond in hydrochloric acid, which is typically depicted as: $\delta^{+}H - Cl^{\delta-}$

Covalent bond

The product of a sharing of electrons, a pure covalent bond has equal sharing, as in N_2, ***but a covalent bond between elements of unequal, but not greatly unequal electronegativity has an unequal sharing of electrons (termed polar covalent). Binary compounds of elements within Groups 13, 14, and fifteen are extensively covalent.***

Electrostatic bond & hydrogen bonding

Molecules of ionic and polar covalent compounds, especially when elements of Groups 1, 15, 16, 17 are involved, are frequently attracted to one another by an electrostatic force. Hydrogen bonding, which is depicted below in the case of water, is one such force.



Molecular orbitals (M.O's). The MO's for H_2 *and (the non-existing)* He_2.

For each atomic orbital co-joined there exists a molecular orbital. Also bonding and antibonding molecular orbitals are generated. In diatomic hydrogen, electrons are preponderantly around and between the two H nuclei. The electrons are most likely to be found in between the nuclei, within the overlapping 1s orbitals, which comprise the football- shaped zone, as shown. With hypothetical He_2, ***the anti-bonding (highest energy)orbital has two electrons, and the lowest energy orbital has two electrons also. This gives a net energy "savings," over two individual hydrogen atoms, of zero. Hence, the*** He_2 ***molecule does not exist. [Generally, the combinations of all possible outer atomic orbitals underpin complex MO diagrams].***

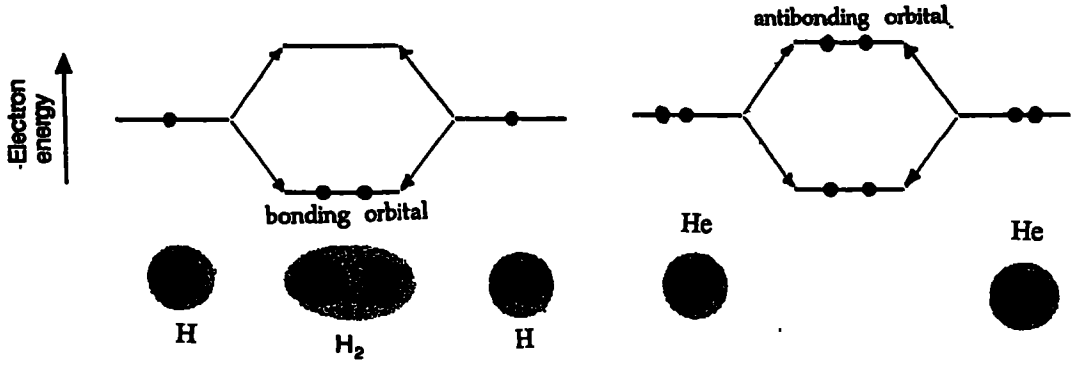


Fig.2. Various types of bonds (re: pages 5, 6, 26)

When two or more highly electronegative elements combine, the nature of the bonding, while it may be partially ionic, may not be beyond question. Unstable liquid nitrogen trichloride, for example, may be viewed as $N^{+3}Cl^{-1}_3$, as Cl^{+1}_3N, or as a mixture of both in equilibrium.

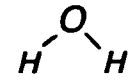
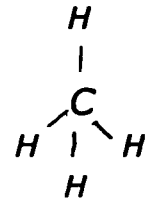
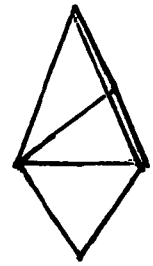
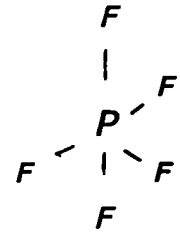
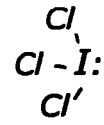
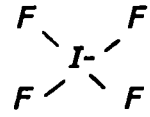
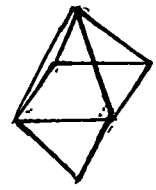
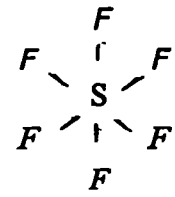
Covalent bonds are predominant when elements of similar electronegativity form binary compounds. The elements in this case share one or more pairs of electrons, in overlapped (molecular) orbitals. Two kinds of such bonds exist: sigma and pi bonds, both arising out of particular geometrical overlapping of s-orbitals and/or p- orbitals (hybridized orbitals). In summary, a covalent bond arises when a donor atom contributes a pair of electrons to a "union" e.g. the addition-compound: $BF_3.OR_2$. A covalent bond arises also when a small highly charged cation (e.g. Be^{2+}) unites with a large anion (e.g. SO_4^{2-}). Binary compounds which are covalently bonded may involve the sharing of one, two, or three pairs of electrons, respectively giving single, double and triple covalent bonds. The higher bond number has the higher bond strength. Covalent bonds are strong, with breaking energies which are in the order of 100 $Kcals.mol^{-1}$. Boron (Group 13), the Group 14 elements (except lead), and phosphorus, arsenic, selenium, and tellurium (Group 15) form extensively covalent compounds, but they have some cationic chemistries.

Molecular orbitals result from various outer atomic orbitals overlapping in one way or another. [MO theory treats bonding as the overlapping of ligand orbitals with central atom orbitals, resulting in a hybrid of one kind or another which has intermediate character re: the respective atomic orbitals. S-, p-, d- outer orbitals produce additional sites, which are (a) bonding molecular orbitals (BMO), and (b) anti-bonding molecular orbitals (ABMO). The theory includes a measure for stability: the bond order (B.O.), which is equal to ½ (the number BMO's minus the number of ABMO's). A bond order of zero means the hypothetical molecule is no more stable than the constituent elements; the molecule does not exist. A bond order of 1 = a single bond, and so on, to a triple bond. MO's account for many different molecular properties which are not adequately explained by the Lewis model. More detailed explanations of MO's are given in chemical texts and in internet chemical sites.

Electrostatic bonds are weak, non-ionic, non-covalent bonds formed between entities which have electrical charges ("Coulombic attraction"); many H, F, O, and N-bearing molecules are so bonded.

Hydrogen bonding is basically electrostatic. Individually, a hydrogen bond is weak (~2 eV), compared to ionic or covalent bonding. (See fig. 2, page 4). Collectively, hydrogen bonding can be very strong, especially in "short-distance repetition" situations, involving O, and N, as exist in proteins. This is reflected in the physical properties of the respective compounds. Hydrogen bonding holds DNA together via the alternating N and O atoms within the helix. Hydrogen bonding in a compound may be relatively weak or strong, depending on the composition of the compound and the electronegativity of the element(s) involved. Water is the classic illustration of strong hydrogen bonding and how it affects physical properties. Water (molecular weight18) has a normal boiling point (bpt.) of 100^0 C. Cf. Hydrogen sulphide, molecular weight 34, Bpt., minus 60.7^0 C. Hydrogen sulphide has a similar shape as water, but S is less electronegative than O. Water has a dipole moment created by: (a) the electron attraction of highly electronegative oxygen, and the ensuing partial electrostatic charge across the O-H bond; and (b) the bent (105^0) shape of the molecule. Hydrogen bonding exists in some solids, liquids and polymeric vapors, but not in a true gas. Studies of infrared spectral changes and X-H stretching and bending frequencies provide reliable evidence of hydrogen bonding in a compound.

"van der Vaals" forces (or London forces) are weak, non-electrostatic forces existing in liquified noble gases, graphite, methyl ethyl ketone, bpt. 80^0 C (cf. diethyl ether, bpt. 10.8^0 C) and other entities.

STRUCTURE	COMPOUND	SKETCH
Linear	*NITROGEN MOLECULE, N_2*	*N ≡ N*
Bent molecule	*WATER MOLECULE, H_2O*	
Trigonal planar	*BORON TRIFLUORIDE, BF_3*	
Tetrahedral	*METHANE, CH_4*	
Triagonal Bipyramidal	*PHOSPHORUS PENTAFLUORIDE, PF_5*	 
T-shaped	*IODINE TRICHLORIDE, ICl_3*	
Square Planar	*IODINE TETRAFLUORIDE ION, IF_4^-*	
Octahedral	*SULPHUR HEXAFLUORIDE, SF_6*	 

[Kekule (wedge-shaped) diagrams when used provide a sense of the 3-dimensional aspect]

Fig.3. Some molecules and their shapes (see Table 1, page 10 for related compositions).

Metal bonds. Metals have an "electron cloud" in a conductive band, and no particular electron is associated with just one atom; the electrons move freely in the band. Metals have temperature-independent paramagnetism. Their atoms are held together by generally strong forces. A metal bond can exist simultaneously between like and dissimilar (metallic) elements. Metal bonds retain their nature in the liquid state. Superconductor metals at very low (*critical*) temperature undergo electron pairing and so exhibit diamagnetism. **Metal bond cohesiveness:** Metals have a wide range of melting point and other properties which depend on the cohesive energy of the interatomic bonds. The transition metals (partially filled d-orbitals) have the highest cohesiveness, as shown by their melting points. These metals have close packed (HCP or CCP) structures. Tungsten (third transition series) has the largest cohesive energy and highest melting point of the metals, 3400 ^{o}C. The transition metals also show high coordination numbers.

Rhenium (Re) has high cohesiveness. Its melting point is 3180°. Rhenium is a rare, naturally occurring element. It is used in making thermocouples and mixed Re-Pt catalysts for petroleum reforming.

Characteristically, metals have each one of their atoms surrounded by a relatively large number of close atomic neighbors, within a crystal lattice. The lattice exists as a close packed form (of which two kinds exist: hexagonal and face centered cubic), or as a non-close packed form (body centered cubic, BCC). Metals in BCC lattice form are hard to "work." This is evidenced by V, Nb, Ta, Cr, Mo and W. These metals are used to make special purpose alloys with extreme hardness and strength at red-heat. Transitions between all three forms of atomic packing can occur at high temperatures.

Alloys. Alloys are formed by fusion of metals. They are classified as (a) interstitial solid solutions, e.g. carbides, hydrides, or (b) substitution solid solutions. The interstitial alloys have different lattices than the parent pure metal. Also, they are more brittle and hard. The substitution alloys are generally structurally like the parent (preponderant) metal. Limits apply to the amount of substitution allowed. The substitution amount depends somewhat on the main valence shown by the minor element and the main element. In general, atoms of similar main valence and size can effect 100% substitution. In other cases, the upper percentage substitution limit which can be tolerated by a stable alloy is determined by the net alloy "electron concentration," which ensues from admixture. Another factor (rule) is: "The electron concentration of the pure parent element may not be reduced."

An alloy which changes from a generally haphazard array into an orderly array after being held at its melting point for some time is termed a "super lattice." The properties (e.g. heat capacity at constant pressure, Cp) of the super lattice differ from the source alloy. Examples of super lattice alloys are Cu-Zn alloy (body centered cubic lattice) and Ag_3Al (face centered cubic).

Alloys can have simple to complex chemistries. The brasses are simple solid solutions of copper and zinc. Simple general purpose alloys include: babbitt alloy; pewter; white metal; bearing metal; and casing alloys. Some alloys contain toxic metals which may be leached by acidic media. For example, an alloy containing antimony, Sb, (some Pewter alloys) in an acid medium produce poisonous stibine, SbH_3.

Special purpose alloys generally have complex chemistries. For example, the very high temperature-high strength alloy Ti-155A comprises titanium and precise but minor amounts of iron, aluminum, chromium and molybdenum.

Outer Electron Orbitals

The 1s orbital has a bi-nodal distribution of the probability of the electron being within a spherical shell, but the 2s orbital is unimodal: both are spherical overall. The dumbbell-shaped 2 p-orbitals are shown in the three planes, z, y,z. The third electron shell of the 3d orbitals are described as double dumbbell and ring and dumbbell shapes, as illustrated. The two lowest energy orbitals (first filled orbitals) are the 1s and 2s orbitals. The diagrams do not represent rigid shells, rather they are the regions with the greatest probability of the electrons being in these "smeared" zones.

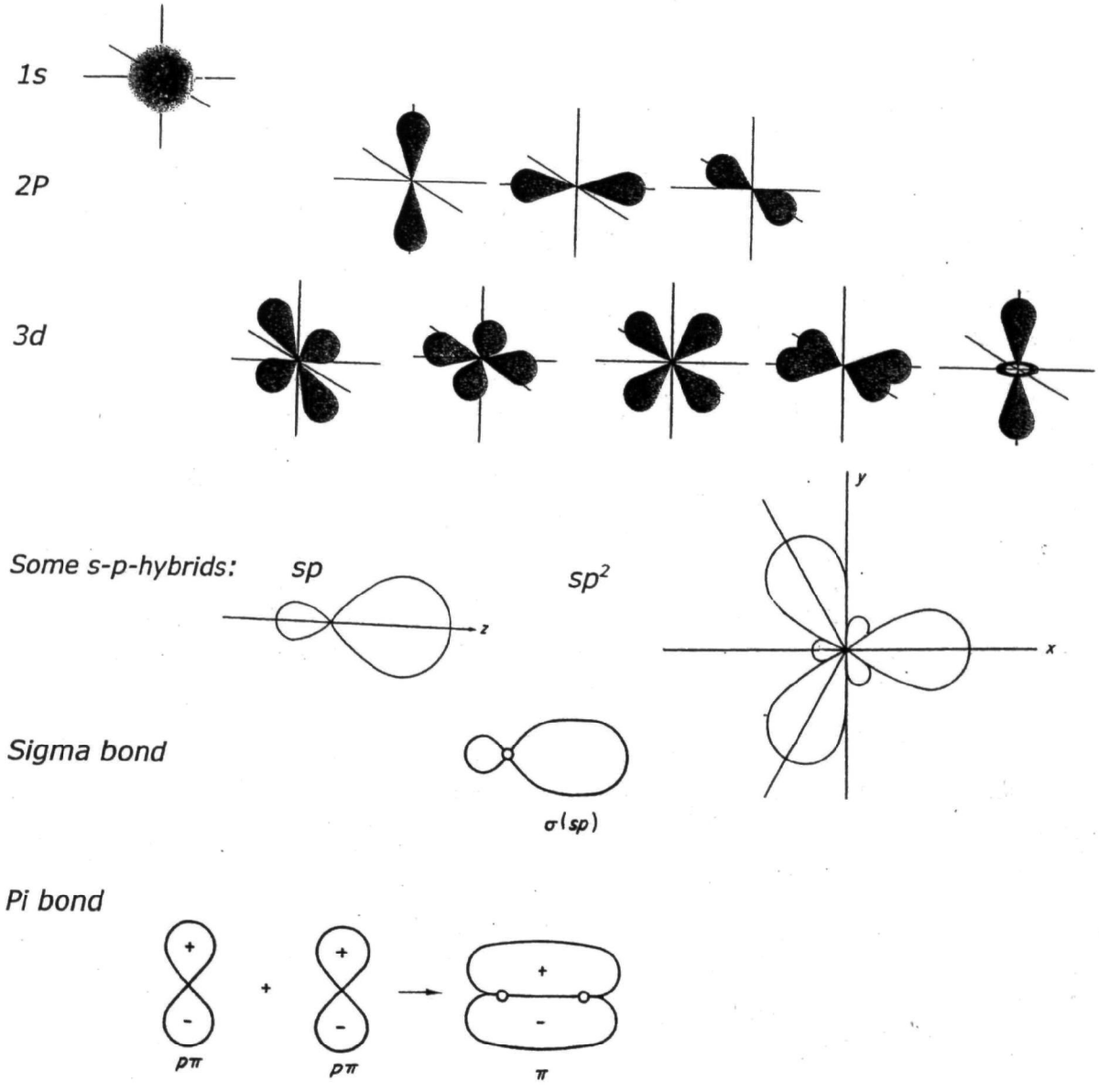


Fig. 4. Some sub-shell orbitals and simple molecular orbitals (with notations)

When differences exist in electronic configuration, preferred oxidation state or atomic size, the permissible substitution percentage of the main element in a stable alloy is limited (by electron density). For example, in alloying copper (ionic radius, 0.96) with zinc (ionic radius, 0.69), zinc may maximally substitute for copper by about 40% by weight before the alloy loses its stability and desirable properties. Germanium alloys with copper with a maximal substitution limit of 12% (germanium).

Orbitals. Electrons in atoms occupy discrete energy levels (orbitals) which represent the probability of an electron being present at any one time at that energy level. See page 12. Quantum numbers (atomic shells, 1, 2, 3 and so on), and sub-shells and respective orbitals describe the quantum atom. Orbitals, in context with the quantum atom, however, are difficult to describe, but they are made understandable by diagrams and the following explanation: In the quantum atom electron orbitals are presented as "clouds," of varying density corresponding to relative probability of the electrons' presence, around a nucleus, with different energy levels and shapes. In molecular (hybrid) orbitals, which are derived from the overlapping of the atomic orbitals of the respective nuclei of a compound, the electrons are located, with varying densities, between constituent nuclei (in which case a filled bonding molecular orbital, BMO, exists), or "along" the sides of these nuclei (when a electron-compound-destabilizing, electron-containing hybrid anti-bonding molecular orbital, ABMO, exists. BMO's and ABMO's can be simultaneously occupied by electrons. A compound with no occupied ABMO's is more stable than one with ABMO occupancy (See "H_2 vs. non-existent He_2" in fig. 2, page 4). The lowest atomic orbital energy levels are the first and second shells —"s" orbitals: 1s, 2s (sphere shaped). The s- orbitals can each accept two electrons (of opposite "spin,"known as magnetic moment; all orbital filling requires opposite spin for the electrons in each pair). Next, energetically comes the ("2p", x,y,z) orbitals — which are three equal-energy, dumbbell-shaped, "sub" orbitals, lying on 3-dimensional, x, y, and z axes. The combined 2 p- orbital capacity is six electrons (three pairs, with each pair having opposite spins). Then comes the third subshell d-orbitals. The d-orbitals have double-dumbbell and ring-and-dumbell shapes (see fig. 4). The combined capacity of the d-orbitals "set" is 10 electrons (five pairs, with each pair of electrons having opposite spins). For simplicity this arrangement may be considered as a set of five, energy level "boxes" — each box having room for two electrons. The energy distribution between the "boxes" (orbitals) may or may not be comparable. Certain ligands create electrostatic fields, around the central atom in a molecular complex, which alter the energy distribution of the d- orbitals and the order of their filling in certain (of d^4 to d^7) situations. [The orbitals of equal energy are termed "degenerate" orbitals]. Strong field ligands, like CN^-, affect (d^4 to d^7) elements/ions in terms of outer electron disposition, magnetism and other properties. See page 52.

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4. Atomic orbitals unite in various ways to form orbital hybrids: blends of different proportions of two or more orbital types. Also, overlapped orbitals axial to a M-X bond are 'sigma bonds' (covalent when p-orbital overlap is involved) bonds; and, those overlapping perpendicular to the M-X axial bond are pi bonds. Hybrids have their own characteristics which determine the spatial arrangement of a compound and other physical-chemical properties (another factor is the number of lone pairs of electrons on the central atom). MO theory, in the most simplistic terms, is that separate atomic orbitals, with respect to electron wave forms rather than discrete electron particles, in overlapping in a molecule, form new molecular orbitals, M-O's, denoted by ω, with numbered suffices. These MO's belong to the entire molecule. Further, the resulting electron densities of the new orbitals are derived from an approximate linear addition of the respective atomic orbitals. For every corresponding atomic orbital involved, two molecular orbitals ensue. The MO's have: (a) energies lower than those of the respective basic orbitals (these MO's are *bonding orbitals*); and (b) energies higher than those of the respective basic orbitals, (these MO's are *anti-bonding orbitals*). In both types, MO's may exist which have identical energy (these are known as *degenerate* orbitals). The filling of the MO's is — first the lowest available energy-orbitals; with the filling following Hunds' rule (maximum of 2e's per orbital). Very complex interactions of MO's occur in many complexes, and M-O energy — orbital calculations generally require computerization. MO theory explains the properties (e.g. structure, intermediate type bond lengths, aromaticity) of inorganic and organic compounds, which cannot be satisfactorily explained by earlier theories.

Orbital Occupancy. Atomic sub-shells and orbitals are discrete energetically and limited in electron-filling capacity and "rules" apply to filling; one is the energetically lowest orbitals fill first (the *Aufbau* orbital filling order), another is (Pauli's exclusion principle), only two *(opposite spin)* electrons per (sub) orbital. Hund's rule also applies: Maximization is required for the number of *unpaired* electrons in the p-, d-, and f- sub-shell orbitals. Multiple-electron atoms and ions are described (in part) in terms of (atomic quantum-allowed) energy levels and atomic shells ('S'), sub-shells, and orbitals and shapes (e.g. s, p, d, f, orbitals) and orbitals directions and hybridization, and electron magnetic spins.

An ("Aufbau") order of orbital-filling by electrons exists (with the sub-shells having different energies): 1s; 2s; 2s, 2p; 3p, 4s; 3d, 4p, 5s; 4d, 5p, 4f, 5d, 6p, 7s, 5f, 6d, 7p, and so on [See page 12]. Note the "upset" above in these orbital energy levels Z=19, 37, 38 (and elsewhere) when a subshell orbital energy "switch " occurs (i.e. for calcium, atomic number 20, the (relatively lower energy) 5p- orbital fills with two electrons before the 4s- orbital). This is due in part to internal nuclear shielding by electrons in inner orbitals. It is important to realize that the above filling order holds for elements, but the order may be altered in a compound, when the central ion is surrounded by "auxiliary-bonded" ligands. For instance, complexed iron can be d^8 rather than d^6s^2 (see page 52).

In summary, the key points of orbital occupancy are: (1) the sub-shells have different energies and electrons enter orbitals and hybridized orbitals with minimal energy; and (2) a comparison of elements belonging to the same PT Group, on the basis of the use of d-orbitals, shows chemical dissimilarities. For example, nitrogen (which does not have d-orbital electrons) does not form the same number or kinds of compounds which its Group neighbor, phosphorus, (which uses d-orbitals) forms.

Molecular geometries (molecular structures). An optimal (least free energy) spatial arrangement occurs for a given number of bonded atoms (valence electrons) and non-bonded pairs of electrons within a molecule. The optimal arrangement is one which provides maximum overall separation between the bonds and the (unbonded) lone pairs of electrons in the molecules. See Table 1.

SOME SIMPLE COMPOUNDS and their GENERAL FORMULA,* in terms of bonding, and unpaired pairs of electrons		OUTER ORBITALS * *	IDEALIZED SHAPE
BCl2	AX2	SP	LINEAR
BF3	AX3E	SP2	TRIGONAL PLANAR
CH4	AX4	SP3	TETRAHEDRAL
NH3 [:NH3]	AX3E	-	TRIGONAL- BIPYRAMIDAL
H2O [::OH2]	AX2E2	-	BENT MOLECULE @ 105° ANGLE
PF5	AX5	SP3D	TRIGONAL-BYPYRAMIDAL
SF4	AX4E	-	SEE-SAW SHAPE
ICl3	AX3E2	-	"T" SHAPE
SF6	AX6	SP3D2	OCTAHEDRAL

* A = CENTRAL ATOM. X=ANION. E= LONE PAIR OF ELECTRONS, [:] ,ON THE CENTRAL ATOM. * * S, P, D, F ATOMIC ORBITALS CAN MIX (HYBRIDIZE) TO ORBITALS. ALSO, THE BOND ELECTRON PAIR AND THE UNBONDED ELECTRON PAIR(S) ARE OPTIMALLY SEPARATED AND THIS AFFECTS MOLECULAR SHAPE.

Table 1. Bonds and lone pairs and molecular shape

As examples: $BeCl_2$, with sp-orbital hybridization, is a linear molecule; BF_3 (sp^2) is a trigonal planar molecule; CH_4 (sp^3) is a tetrahedral shaped molecule; and PF_5 (sp^3d) has a trigonal bipyramidal shape.

Electronegativity. Electronegativity is measure of the propensity for an element (or ion) to gain an electron. The **least electropositive of the more common elements** is potassium. [The least electronegative element is cesium]. The **most electronegative** element is fluorine. [The halogens in general are the most electronegative elements.[5] The reason for the halogens' high electronegativity is that each halogen is just one electron short of its corresponding noble gas configuration].

The noble gases have zero electronegativity. ["Noble" here means unaffected by mineral acids. The term is preferable to "inert." Also, these gases have a filled sub-shell orbitals, for example helium, s^2]. In addition to having zero electronegativity, the noble gases have low electrode potentials and high (>10 eV) ionization potentials. Some of the noble gases form a few stable (and also some unstable) compounds with fluorine and oxygen: XeF_2, (crystals); XeF_4 (crystals); XeF_6 (crystals); $XeOF_4$, which are strong oxidants and fluorination compounds, and which are used in organic synthesis.

A plot of electronegativity versus Z (the atomic number, the number of protons in the nucleus) illustrates the range (Table 2).

IUPAC GROUP	ELEMENTS (A to B, inclusive)	RANGE	IUPAC GROUP	ELEMENTS (A to B, inclusive)	RANGE
1	H [H, 2.2] Li-Fr	0.97-0.86	10	Ni-Pt	1.35-1.44
2	Be-Ra	1.47-0.97	11	Cu-Ag	1.75-1.42
3	Sc-Y	1.2 -1.11	12	Zn-Hg	1.66-1.44
4	Ti-Hf	1.32-1.23	13	B-Tl	2.01-1.44
5	V-Ta	1.45-1.33	14	C-Pb	2.5 -1.55
6	Cr-W	1.56-1.4	15	N-Bi	3.07-1.67
7	Mn-Re	1.6 -1.46	16	O-Te	3.5 -2.01
8	Fe-Os	1.64-1.52	17	F-I	4.1 -2.21
9	Co-Ir	1.7-1.55	18	He-Rn	Zero

Notes: THE PT-GROUPS ARE INCOMPLETE. THE OBSCURE ELEMENTS ARE EXCLUDED.
THE (L. PAULING) DATA WERE REFERENCED TO THE COMMON OXIDATION STATES.
FOR EXAMPLE +1 FOR GROUP 1 AND +2 FOR GROUP 2 AND THE 1ST TRANSITION SERIES ELEMENTS. AND +3 FOR BORON AND ALUMINUM, ETC.

Table 2. Electronegativity ranges for selected elements in the IUPAC-PT Groups

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5. Some halogens yield stable oxy-compounds (e.g. oxides, iodates, and bromates). ClO_3 and ClO_2 exist and are strongly oxidizing. Chlorates (ClO_4^-) are stable, but powerful oxidants. Hypochlorite and hypobromite ions are stable in solution. No "hypo-iodite" exists. The oxy-halides exhibit formal, positive halogen oxidation numbers. Bromine and iodine, separately, exhibit O.N.+1 in some complexes, e.g. $Br^+(pyr)_2ClO_4^-$ (pyr = pyridine). The ICl_4^- ion is square planar because of orbital hydridization, for example configuration $D^{10}S^2P^2$ excited to $D^{10}SP^1D^1$. A few inter-halogen compounds have formal positive halogen oxidation states, e.g. CLF_3.

Element	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f 5g
1. H	1				
2. He	2				
3. Li	2	1			
4. Be	2	2			
5. B	2	2 1			
6. C	2	2 2			
7. N	2	2 3			
8. O	2	2 4			
9. F	2	2 5			
10. Ne	2	2 6			
11. Na	2	2 6	1		
12. Mg	2	2 6	2		
13. Al	2	2 6	2 1		
14. Si	2	2 6	2 2		
15. P	2	2 6	2 3		
16. S	2	2 6	2 4		
17. Cl	2	2 6	2 5		
18. Ar	2	2 6	2 6		
19. K	2	2 6	2 6	1	
20. Ca	2	2 6	2 6	2	
21. Sc	2	2 6	2 6 1	2	
22. Ti	2	2 6	2 6 2	2	
23. V	2	2 6	2 6 3	2	
24. Cr	2	2 6	2 6 5	1	
25. Mn	2	2 6	2 6 5	2	
26. Fe	2	2 6	2 6 6	2	
27. Co	2	2 6	2 6 7	2	
28. Ni	2	2 6	2 6 8	2	
29. Cu	2	2 6	2 6 10	1	
30. Zn	2	2 6	2 6 10	2	
31. Ga	2	2 6	2 6 10	2 1	
32. Ge	2	2 6	2 6 10	2 2	
33. As	2	2 6	2 6 10	2 3	
34. Se	2	2 6	2 6 10	2 4	
35. Br	2	2 6	2 6 10	2 5	
36. Kr	2	2 6	2 6 10	2 6	
37. Rb	2	2 6	2 6 10	2 6	1
38. Sr	2	2 6	2 6 10	2 6	2
39. Y	2	2 6	2 6 10	2 6 1	2
40. Zr	2	2 6	2 6 10	2 6 2	2
41. Nb	2	2 6	2 6 10	2 6 4	1
42. Mo	2	2 6	2 6 10	2 6 5	1
43. Tc	2	2 6	2 6 10	2 6 6	1
44. Ru	2	2 6	2 6 10	2 6 7	1
45. Rh	2	2 6	2 6 10	2 6 8	1
46. Pd	2	2 6	2 6 10	2 6 10	
47. Ag	2	2 6	2 6 10	2 6 10	1
48. Cd	2	2 6	2 6 10	2 6 10	2
49. In	2	2 6	2 6 10	2 6 10	2 1
50. Sn	2	2 6	2 6 10	2 6 10	2 2
51. Sb	2	2 6	2 6 10	2 6 10	2 3
52. Te	2	2 6	2 6 10	2 6 10	2 4
53. I	2	2 6	2 6 10	2 6 10	2 5
54. Xe	2	2 6	2 6 10	2 6 10	2 6

Note the energy level - main shell number 'switch" at z =20 and elsewhere.

Fig. 5. Some (ground state) electronic configurations (re: pages 9, 10)

Electronegativity differences and ionic bond character. As the electronegativity difference between the elements of a binary compound decreases the ionic character of the single bond rapidly decreases. A large difference in electronegativity accounts for the strong, polarized union which occurs between relatively highly electropositive and highly electronegative elements. A plot of electronegativity versus atomic number (a seesaw profile) helps in understanding why elements bond in particular ways, and why some anticipated compounds do not exist. When the electronegativity difference is about 2, the single chemical bond between the two elements is substantially ionic. At an electronegativity difference of 3, the character of the bond is essentially ionic. Ionic *and* covalent bond character co-exists in most compounds.

Electronegativity and displacement of a cation from solution. In general, a more electropositive (less electronegative) cation will displace another cation from solution.

Electron Affinity: a concept akin to, but somewhat different from, electronegativity. It is expressed in terms of the energy released when a neutral atom forms an anion. The main Group elements differ in being able to form a negative ion from a neutral one. A large negative enthalpy change, for a neutral ion forming a negative ion, is indicative of high electron affinity. Chlorine readily accepts an electron (with a large negative enthalpy change of about 3.6 eV/atom), and is said to have high electron affinity. Sodium, on the other hand, does not have any degree of electron affinity; the Na^- ion does not exist. Similarly, the rest of the Group 1 elements, the Group 2 elements, and the noble gases have no significant electron affinity. Electron affinity (E.A.) can only be measured indirectly. Also data are only available for the more electronegative elements (E). See table 3.

E	F	Cl	Br	I	O	S	Se
E.A. (KJ/mol)	-328	-349	-325	-295	-141	-200	-195

Table 3. Selected elements and their electron affinity values

Oxidation number or state. The oxidation number (O.N.) or state is the electronic configuration of the element, when one or more electrons "relocate" from or to that element. The highest O.N. is eight (e.g. ReO_4 and OsO_4, a *volatile* oxidant, which is extremely toxic via all routes of uptake, including the eyes). Oxidation number is primarily a stoichiometric concept. It is used, however, as a "formality" in describing a charge on an atom, a cation, an anion, or an atom which is central to a coordinately bonded molecular complex. For example, elemental calcium is described as oxidation number zero, whereas, the (aquo) Ca^{++} cation is described as "calcium, oxidation number two." For many *organometallic* compounds, the (M) O.N. is low, even negative. The usefulness of O.N. re: these complexes is limited.

Redox reaction. "Redox" is simply the application of electrode potential values (see page 14) to comparing the equilibria of simultaneous reactions involving respective oxidation state changes, relative to the standard hydrogen electrode (SHE). It may be best explained by example: The water reaction of **Fe** (O.N. 3, ferric ion) and **S** (O.N. -1), as hydrogen sulphide, yields **Fe** (O.N. 2, ferrous iron) and **S** (O.N. =0, colloidal sulphur). The redox principle explains why *ferric iodine* does not exist, but *ferric chloride* ($Fe^{3+}Cl^{-1}_3$) exists. The ferric ion is too strong an oxidant, and the iodide ion is too strong a reductant for these two ions to co-exist in water. Redox reactions are important in regard to waste water and river and stream chemistry. They are pH-, relative concentration-, and temperature- dependant. Some are mediated by water microorganisms. Common Redox water chemistry includes: the **Nitrogen Cycle** (reduction of nitrate to nitrite and oxidation of ammonia); and the **Sulphide-Ferric** system (reduction to colloidal sulphur by $Fe(III)_{aq}$). Fe(II) is more readily oxidized by oxygen in neutral rather than acidic water.

Electrode Potential. Electrode Potential (E.P.) measurements are used in water chemistry for such things as sulphide evaluation and determining whether or not sulphide can be eliminated chemically. EP measurements outside of a laboratory setting, however, are difficult to make. The principle may be explained in terms of: (a) a reference element (hydrogen) giving up electrons in an equilibrium condition (at 25°C, 1 bar) in (1 Normal) acid solution; and (b) the half cells of a "battery." A battery comprises an element or positively charged ion, accepting electrons from an element/ion undergoing oxidation and giving up electrons: a voltage potential across the system. The reference half-cell is the standard hydrogen electrode—the "SHE." [A half-cell electrode potential can be either positive or negative re: the SHE, which has, by definition, a potential difference of zero volts: $2H^+ + 2e = H_2$. E^0 (E nought) = 0.000, at 25°C, 1 bar]. Other reference half-cells exist, e.g. the calomel glass electrode. When electron transference occurs and one mole per liter is the concentration of the charged ion being acted on, by definition, the associated voltage potential is E^0. At less than unity concentration, the (half-cell) voltages (E) are established (for the specific reaction, written as a reduction) by the Nernst equation: $E = E^0 + 2.3\ RT/\ n\ F \log [M^+]$. R is the gas constant (1.98 cals / mol / degree C). T is the absolute temperature (°C + 273). "n" is the number of electrons involved. 'F' is the *Faraday* unit of charge (~95,600 coulombs). "[]" represents concentration (which in a dilute solution is practically the same as ion activity). The IUPAC convention (*reduction to the RHS of the equilibrium*) applies. For strong oxidants, E^0 values are high and positive. For example, consider the following two reactions: (a) $O_3 + 2H^+ + 2e \Leftrightarrow O_2 + H_2O$. $E^0 = 2.076$ v; and (b) $F_2 + 2e \Leftrightarrow 2F^-$ = 3.0 v. Some (RHS reduction-written, metal as well as non-metal reactions, have negative values of E^0 re. the SHE. For example, for $Mg^{2+} + 2e^{-1} \rightleftharpoons Mg_S$, $E^0 = -2.37$ v; and for the equilibrium $Zn^{2+} + 2e^{-1} \rightleftharpoons Zn_S$, $E^0 = -0.76$ v. [The negative sign indicates these particular (metallic) elements have a greater tendency to give away electrons than has hydrogen gas]. When it is convenient, an equilibrium reaction may be shown as a left to right oxidation, in which case the sign of the respective, assigned E^0 must be reversed. Also, it is noted that: (a) if complexation by or ligand occurs during the reaction, the reported E^0 may not reflect the actual chemistry; and (b) pH, the particular anion, and temperature affects the particular equilibrium and, hence, the electrode potential. E^0 standard data for some common equilibria are provided in Table 4 (note the change of sign, from metals to non-metals) and other E^0 data, with E^0 temperature coefficients ($\delta E^0/\delta T$, in the range of about 10^{-3} to 10^{-5} v/°C) are given in the *Handbook of Chemistry and Physics.* In summary, some of the practical aspects of Electrode Potential are:

1. For METALS: A high positive E^0 indicates substantial ***unreactivity*** (re: reduction).

   Note. Unreactive gold: $Au^{+1} + e \rightleftharpoons Au$. $E^0 \sim +1.7$ v. Cf. reactive lithium: $Li^{+1} + e \rightleftharpoons Li$. $E^0 \sim -3.0$ v.
2. For NON-METALS: A high positive E^0 indicates substantial *reactivity:* $F_2 + 2e \rightleftharpoons 2F^-$. $E^0 \sim +3.0$ v.
3. ELEMENT DISPLACEMENT: An element with a higher negative E^0 will displace from solution one with a lower E^0.
4. In a redox (page 13) reaction, a difference between the two respective E^0 values of about +0.4 v indicates the respective reaction will go to virtual completion. For example, with due rearrangement for the redox, Fe(II) ⇒ Fe (III), *written left to right as an oxidation, note sign change,* $E^0 = -0.77$, and with (acid) permanganate, Mn(VII) ⇒ Mn(II), $E^0 = 1.51$ v. Whence for the overall reaction, E^0 is: $-0.77 + 1.51 = 0.74$, hence acid permanganate will completely oxidize ferrous iron (in acidic solution).
5. Reaction kinetics, not the E^0 cell value determines the rate that a redox proceeds.

Element	K	Ca	Al	Zn	Cr	Fe	Pb	Cu, (Ag, Au, Hg)	I	Cl	F	H
E^0 (V)	-2.9	-2.8	-1.7	-0.76	-0.74	-0.44	-0.13	+0.34, (+0.80)	+0. 5	+1.4	+2.9	0.00

Table 4. E^0 values for some common elements

Acids may be represented as HX, where X can be "multi-elemental' and the acid can be an organic acid. Acids are described as "strong" or "weak," according to their particular media. This may be shown experimentally by a plot of electrical conductance versus concentration and in studies of the rate of acid-catalyzed reactions. Acids are not classified as weak or strong on their ability to attack one substance or another. H^+ activity (bond dissociation) depends in part on the strength of the bond between H and X in the particular solvent. Another factor is the respective "ion hydration energies" (entropy of hydration).

Strong acids. Electrical conductivity measurements and also reaction kinetic studies of protonation-dependant reactions, over a wide range of concentrations of acids of comparable molarity, show two general, distinctive patterns (of proton activity), which a simple pH assessment, done on less than full-strength acids, does not disclose. Acids are differentiated as strong or weak. The ability of an acid to attack a metal even in a dilute solution is not a criterion of acid strength. Designated strong acids include: $HCLO_4$ ($HCLO_4^-$ is the "chlorate ion"); HNO_3; and HCl, HBr and HI. [HF is not described as a strong acid, notwithstanding that it can attack glass. All acids *are* corrosive to one substance or another].

Halogen substituted organic acids can be strong acids. While many organic acids have pKa values ~ 4 (see below), halogen substituted organic acids may be strong acids, when the halogen atom is just one carbon removed from a -COOH group or an $-SO_3H$ group, or is otherwise separated from these acidic groups by alternating single and double-bonded carbon atoms in the molecule (which involves π bonds). Trifluoracetic acid, CF_3COOH, is one the strongest acids known. This is due to the F "pull" on electrons, away from the O-H bond. Cf. CH_3COOH, pKa = 4.15.

Weak inorganic acids. Weak acids include acetic acid, carbonic acid, hydrofluoric acid, and nitrous acid. Weak acids exist as an equilibrium, $HX \rightleftharpoons H^+ + X^-$, between undissociated acid (HX) and $H^+ + X^-$ (which is termed the conjugate base). The equilibrium is concentration-dependent, that is, the concentration of a weak acid in water affects the equilibrium. The equilibrium is: Ka = ([H+] x [X-]) / ([HX]), where "[ ]" is "concentration." Ka which can be determined experimentally. It is conventional to quantitatively describe a weak acid by pKa. Pka = -log Ka. Note the similarity to pH. Weak acids have values of Ka <<1 and Pka values, at 1 Normal concentration, of about 3 to 4. For example, acetic acid, 4.1; HF, 4.15; and nitrous acid, 3.35.

An acid may undergo more than one dissociation. For example, the amino-acid alanine has two pKa values, corresponding to the two-step dissociation shown. Similarly, phosphoric acid, H_3PO_4, has three pKa values, corresponding to the three possible stages of dissociation involving a proton. The dissociation is higher for the process with the lower pKa value. See page 48.

Alanine: NH_3^+-$CH(CH_3)$-$COOH$ $[-H^+] \Leftrightarrow$ NH_3^+-$CH(CH_3)$-COO^- pKa = 2.35.
NH_3^+-$CH(CH_3)$-COO^- $[-H^+] \Leftrightarrow$ NH_2^+-$CH(CH_3)$-COO^- pKa = 9.87.

Lewis acid and base. (See page 16). A molecule with a vacant orbital may accept an *electron pair*: it acts as an acid. BF_3 is a Lewis acid. It is electron deficient, two short of an octet[6]. It accepts two electrons to form an "octet." **Electron pair acceptance = Acidity**.

A Lewis base is a compound which donates an electron pair in bonding, e.g. Cl^-, NH_3, H_2O, and OH^-. Note, BF_3 (acid) + $:N(CH_3)_3$ (base) → $BF_3 \cdot N(CH_3)_3$ (adduct). The lone pair (:)on the nitrogen 'joins" with the **B** atom. See page 16.

6. The "Octet" rule is an early, formal bonding model which is still in good standing. It deals with bonding and non-bonding pairs of electrons. It "shows" how single, double and triple bonds in a compound, and resonance between molecular structures, which contributes to the stability of the compound, may arise.

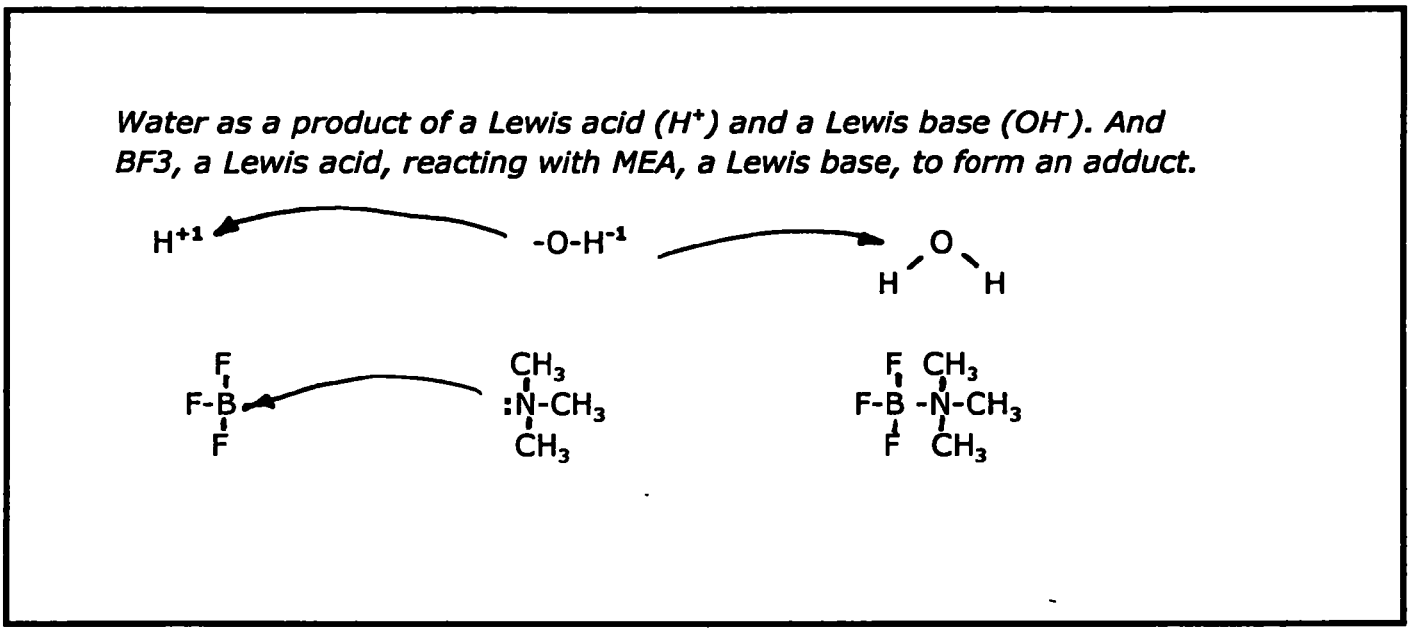

Fig. 6. Lewis acid. Lewis base. Related adducts.

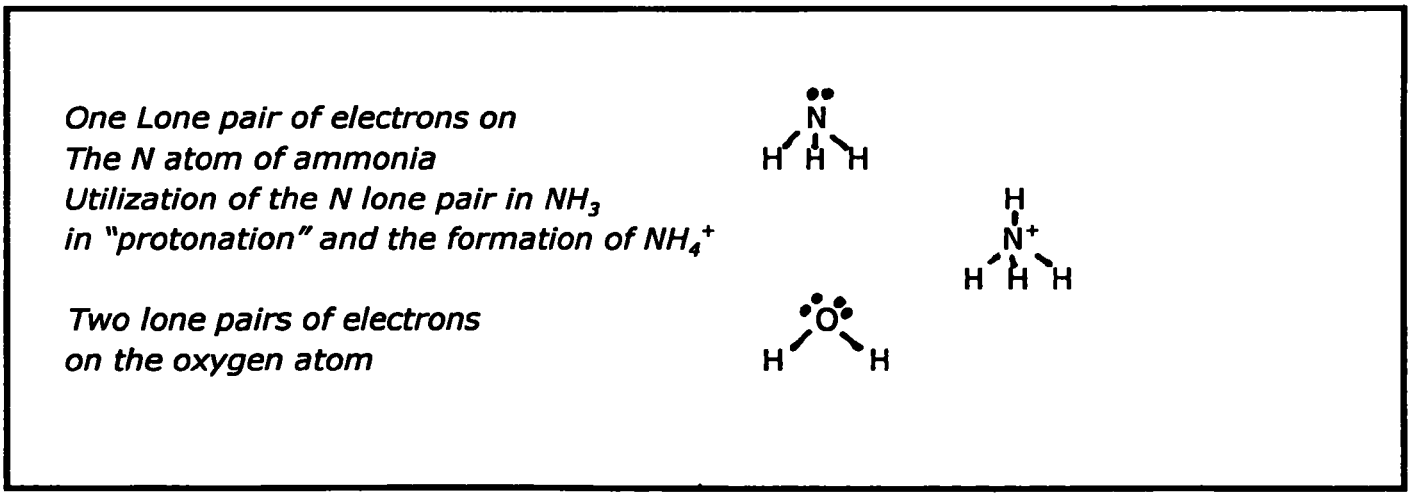

Fig. 7. Lone pairs of electrons on N and O. Protonation of the nitrogen atom in ammonia.

An example of lone electron pair bonding is seen with nitrogen ($1s^2,2s^2,2p^3$), as ammonia, bonding with hydrogen. Nitrogen in ammonia has one lone pair. With electron deficient molecules like BF_3, ammonia (via the N lone pair) forms the adduct: $BF_3 \cdot NH_3$. See fig.7, page 16. The bonding of N-H in ammonia proceeds via trivalent nitrogen and hydrogen atoms which stoichiometrically contribute three electrons/nitrogen to three bonds — stoichiometry is the quantitative relationship of elements and compounds.

Lone pair of electrons and protonation. A pair of outer orbital electrons not involved in bonding is a "lone pair"(*shown by ':' after the central atom).* A lone pair can act as a base, the lone pair can bond with a positive ion, like H^+, to form a new cation. More than one lone pair may reside on an atom. For example, the **O** atom in H_2O has two lone electron pairs. Electrons involved in either ionic or covalent bonding are those that occupy the outermost or the next outermost shells. Electrons in deeper shells are too tightly held to chemically interact. However, the actual number of electrons in the outermost shells do not always determine the number of bonds which can be made. Some of these outer electrons may lie in orbitals that are not involved in bonding. A lone pair of electrons on a central atom/ion does not take an immediate part in bond-forming, but it does affect the geometry of the molecule/ion. [Table 1].

The pH concept. The entire concept of pH is based on the existence of hydrated hydrogen cations[7,8] (H_3O^+) and hydroxyl (OH^-) ions, in only very slightly dissociated water. Further to the point of water dissociation and the (mathematical) product of dissociation: Water exists in equilibrium with H+ and OH- ions (the equilibrium is far to the left), as follows: $H_2O \leftrightharpoons H^+ + OH^-$. This is expressed in terms of an equilibrium constant, Kw, as follows: $\{[H^+] \times [OH^-]\} / [H_2O]\}$. [$Kw \approx 1x10^{-14}$]. Note that "[ ]" signifies concentration (e.g. gram ions of H^+ in a liter of water at 20°). With water the concentration of the *undissociated* water molecules greatly exceeds the (co-equal) concentrations of the two ions. The product of dissociation is written, in this circumstance, as: $[H^+] \times [OH^-] \approx 10^{-14}$. $[H^+] = 10^{-14}/[OH^-]$.

In non-aqueous systems, pH is not used. Instead a function called the Hammett Acidity Function (Ho) applies (an explanation, however, is not within the scope of this presentation). Upon extensive water-dilution of the (non-aqueous) system, Ho and pH attain the same value.

The important practical aspects of pH are: (a) "pH" is defined as "minus the log (to base 10) of the concentration of the hydrogen ion in gr.ion/liter terms. [H+ gr.ion/l], or, exponentially, as 10^{-x},where x is the pH. Thus, pH = - log [H+] = 10^{-x}. The concentration of hydrogen ion is expressed in terms of "gram ion per liter." (b) pH only applies to relatively dilute water solutions; (c) the pH range is 0 (most acidic) to 14 (most basic); (d) pH = 7 = "neutrality;" and (e) water dissociates at room temperature and the mathematical product of the concentration of the ions (H^+ and OH^-) is approximately 10^{-14}.

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7. As an example of pH calculation, a solution of 0.019 gram of 100% hydrochloric acid (a strong acid, fully dissociated: [HCl] = [H+]), in one liter of water, has a gr. ion concentration of [0.019/36.5 (the gram mole weight), gr.ion /liter]. This equals 10^{-pH}: 0.019/36.5 = 10^{-pH}. Taking logs (base 10) on both sides of the equation we get: log 0.019 - log 36.5 = -pH, or pH = log 36.5 - log 0.019 = 3.28. For determining the pH of an alkaline solution: consider a 2 gram/liter solution of NAOH, which is 2/40 (gr.mole OH^-/liter): $[H^+] = 10^{-14}/[OH^-] = 1 \times 10^{-14}/.5 \times 10^{-1} = 2 \times 10^{-13}$, when pH = 13 - log 2 (remember the definition, hence the change from + log 2 to - log 2) = 12.7 pH.
8. A relationship exists in the case of a weak acid (or base) re: pKa (or pKb) and pH. For $HA \leftrightharpoons H+ + A^-$, $Ka = ([H+] \times [A^-])/[HA]$. $Ka/[H+] = [A^-]/[HA]$. Multiple x -1: $-Ka/[H^+] = - [A^-]/[HA]$. Take logs: -log Ka + log H+ = - log$[A^-]$ /[HA]. Rearrange: -log Ka = (-log H+ - log[A-])/[HA]. pX = -log X, hence pKa = pH -log [A-]/[HA]. This gives a quantitative assessment of the impact on adding a strong acid to a solution of a weakly dissociating acid. As [H+] increases (more acid added) the dissociation of the weak acid gets less. When pH << pKa for a particular proton liberation, no corresponding 'HA' dissociation occurs. When pKa =pH, then $[H^+] = [A^-]$. The same concept applies to a weak base (b), since pKb = 1/pKa = -logKb. A weak base has a Kb <<1.

Chemical buffers

In many biological and analytic chemical reactions the pH of the system must be maintained (buffered) within a narrow range for the reaction to occur at a useful rate. Numerous buffer preparations are commercially available. They are used in water chemistry, chemical testing, and general pH control. An example of a biological buffer is: $H_2PO_{4\,(aq)}^- \leftrightarrows H^+_{(aq)} + HPO_4^{2-}{}_{(aq)}$. This (dihydrogen phosphate) system controls cellular fluid pH. Another example of a biological buffer is the carbonic acid system, which regulates blood plasma pH (to about pH 7.4).

Aqueous solutions with a pH of between about 2 to 12 (this excludes concentrated strong acids and base) are often buffered. That is, by the use of suitable chemical buffers, they are made resistant against a major pH change from a significant addition or removal of hydrogen ion.

For the change in pH to be minimal for an added amount of acid or base, the buffer should: (a) have a pK value numerically about equal (±1 unit) to the pH of the solution; (b) have an appropriate acid and conjugate base concentrations—usually about 0.01 - 0.1 molar (it is not critical, except that the concentrations need to be known in order to calculate the buffer pH, see example below); and (c) comprise a suitable acid-base conjugate pair, with the two respective species existing in reasonably comparable concentrations. The basic reason a buffer system works is that its equilibrium shifts as H^+ is added or removed and it holds [H] steady over its application range.

As an example of buffering: for acetic acid, represented by $HA \leftrightarrows H^+ + A^-$, the un-ionized HA and the A^- anion constitute the acid-base pair. The A^- is the conjugate base. The $Ka_{(25°C)}$ of the acid, is 1.75×10^{-5} (therefore its pKa = 4.756). A solution made of equal parts of 0.01 molar acetic acid and 0.05 molar sodium acetate has a respective pH, which is calculated as follows:

$1.75 \times 10^{-5} = Ka = [H^+] \times [A^-]/[HA]$. $[H^+] = 1.75 \times 10^{-5} \times [HA]/[A^-] = 1.75 \times 10^{-5} \times (0.01)/(0.05) = 3.5 \times 10^{-6}$. And $pH = -\log [H^+]$, hence $pH\ (_{buffer}) = 5.456$.

Some common acid-base pairs and their buffering ranges are given in Table 5.

BUFFER (ACID & CONJUGATE BASE)	USEFUL BUFFERING RANGE @ 25°C
Citric acid-citrate (Na)	3.0 - 6.0
K_2H phthalate-NaH_2orthophosphate	5.8 - 8.0
Na tetraborate-hydrochloric acid	8.1 - 9.2
Na tetraborate-sodium hydroxide	9.3 - 10.7

Table 5. Some common acid-base pairs and their buffering ranges

Acid Equivalent Weight. The acid equivalent weight of a substance is that weight of substance which can provide one mole of H^+ ions in the particular media. Historically, the principle is associated with inquiry by M. Faraday into the (redox) reaction involved in the sulphuric acid battery:

$Zn^{2+} + Cu \leftrightarrows Cu^{2+} + Zn$ (note the 2 electrons transferred to zinc per one molecular weight of copper).

Acid rain and its impact. Acid rain develops from solvation of airborne (acidic) oxides of sulphur and nitrogen, each of which forms two or more oxides. These gases arise from natural processes, as well as from fossil fuel burning. Power generators and municipal incinerators create acid oxides (and other major pollutants) in massive quantities. Some of the acid oxides are oxidizing and some are reducing, depending on their chemical environment. These oxides, on hydration, lead to acid rain. Acid rain destroys ancient limestone artifacts and buildings, leaches cations from soils, and acidifies many bodies of water, including streams and ponds. Acidic moieties can migrate large distances in the atmosphere. Certain cations, which are leached out of soil by acid rain, are essential for plant growth. These include the cations of sodium, calcium, and magnesium. Certain toxic cations, which are normally immobilized in soil, are leached by acid rain contacting siliceous soil and organic acids in soil. Toxic cations which are leached out of soil by acid rain include aluminum, lead, and mercury. Acid rain may be especially harmful when affected soils do not have a calcium carbonate subsurface (to neutralize the acids). Few places in the United States have an alkaline soil substrata.

Effective prevention. The effects of acid rain are unstoppable and the whole-scale neutralization of acis rain is economically infeasible. Effective prevention, inevitably, must be centered around a concerted effort: to reduce (S, N) oxide emissions; apply the best available technology, in a cost effective way, to power generation and waste incineration processes, and educate the public to the magnitude of the problem and the need for informed public activism.

Gibbs Free Energy. Reaction Feasibility. Catalysis

The second law of thermodynamics relates change, Δ, in a quantity known as Gibbs Free energy 'G' to changes (Δ's) in (a) the enthalpy ('H,' heat content), and (b) the entropy, 'S,' multiplied by the absolute temperature,'T' (with respect to a closed system at constant pressure and temperature — with heat being able to leave). Entropy, S, is a quality of randomness. A highly structured entity, like crystalline salt, at very low temperature, has little entropy, and a gas at very high temperature has very high entropy.

In many reactions of interest, and in certain circumstances, the contribution of TΔS to Δ G may be minor compared to the enthalpy change (ΔH) in the reaction: $\Delta G = \Delta H - T\Delta S$. [Absolute values of the factors are not determinable; only changes in their values are determined].

For the chemical reaction A + B ⇌ C + D (and others with a different stoichiometry), at equilibrium, the value of ΔG is zero. Also, for a reaction to be feasible, ΔG is negative.

The second law of thermodynamics does not 'say' whether or not the reaction will proceed. It does not deal with the kinetics of the reaction. It only 'says' whether the reaction is feasible. As a practical matter, when the (derived) heat of reaction is high the reaction can probably proceed. The determinative factors are available for many reactions in reference chemistry texts, and equilibrium constants (Ka) can be determined experimentally or indirectly calculated. Even for a thermodynamically feasible reaction to proceed, the reactants must undergo change and energy is needed to overcome the associated kinetic barrier before the reaction can proceed. For example, in a reaction involving hydrogen gas, the hydrogen molecule bond breaks and forms two hydrogen atoms, and uses energy.

When all the reactants and products (i.e., A, B, C, D) are at a molar concentration, the term G_o is employed to represent the Gibbs free energy. At equilibrium in the reaction, $\Delta G = \Delta G_o + 2.303\ RT \log Ka$. And since at equilibrium $\Delta G = 0$, then $\Delta G_o = -2.303RT\log Ka$. When Ka is known (determined experimentally), ΔG_o may be established and ΔG may be calculated for a given circumstance.

Catalysts. Catalysts are required to initiate some reactions. A catalyst is a substance which lowers the energy barrier to the reaction proceeding, but it does not alter the reaction equilibrium. The catalyst provides an enormously large surface area on which transitory chemical and/or physical adsorption, of one or more reactants, occurs. The catalytic process may be described as follows: as the inter-atomic bonds of each reactant's atoms weaken, the free energy *increases (*the kinetic energy barrier to the overall reaction is lowered). The reactants are acted upon in such a way that the original barrier is effectively surmounted. An analogy is that of a ball rolling downhill, being stopped by a bump in the road, and needing a shove to get it over the bump—when it accelerates on its way to a lower section of road. The catalyst provides the 'shove.'

Biocatalysts (i.e. enzymes, plants, certain antibodies and engineered genes) are now widely employed to produce more of one form than other when such forms of a product of reaction exist (e.g. selective enantiomorph production). Catalysts in nature, enzymes, are highly specific to one or a few biological reactions (homo-catalysis). The natural catalysts can cause chemical reactions to selectively occur (which organic chemists find generally hard to do without resorting to using natural products). Man-made catalysts are generally non-reaction specific. However, they are often only applicable to reactions which are chemically alike. The petroleum industry, the drug industries, and some others have engineered highly-efficient, substrate-specific, action-specific (homo-) catalysts.

Autocatalysis. A product of a reaction may actually accelerate the reaction. This is "autocatalysis.' Autocatalysis is now used to increase production yields of one desirable (usually a drug) enantiomer over another.

An enantiomer is a form of a compound which has the same molecular formula as another form, but with a different spatial arrangement, which may have special biological and/or physical properties. For example, the herbicide *Dichlorprop* is a racemic mixture, but only one form (enantiomer) is active in killing weeds. Selective enantimorphic production of dichloroprop is of interest to environmentalists, as a way to minimize pollution. Many similar examples exist.

Atomic packing arrangements. The structure of an element or alloy at different temperatures is of primary importance to metallurgists seeking optimum alloy performance in hostile environments.

Let a sphere represent an atom. If a two-direction, single extended layer of spheres, all in contact with one another, is overlaid by a similar layer so that it fits as closely as possible and a third such layer is overlaid on the former double layer, also closely fitted, then two kinds of (3-tier) arrangements exist: (1) the *first* (A) and the *third* (B) arrays of spheres are directly in line, i.e. ABABAB. This combined array is described as hexagonal close-packed, (HCP); and (2) the *third* array (in this instance C) is displaced, with respect to the *first* array, by half a sphere diameter, i.e. ABCABCABC. This combined array is described as **"cubic close-packed"** (CCP).

Both HCP and CCP arrangements are fully symmetrical and maximally packed (maximal density). The HCP and CCP close-packed arrangements (a) differ between themselves in the numbers of tetragonal spaces which occur between the layers of spheres, and (b) have the "same nearest neighbor" arrangement: each atom is surrounded by 12 nearest neighbors: six in the same layer as that atom, and three above and below that atom (which is true for any close-packed arrangement). Within these close-packed arrangements are two different kinds of distinctly shaped spaces (holes), between spheres, which may be occupied by other atoms of a size which does not strain the spatial arrangement. The two distinctly-shaped holes, within a three tier (and the multilayered) close packed atomic array, are: (a) octagonal holes, and (b) tetrahedral holes. There are twice as many tetrahedral holes as there are octahedral holes.

The presence of octahedral and tetrahedral holes in a CP structure makes for some complex compound structures, including layered molecules, many of which involve partial filling of both types of holes which exist in the multi-tiered array.

A third, non close-packed, atomic stacking arrangement exists: the "Body Centered Cubic" (BCC). The BCC atomic arrangement has each atom surrounded by 8 nearest neighbors, cf. "12 nearest neighbors" for the close packed HCP and CCP lattices. Metals in the Body Centered Cubic lattice form are much harder to "work" than metals in either the HCP or CCP lattice forms.

Dominant structural arrangements exist for some elements. The CCP structure dominates the first transition metals. However, the BCC structure is common to V, Nb, Ta, Cr, Mo, and W. These metals are normally very hard to 'work.' An element can have one or more atomic packing arrangements, and one form may be predominant in a specific temperature range. Some metals exhibit two stable structures, depending on the respective temperature and treatment. As examples: (a) Li and Na are BCC *and* HCP; (b) Ti, Zr, and Hf are BCC *and* HCP; and (c) Fe is CCP *and* BCC.

A *compound* need not adopt the structural form of any of its *constituents*. Little if any predictability exists solely on the basis of constituency. When a compound exhibits low polarity, it is quite likely to be covalently bonded. When a compound is highly polar, it is likely to exist as an infinite array of the atoms of one of the component elements.

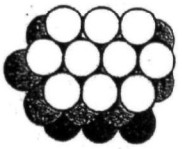
Crystal Lattices. Compounds exist in several dominant structural arrangements which characteristically allow different numbers of ions to surround another atom/ion— a situation which is referred to as the "coordination." **The common types of crystal structures** are named after structurally similar common compounds. For example, **NaCl** (rock salt, C.N. = 6); **CsCl** (cesium chloride, BCC, C. N. = 8), and **CaF_2** (fluorite, C. N. = 8). Other common, important crystal structures are: **Rutile** (TiO_2), which is the main source of titanium; **Zinc Blende** (ZnS), whose structure is a face centered cubic with half the sulphur lattice tetrahedral holes filled symmetrically by Zn atoms; and **Wurtzite** (hexagonal ZnS). Other fairly common structures are: **Corundum**, after Al_2O_3 (O atoms in a HCP structure with two-thirds of the octahedral holes filled with Al atoms, e.g. Hematite, α Fe_3O_4, is "corundum"); **Spinel**, after $MgAl_2O_4$, a naturally occurring mineral; **Ilmenite**, after the naturally occurring mineral of the same name: Fe(II)Ti(III)O_3; and **Perovski**, with the form of ABO_3 ("A" is the smaller cation and it is at the center of a cube, and "B" is the larger cation and it is at the corner of the cube, and the "O" (oxygen) atoms are at the cube face centers). The complex fluorides $KMgF_3$ and $KZnF_3$, and calcium titanate and tungstate, are "**Perovski.**" [See page 28]. **Some compounds have "anti-" structures.** For example, Na_2O has an "**antifluorite**" structure — with the Na^+ cations residing in the tetrahedral holes of the lattice of the oxygen ions.

Polymorphism. A substance may have the same composition but different structures. For example, the compound (Zn, Fe),S exists as (CCP) *spharlerite* (a mineral), as well as (HCP) *wurtzite* (a mineral).

Isomorphism. Some minerals have the same structure but different compositions, e.g, NaCl as *halite*, and PBS as *galena*. This relationship is not obvious from the formulas. In isomorphism, ion size and relationships are more important than chemical similarity. Note **Ca** and **Mg** have about the same chemistry, but different ionic sizes. They do not form isomorphous (same form) compounds.

Preferred structure. The preferred ionic crystal structure for a compound is the one which provides the greatest stability—which is the same as the one with the least free energy.

CUBIC CLOSE PACKED (CCP) — PLAN VIEW



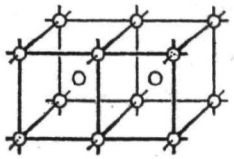
THE CPP 3-TIER ARRANGEMENT IS "ABC."

HEXAGONAL CLOSE PACKED (HCP).

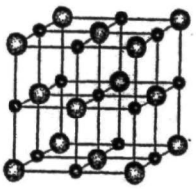
THE REPEATING HCP-STACKING ARRANGEMENT IS "ABABAB" [Description at page 20].

BODY CENTERED CUBIC (BCC)

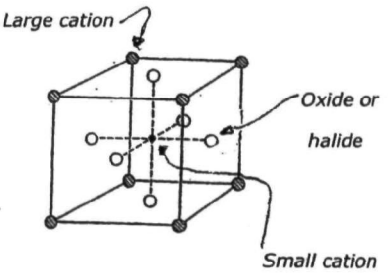
(NON CLOSE-PACKED)



NaCl (Rock Salt) lattice.

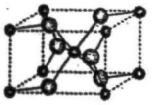


(Small spheres are metal atoms)

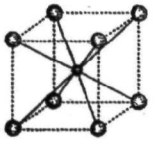


Perovskite ($CaTiO_3$)

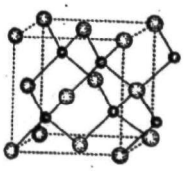
(Some other lattices).



Rutile (titanium dioxide)



Cesium chloride

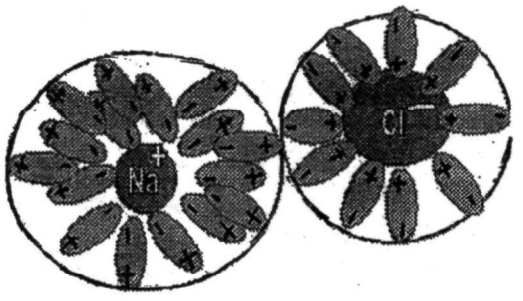


Zinc sulphide

Fig. 8. Some lattice types (re: page 21)

Na ion hydrated and Chloride ion hydrated in NaCl aq. Note the (representative) larger size of the Cl ion, with less water ligands and the clustering within in the Na ion hydration shell.

Ions and their hydration shells move together in passing through membranes, and in other transport phenomena.



Note the reported electron density profile of the water ligand is not oval, as shown, rather it is as follows:

Fig. 9. Ion and compound hydration (re: page 25)

Lattice formation energy (also called *energy of crystallization*). Energy "holds" the lattice together. This energy is the enthalpy change (negative) which ensues when the lattice is formed from its 'parts.' The strength of the lattice depends on: (a) the (positive effect) force of attraction between the two oppositely charged ions); and (b), the (negative effect) force of repulsion between the same two ions when they come close together. With the first factor, as the coordination number increases for the ion, the ionic force increases, and with latter factor, the repulsive force increases rapidly as the ions "squeeze together." The relative ion sizes (of same charge) determine the (least energy) crystal arrangement.

The lattice formation energy has a negative heat change value. As an example, the reported lattice formation energy of sodium chloride is minus 788 KJ. mol^{-1}. The lattice formation energy is determined indirectly using Hess's law, in the form of a Born Haber cycle. [This 'cycle' takes into account the energies used or released in the attaining the various physical states and stages involved, from start to finish, in forming the lattice, regardless of the routes involved. For more on this topic consult "Hess's Law and the Born-Haber Cycle"].

Lattice formation energy increases as the ion size decreases and the ion charge increases. For example, LiF, -1036 kJ. mol^{-1}; KF, -821 kJ. mol^{-1}; MgF_2, -2957 kJ. mol^{-1}; MgI_2, -2440 kJ. mol^{-1}.

The Lattice Energy is the measure of the strength of the lattice. It is the amount of energy which is required to separate the solid lattice into its gaseous parts. The lattice energy value is always positive.

General Lattice Types. Lattices in the solid state are: ***ionic*** (e.g. NaCl); ***homopolar*** (covalent bonded, generally high melting, e.g. diamond); ***molecular*** (separate molecules held together by van der Vaals forces, e.g. solidified methane); or ***metallic*** (band of electrons, none of which belong to any one atom).

The **Goldschmidt rules** apply to the kind of lattice structure than ensues from the chemical union of one element with another. For example, a BCC lattice (described as 8:8 coordination, each atom has 8 nearest neighbors, e.g. NaCl) is formed for AB, a binary molecule, when the ionic radius ratio (rA/rB) range is 1 to 0.73; and a face centered cubic structure (6:6 coordination, e.g. cesium chloride) is associated with a reported ratio range of 0.73 to 0.41.

The key point on lattices is that lattice properties are determined by the sizes, shapes and numbers of the ions involved, not by the chemical properties of the ions. The maximum number of ions in contact with the smaller ion, usually the cation, while preserving electrical neutrality, controls the lattice type.

The **Coordination Number** (C.N., also called the "Goldschmidt number"). Coordination number is a factor of lattice structure. It is the number of ions or molecules which can fit closely around a central common atom. The C.N. depends on the size of the radius of the ion, around which other ions of "unit" radius can be arranged to be "just-touching."

For the non-transition elements, with a binary compound, the size of the ions involved determine the Coordination Number and, hence, the stereo-chemistry of the respective compounds.

With the transition elements, d-orbital filling affects the stereo-chemistry.

The energy available from uniting one ion with another of opposite charge (the lattice formation energy) is a factor in the stable oxidation number(s) of the cation. Another factor is the energy available from ion solvation. Together, the lattice formation energy and the ion solvation energies may or may not be more than the energy required ("compensation") for a particular (first, second, third) ionization potential. The energy involved in remotely separated gaseous atoms uniting to form a lattice (AH negative), together with the ion solvation energy (AH negative), may compensate for the energy required for a particular ionization stage to take place. This may facilitate the formation of a respective compound. An ionic bond with a particular cation in a particular positive oxidation state will not occur if the respective ionization potential is too high to be "compensated" for by the ionic lattice energy and the ion solvation energy. Of course, a *non-ionic* bond may occur (but not when a redox situation prevents its stable existence). With boron trifluoride, BF_3, the B-F bonds are not ionic; the ionization potential involved in forming the B^{3+} ion is too high to be offset (compensated for) by the corresponding lattice energy and solvation energy. [The BF_3 molecule is a trigonal planar molecule. The **B-F** bonds are all covalent, via SP^2 hybridization. The molecule is a Lewis acid and forms many adducts with electron donor- molecules or radicals. See fig. 6, page 16]. Reported minimum radius of an ion just touching an ion *of unit size*, and the corresponding "Goldschmidt Coordination" and lattice structure are given in Table 6.

COORDINATION	LATTICE	RELATIVE RADIUS
8 fold	cubical	0.732
6 fold	Octahedral	0.414
4 fold	Square Planar	0.414
4 fold	Tetragonal	0.275
3 fold	Triangular Planar	0.155

Table 6. Coordination number, lattice structure, and minimum ion relative radius

Ionization Potential. The energy associated with loss of an outer orbiting electron from an atom is termed the "ionization potential, I.P," which is expressed in terms of "electron volt per atom" (eV = 23.9 Kcal/mol. = 96.48 KJ/mol. [This "atom-to-mol." conversion reflects the Avagadro number, N_A. N_A iIs the number of atoms in *any* mole, which equqls = $6.02252 \times 10^{23}.mol^{-1}$]. The I.P. can be a factor of an element's preferred oxidation state. The I.P. is affected by the degree of nuclear shielding that exists from the respective presence of inner orbital electrons. Ionization potential data explain why, in Groups 1 and 2, significant variation in physical and chemical properties exist between the first element in the Group, compared to rest of the elements in the Group (the rest are alike). The Group 1 elements only form stable compounds, with the cations in O.N. +1, e.g. Na^+, as in Na^+Cl^-. No oxidation state other than +1 is known for Group 1 binary compounds. The elements in Group 1 have very high **second** ionization potentials, e.g. Na: 2nd IP ~ 47 eV. The 1st I.P. for sodium is ~5eV. The higher 1st IP values are seen with helium and the noble gases, e.g. helium, ~25 eV; neon, ~23 eV. The lower 1st IP values are seen with the alkali metals, e.g. lithium, 1st IP ~5 eV. In general, the 1st IP values decrease as the atomic number of the element in a Series increases. The second and third (and so on) ionization potentials also increase sequentially.

Ion hydration. Ion hydration is an active area of research and interest for biochemists, neuro-chemists, and others. It is a basic part complete solvation. Ions are surrounded by a shell of H_2O ligands (L). The respective aquo-complexes are dispersed in water: $M^{z+ (or -)} + nL = MLn^{z+ (or -)}$.

Reportedly, virtually all ions in water are hydrated, except Rb+ and Cs+, which are large, low-power-polarizing ions. Ion hydration is energetically favored (negative enthalpy), strongly so for Fe(III) and Al(III). Also the (negative) enthalpy of M-L formation, for the alkaline earths and the halogens, are comparable. The bonds in the aquo-ion are ion-dipole bonds, however, the bond lengths are indeterminate, but several angstroms. Ions move with their hydration shells. The relatively negative surface of the oxygen atom in each water ligand is directed toward a cation, and away from an anion. The number of water ligands in the ion complex depends on the size and charge of the central ion. Symmetrical distribution occurs when the number of ligands is relatively small, but asymmetrical distribution, including clustering, also occurs. The water ligands in a complex may be replaced by a ligand which bonds stronger to M than water, e.g. ammonia: $Cu(H_2O)_6 + 6\ NH_3 \rightarrow Cu(NH_3)_6 + 6(H_2O)$. Water dissociates very slightly and it is hydrated by itself: $2H_2O = H_3O^+ + OH^-$, and $H_3O^+ + H_2O = H_5O_2^+ + OH^-$ (hydroxyl ion). Ion solvation is a factor in an element existing in a particular oxidation state. The (-ve) energy associated with ion solvation depends on the ion, but it is in the order of (-)1000 KJ/mol. Ion hydration is a factor in the "strength" of an acid. For example, F^- ion hydration is strongly energetic (negative heat change); this tends to cause dissociation of HF, but, in this particular case, it is not enough to cause all the **H** to **F** bonds to dissociate. The strong H-F bond makes HF a relatively weak acid, but one which is corrosive: HF attacks glass (to give SiF_6^-). Hydrofluoric acid can be handled in copper, monel or PTFE vessels.

Molecular compounds with water. Stable hydrated inorganic compounds exist with various types of bonding involved and with the water tightly bound to the molecule. An example of a molecular water compound (aquo-compound), of which a great many exist, is $[Be(H_2O)_4]Cl_2$ (made via the exothermic addition of beryllium chloride to water). $[Be(H_2O)_4]Cl_2$ is a stable compound. It can be crystallized from solution using HCl. The $Be(H_2O)_4^{2+}$ aquo-ion forms numerous crystalline salts. Another example of a molecular water compound is $Na_2SO_4.12H_2O$. In this molecule, the water molecules occupy definite positions within a "rock salt" crystal structure. Another example is BF_3-H_2O (M.P. 10.2^{0}C). The water molecules in these particular examples are firmly attached, but in some other water compounds, varying degrees of water-binding strength occurs. Thermal gravimetric analysis, TGA, may be used to determine the stability of a molecular water compound. Also, a plot of "melting point vs. gram mole percent water" may be used. For example, for ferric chloride in water, a plot of "melting point vs. gram mole percent water" shows four minima. Each one corresponds to the existence of a pure hydrate: $Fe_2Cl_6 \cdot 12\ H_2O$; $Fe_2Cl_6 \cdot 7H_2O$; $Fe_2Cl_6 \cdot 5H_2O$; and $Fe_2Cl_6 \cdot 4H_2O$.[9]

Electroplating. Faraday's law. The Electrochemical Equivalent

One Faraday = 96,500 coulombs of charge. One coulomb = one ampere.second. One gram equivalent = {[Atomic Weight] / [Valence Number (in the reduction reaction)]}. One Faraday will 'plate out' one gram equivalent of the element, using an appropriate cell. In silver plating { $Ag^{+1} + 1e = Ag\ (s)$}, for example, the silver gram equivalent is {107/1=107}, and 107 grams of silver deposits with the utilization of one Faraday of energy. The "**electrochemical equivalent - K**" is the "gram equivalent divided by the Faraday." For example, <u>for silver</u>, K = 107.88/96500 = 0.001118 (gram equivalent/Faraday). When 'current and time' is known, the deposited amount may be calculated. Thus, the silver deposited by 10 amps for 2 hours, is: (107x10x2x60x60)/96,500=79.86 gm. [The cell is not 100% efficient, due in part to electrode surface and charge distribution effects, including gassing and an associated over-potential].

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9. Other <u>concentration terms</u> are applicable, for example: *molar concentration* — the number of mole weights of solute/ liter solution; *normality* — the number of solute mole equivalents per liter of solution (formula weight/number of the charge on the atom involved, e.g. for Al^{+3} this equals one third of its atomic weight); *mass percent* — grams of solute per 100 grams of solution X 100; and *volume percent* — milliliters (ml) of substance per 100 mls of solution X 100.

Hydrogen. Hydrogen exists as dihydrogen (H_2, the common, no-neutron, diatomic molecule), deuterium (naturally occurring in trace amounts in hydrogen), and tritium (an isotope created by upper atmospheric cosmic radiation of nitrogen). Dihydrogen has a molecular orbital arrangement of only bonding orbitals occupied by electrons. No antibonding molecular orbital occupancy arises, hence the stability of H_2. All of the isotopes of hydrogen (and for that matter any other element) behave identically chemically, with the exception of "rate of reaction," which is mass-dependant. Isotopic physical properties of an element are slightly different from one another because these properties are atomic mass-related. [Hydrogen has been proposed as an alternative to gasoline for automobiles. The potential for an adverse effect on the ozone layer, however, is unclear]. **Hydrogen predominance:** Hydrogen, reportedly, accounts for most of the atomic content of our universe.

Hydrogen-carbon bonding. Hydrogen and carbon form millions of compounds, most of which are non-ionic. They are essentially covalently bonded. An "electron-pair" bonds the elements. No "loss" or "acquisition" of a single electron is involved. The reason for this extensive degree of covalent bonding is hydrogen's very high first ionization potential, which is actually higher than that of the noble gas zenon.

Hydrogen-highly electronegative element bonding. Hydrogen bonds with highly electronegative elements, like fluorine, oxygen and nitrogen, to form ionic compounds, via $H - e \Rightarrow H^+$ cation. [The H^+ cation exists in water as hydrates: H_3O^+, $H_5O_2^+$].

Hydrogen embrittlement. Hydrogen embrittlement of metals is seen as a cause of failure in many investigations of chemical and industrial plant accidents. Hydrogen embrittlement of steel and high strength or high temperature alloys is a major concern in industrial manufacturing, chemical plant operation, and airframe construction. The phenomenon involves nascent hydrogen gas (and/or methane formed by the nascent hydrogen) penetrating inter-granular zones or sub-surface cracks, with localized high pressures. Hydrogen sources, involved in embrittlement of vulnerable alloys, include hydrogen sulphide (also called sulphur embrittlement), hydrogen in welding rod coatings, and hydrogen in chrome-electroplating cathodes. Special pre- and post- treatments can prevent hydrogen embrittlement of susceptible metals which are to be used in high stress or chemically severe environments. In some instances, such treatments are required by national codes. No one method is satisfactory for evaluating hydrogen embrittlement. A battery of tests is used. This includes: the notch sample-200 hour load test; other low cycle fatique tests; and scanning electron microscopy, using a surface-polished and sometimes a chemically-etched specimen, for detecting inter-granular changes.

Hydrides. With highly electropositive elements (e.g. sodium), hydrogen forms ionic hydrides. The ionic bond character relates to hydrogen acquisition of an electron, e.g. $H + e \Rightarrow H^-$.

The hydrides of Group 1 and Group 2 elements are mostly ionic and reactive. The hydrides of the first transition metals are numerous, stable and often interstitial. For these metals, the "ratio of ionic sizes," rather than normal valency, controls molecular composition, bond character and properties.

Hydrides exist with little ionic bond character. These include water, methane, arsine (AsH_3 but no dihydride), phosphine (PH_3) and diphosphine, (P_2H_6), boron, aluminum, gallium, indium and thallium (unstable) covalent-bonded. Polymorphic hydrides exist, e.g. diborane, B_2H_4. No simple BH_3 molecule exists, but adducts of BH_3 exist. See page 42.

Carbon. $1s^2 2s^2 2p^2$ (in the ground state, with two unpaired p- electrons, following Hund's rule). Carbon chemistry is characterized by carbon's unique ability to form millions of organic compounds by using a multitude of orbital hybrids (s-, p-, d-orbitals), which carbon generates to a degree not shown by any other element. In the IUPAC PT format, carbon is the first element of Group 14. See Table 7.

(Atomic number ⇨)	**6**	**+2, (⇦ oxidation states of stability)**
(Symbol ⇨)	**C**	**+4, (⇦ Ditto)**
		-1. (⇦ Ditto)
(Atomic weight ⇨)		**12.011 (⇦ uneven number reflects isotope contributions)**
(Electron configuration ⇨)		**2, 4. (⇦ 2 electrons in the "1S" atomic orbital, 2 in "2S" and 2 in "2P.")**

Table 7. Carbon

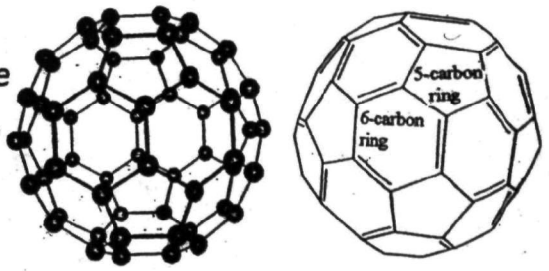
By convention, the carbon-12 isotope (C=12) is the standard of atomic weight (also called the 'average mass number.') It applies to all elements. The atomic weight of carbon itself is 12.001, which reflects with the presence of carbon-12, carbon-13, and carbon-14 isotopes. [See "Some notes on radioactive isotopes," page 56]. **Methane,** CH_4, is the simplest stable carbon compound. [The C atom orbitals are hybridized, SP^3). An unstable simple carbon-hydrogen compound, CH_2 has been reported. Its outer electron configuration, $[1s^2]\ 2s^2,\ 2p^4$ is electron deficient, however. It is two electrons short of an $[1s^2]\ 2s^2$-$2p^6$ "octet" (which corresponds to a stable bonding configuration). **Fullerenes (C_{60} and C_{70}), a basic form of carbon:** Carbon forms a great many cyclical, cage-like and tube-like compounds — Fullerenes, generically termed carbon-based nanostructures (with single and double bonds), discovered in the early 1960's. The most famous fullerene is the "C_{60} - Buckmaster Fullerene," also known as the "Buckysphere." It was named after Buckmaster Fuller's giant Geodesic structure, which it structurally closely resembles [See fig.10]. This giant Geodesic structure was exhibited in the 1967 World Fair in Canada. A host of C_{60} and C_{70} Fullerene compounds and some salts (e.g. $C_{60}K_3$, with the K^+ ion inside the cage) exist and are used for special purposes, such as polymerization of olefins and formulating lubricants. Also, bundles of carbon nanotubes are of interest in extreme-sensitivity (stress, temperature, pressure, and fluid motion) space sensor technology. **Catenation** is the distinctive, but not unique ability of carbon to form massive chains and rings by virtue of multiple orbital hybrids. See Table 8.

1S	2S	2P	Hybrid	Comments
⇅	⇅	↑ ↑	SP	(A). 3 possible orbital arrangements for the Carbon atom (which has 6 electrons) and the (shown) four electrons in the 2nd shell, and their SP SP^2 SP^3. [Hunds' law controls atomic orbital filling].(B). SP^2 hybridization for all carbon atoms, with pi bonding,is one of two essential requirements for aromaticity (and extraordinary stability) in a cyclic hydrocarbon molecule, e.g. benzene, or cations or anions, like the cycloheptatriene cation. [The other essential criterion for aromaticity is the pi electrons must = 4n +2, per Huckel's rule; for benzene, the number of pi electrons = 4x1+2 = 6].
⇅	⇅	↑ ↑ ↑	SP^2	
⇅	⇅	↑ ↑ ↑	SP^3	

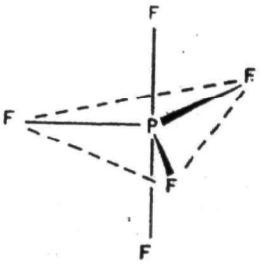
Table 8. Carbon S - P orbital hybridization

Carbon Oxides, Sulphides, and Halides. Stable carbon monoxide, carbon dioxide, carbon disulphide, and carbon oxysulphide, COS, exist and are toxic —except for carbon dioxide, which is a simple asphyxiant. Carbon monoxide (C, O.N. 2) on burning yields carbon dioxide ,C, O.N. 4. (CS also exists). Carbon monoxide is poisonous because it interferes with oxygen to blood binding. $CX_{4(\text{All halogens})}$ exists.

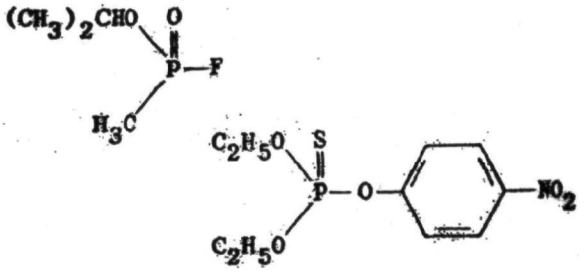
The C60 Fullerene carbon allotrope. Note the close resemblance to a soccer ball construction. The (C60 and the C70) stable carbon structures are "valence-balanced," via 12 five-membered cyclic "faces" (panels) with a variable number of other six-membered "faces" and with conjugated (=-=) double-single bonds. (Page 27).



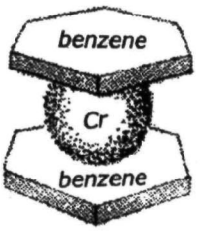
PF_5 molecular shape (page 47).



The structure of Sarin (with ionic P-F bond which is readily hydrolyzed). Cf. Parathion (a water insoluble, thionic acid ester). Both are organo-phosphorus compounds which are toxic by cholinesterase inhibition.



Cr (benzene)$_2$: A historical sandwich complex (re: page 54).



Ethylene diamine tetra acetic acid and EDTA-calcium complex. Ca-EDTA is stable only at high (>9) pH, when EDTA (acid) exists as $[EDTA]^{4-}$. Note, Ca is O.N.+2. (Page 52).

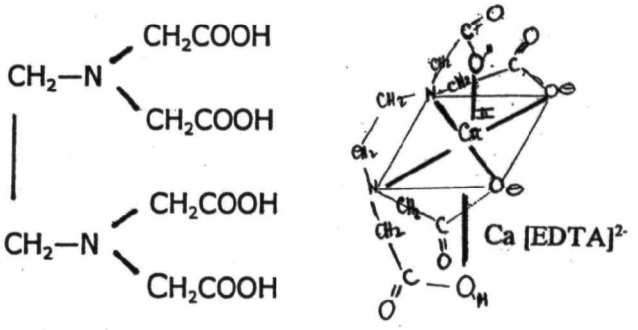


Fig. 10. Miscellaneous diagrams (individually referenced to subject and page)

Carbides. Carbides are formed between carbon and many elements. The carbides of the elements of Groups 1, and 2 are ionic and reactive. In water they yield acetylene (indicating a C_2^{--} ion) and/or similar "allylenes" (indicating a C_3^{---} ion). Other carbides exist as interstitial compounds, many of which are refractory and electrically conducting. For example, tungsten carbide (W_2C) and molybdenum carbide (Mo_2C) are cutting tool materials which are not affected by dilute acids.[The carbon atoms reside inside an extended array of metal atoms]. A carbide need not be interstitial, however, to be hard and refractory. For example, chromium forms several non-interstitial, refractory carbides. Still yet other arrangements exist for large cations (as complicated structures). In (stable) iron carbide, Fe_3C, the C atoms reside inside a trigonal prism. Iron carbide reacts with acid. See fig. 10. The nature of the carbide depends on: (a) the relative atomic radii of the two components; and (b) the relative component negativities. Two conditions exist with an interstitial carbide (MX). The atomic radii ratio (Rx/Rm) must not exceed about 0.6, which translates to the metal atomic radii reportedly being ≥ 1.4 Angstrom. Also, the electronegativity difference must be small. With an interstitial carbide, typically, the metal exists as a cubic closed pack lattice, and the carbon atoms occupy the lattice's octahedral holes. Metals which form interstitial carbides include: **Mo** (atomic radii 1.4 A^0) and **W** (atomic radii 1.4 A^0). Metals which do not form interstitial carbides include **V, Cr,** and **Mn** — their atomic radii are <1.4 A^0.

Carbide embrittlement. Carbide embrittlement of structural steels and alloys is a major concern in the manufacturing, chemical, and construction industries. It is a cause of many structural failures. The phenomenon involves iron and other metal carbides forming in inter-granular zones, causing a granular discontinuity and loss of ductility and other desirable properties. It often results from improper heat treatment and poor mixing in manufacturing. Various methods are used to evaluate carbide embrittlement. They include the techniques used to evaluate hydrogen embrittlement. Secondary ion mass spectroscopy (SIMS) is used extensively. Notch-sample and extended time-load tests are used, and optical microscopy (at 10 to 300 magnification) of polished surface specimens is used universally.

The Periodic Table

The (reduced) IUPAC 1989 version of the Periodic Table (fig. 1) is used in the subsequent sections.

The IUPAC format[10] of the Table particularly depicts hydrogen as shown in Table 9.

(Atomic number ⇨)	**1**	**+1,**	**(⇦ oxidation state)**
(Symbol ⇨)	**H**	**-1.**	**(⇦ oxidation state)**
(Atomic weight ⇨)	**1.00794**		
(Electron configuration ⇨)	**1**		**(⇦ one electron in 1-S shell).**

Table 9. Carbon.

The atomic number (Z) of the element is the number of protons (p) in its atomic nucleus. **Z** is balanced by an equal number of electrons. [Atomic number defines an element]. **The element symbol** is usually the first two letters of the Latin or Greek name, e.g. Fe (iron), "ferrum." **The mass number (A)** is the number of protons *and* the number of neutrons (n) in the nucleus. [Mass number defines an isotope].

10. The first modern-type Table was constructed by Mendeleef in 1886. It was a remarkable accomplishment given that atomic weights were unknown at the time, only about sixty elements were known at that time, and Meneleef left places in the table for, and correctly predicted the existence of elements, which would only be found decades later.

The atomic number (also called the average mass number, or the atomic weight) is the total mass of the element. It is based on carbon =12 (an international standard).

Isotopes (with a reference to radiometric dating). Consider carbon, one isotope one isotope of which is ^{14}C. It has the same number of (6) protons, but a different number (8) of neutrons in the nucleus, as the ^{12}C isotope of carbon (6 protons and 6 neutrons). An isotope of an element has a common **mass number** (protons + neutrons), but a different **atomic number** (protons only). The isotopes of an element have virtually identical chemical properties, but some generally slightly different physical properties. Also, elements with even-numbered atomic weights tend to have more isotopes than odd-numbered elements. Additionally, isotopes with an even number of neutrons tend to be relatively more stable. Most isotopes are stable, but the isotopes of the heavier elements are generally unstable (radioactive). Particles may be ejected or absorbed by their nuclei (with a balance being attained between the nuclear charge and the "mass-energy," via the Einstein equation, $E = MC^2$). This can result in various products (daughters), via electron (beta, β) capture, electron (β) decay (emission), or by the emission of a heavy particle, an alpha particle, which comprises 2 protons and 2 neutrons. Radioactivity may be accompanied by a release of energy from the parent core (gamma emission). The orbiting electrons are not involved in radioactivity (other than intra-electron capture). Radioactive isotopes have characteristic half-lives, some of which are very short and some others are very long (several thousand to several billion years). A half-life is the mean time for half of the initial amount (the number of atoms originally present) of isotope to decay. After 7 half-lives, the respective isotope has decayed by more than 99.2 percent.

Naturally occurring ^{14}C (β decay, half-life 5730 years, daughter: nitrogen-14) is used to radiometrically date cloth, wood and organic matter, of about 100 to 70,000 years old. Naturally occurring ^{40}K (β decay and β capture, reported half-life =1.3 billion years, with the daughters, respectively, being argon-40, and calcium-40) is used, in conjunction with ^{40}Ar, in the radiometric dating of rocks, ice and artifacts, with an age in the range of about 10 million to 5 billion years (see page 56).

Oxidation number/state (other than zero) is the electronic configuration of the element, when one or more electrons "relocate," via ionization, from or to the element. For example, sodium metal is oxidation number 0. Upon a "one outer orbiting electron loss" (oxidation), it becomes Na^+, oxidation number =1. Sodium is too electropositive to form a negatively charged ion (an anion). Fluorine (0), on the other hand, readily acquires an electron and thereby undergoes a reduction in oxidation state to O.N.-1.

Oxidation number reflects stoichiometry, which is the relative quantities of reactants and products in a reaction. It is not reflective of chemical bond type or molecular geometry. Moreover, it is not meaningful when the compound in case has no stoichiometric composition (e.g. Fe_6S_7). A formal oxidation number does not necessarily indicative of the charge distribution in a compound. For example, in dichlorine heptoxide, Cl_2O_7, the Cl ion has an O.N. of +7, but there is very little evidence for the halogens resembling metals.

Electron configuration refers to the "post-noble gas core" outer atomic orbitals' electron filling order.

Table organization. The Period Table is an arrangement of the elements in terms of Groups (columns) and Series (rows). Currently, there are 110, *IUPAC-established* elements. The Series differ between themselves in the number of electrons in the principal atomic shells. In comparing the atomic number differences between the Series, and hence, the number of electron differences between them, one sees that the electron "build-up" is: 2, 8, 8, 18, 18, and 32. This "build-up"reflects the increasing complexity of the electron orbitals with increasing atomic mass.

About 80% of the elements are metallic, either in the elemental state (oxidation number zero) or in one of more compounds (with the cation having an oxidation state of plus one or higher). Even iodine, while it generally forms iodides and exhibits non-metallic behavior, acts metallically in forming I^+ compounds, like **ICl**.

The PT Series reflect the similarities of the elements within each Group in terms of electron configuration, as well as physical-chemical properties.

Atomic shells, sub-shells and orbitals exist in a probabilistic sense. The outer sub-shell orbitals occupied by electrons influence the respective molecular bonding, structure, and other properties. The energy separating the sub-shells and their orbitals decreases with increasing shell number.

A fundamental aspect of the Table is that the disposition of the elements is dictated by their chemical and physical behavior and by the properties of their ions. The position of an element in the Table generally indicates the main valency and other properties of the element in binary compounds. In the case of the centrally located Groups, main valence and compound properties are less clear from the location. The occupancy of the d- orbitals, with associated extra-stability of empty, half-filled and fully-filled orbitals, and other factors affect valency.

Elemental chemical and physical behavior is affected by: (a) the size of the respective ion; (b) the charge on the ion; and (c) the **polarizability** (electron distortion) of the element involved.

Polarizability means the tendency of the electron cloud around the molecule to be distorted (over and above any existing distortion from electronegativity differences between the bonded ellements) by an external electrostatic force. The larger the atomic size, the greater is the elemental polarizability, e.g. compounds of S^{-2} are more polarizable than compounds of O^{-2}.

Numerous Periodic Table-formats exist. They all display the elements in vertical Groups, and in horizontal Series.

The 1989 IUPAC (International Union of Pure and Applied Chemistry) PT format is more informative than many of the earlier versions of the Table. It is still not yet used universally, however. It organizes the elements into 18 Groups and 7 Series. It provides information on each element's atomic number, symbol, atomic weight, stable oxidation states, and electron configuration. [A few other formats provide even more information, e.g. crystal structure, ionic radius, electronegativity, and the first ionization potential].

Atomic properties include: atomic number (symbol Z, representing the number of protons in the nucleus); elemental isotopic composition; electron occupancy of outer atomic orbitals (surrounding a noble gas type, electron-filled core); stable oxidation states; and other physical-chemical factors. Atomic properties affect, to one degree or another, the formation and the properties of molecular compounds and *molecular complexes* (which are, of course, molecular compounds).

A striking aspect of the of the earlier Tables is that their Groups are in accord with current knowledge of "electron sub-shell-and-orbital" characteristics (which determine the chemical and physical properties of compounds). The element electron arrangements, in terms of Groups, Series, and sub-shell electron orbitals are illustrated, in part, in figure 6.

Perusing a Periodic Table (PT) is an excellent way to understand environmental chemistry. Reviewing the Table in the light of what is known about the major environmental challenges, shows that less than fifteen percent of the elements, in one form or another, account for almost all of the current environmental and occupational hazards. Of course, a plethora of compounds are involved in environmental and occupational health issues. The reason is simple and two-fold:

1. Many of the elements are either too rare (e.g. the lanthanides and actinides, but also other elements), too precious (gold, platinum), too reactive or uncommon (cesium), or too inert (krypton) to account for major environmental problems.

2. The elements in general enter into a myriad of singly or multi-bonded arrangements with other elements totaling millions of compounds, the vast majority of which pose no known serious environmental or occupational health threats.

Insight into chemical properties is gained by comparing and contrasting elemental data. These data include:

- Electronegativity (scale 0 to 4)
- First (and second, etc.) ionization potentials (energy, expressed in "electron volts," eV).
- Stable elemental oxidation states.
- Ionic radius (measured spectroscopically, in Angstom units, $A^0 = 10^{-10}$ meter).
- Crystal structure.

The bond character of a binary compound is dictated by the difference in the electronegativity of the elements involved. Using the available data, one can "visualize" particular binary compounds as exhibiting either extensive, moderate, or virtually no ionic-bond character.

"Ionic radius versus Z" data together with first, and second (and sometimes the third) ionization potential information, provide a basis for anticipating the properties of a binary compound.

Selected ion size data, derived from X-ray analysis by L. Pauling, are given in Table 7.

Ionic radii, electronegativity, and ionization potential do not solely determine properties. Bond type and strength, molecular structure, lattice energy, and energy of ion solvation are other factors.

A well-evidenced trend to be seen in the Table is the way distinctly different physical and chemical properties arise with the first element of a Group, compared to the subsequent, larger atomic number-elements in that Group. This phenomenon occurs across many of the Groups.

ELEMENT	O.N.	IONIC RADII, A°	ELEMENT	O.N.	IONIC RADII, A°	COMMENT
H	-1	2.08	Pb	+2	1.21	S = SAME OXIDATION NUMBER AS SHOWN IMMEDIATELY ABOVE
F	s	1.36	Pb	+4	0.84	
CL	s	1. 81	Mn	s	0.8	
Br	s	1..95	-			LISTS ARE NOT IN P.T. GROUP ORDER, NOR ARE FULL GROUPS SHOWN.
I	s	2.16	Zn	s	0.69	
			Cd	s	1.03	
			Hg	s	0.93	
O	-2	1.4	Fe	+2	0.78	THE VALUES SHOWN ARE THOSE REPORTED BY L. PAULING. SOME DIFFERENT VALUES HAVE BEEN REPORTED BY OTHER SCIENTISTS, BUT MOST OF THEIR VALUES ARE CLOSE TO THE PAULING' VALUES.
S	s	1.84	Co	s	0.74	
Se	s	1.98	Ni	s	0.69	
Li	+1	0.6	Bi	+3	0.20	HIGH FORMAL OXIDATION STATES DO NOT NECESSARILY MEAN THAT AN ION OF THAT CHARGE EXISTS, RATHER THE VALUE REFLECTS A SYSTEMATIC FORMALITY.
Na	s	0.95	Al	s	0.50	
K	s	1.33	Tl		0.95	
Cu	+1	0.96	C	+4	0.15	
Ag	s	1.26	Si	s	0.41	
			Ti	s	0.68	
			Ce	s	1.01	
			Sn	s	0.71	

Table 10. Selected Ion Radii (after L. Pauling)

Lithium, the first element of Group 1, resembles magnesium (second element of Group 2). Other examples are: beryllium (Group 2) resembles aluminum (Group 13). Also, boron, the first element of Group 13, resembles silicon, the second element of group 14.

In Group 2, beryllium stands out from magnesium, calcium and the other elements in this Group because beryllium oxide, BeO, is refractory. It resembles aluminum oxide, Al_2O_3 (Group 13).

In contrast to beryllium, magnesium oxide, MgO, forms insoluble magnesium hydroxide, $Mg(OH)_2$. [Mg^{2+} charge/radii ratio = 2.6]. And calcium oxide, CaO, forms soluble calcium hydroxide, $Ca(OH)_2$. [Ca^{2+} charge/radii ratio = 2.0].

The beryllium cation has an exceptionally high "ion charge-to-ion radius" ratio. [Be^{2+} = 5.9, comparable to Al^{3+} = 6]. This and other energy-type factors account for the differences.

Notes on the physical properties (boiling point, volatility, etc.) of some elements, in context with the Periodic Table (in descending order of Group number)

At this juncture physical-chemical properties, in context with the Table, are briefly discussed.

The noble ("inert") gases. The noble gases (Group 18) are monatomic. No molecules are formed in any phase. In the solid phase the noble gases exist as a close-packed arrangements of unbonded atoms. Some stable compounds of the noble gases exist, e.g. XeF. The prefix "inert" is not preferred simply because such compounds exist.

The halogens (Group 17), as elements, exist essentially as diatoms (e.g. F_2). Iodine dissociates at low temperature: $I_2 \Leftrightarrow 2I$. As solids, the halogens have crystal structures, in which the "nearest neighbor-to- the next nearest neighbor" ratio increases with increasing atomic number. For example, F, ratio = 1.4; and I, ratio = 1.33.

As a rule, elements in Groups become relatively more metallic as the value of this ratio approaches unity. Iodine (the least electronegative of the common halogens) shows metal-like properties in some compounds, e.g. I^+Cl^-, which is stable, and $I^+(py)NO_3$. [py = pyridine].

The "oxygen group" (the "Chalcogens," **Group 16)** elements exist in di- and poly- atomic forms. They exhibit some ring and long chain structures. Oxygen O_2 (dimer) is the most plentiful element and is paramagnetic. [This is not expected on the electron pair bonding theory, but it is explained by molecular orbital (M.O.) bonding theory. In the former case, two unpaired electrons per oxygen would "pair" with the two other unpaired electrons in the other O atom, so that no unpaired electrons exist. Thus, the dimer would be diamagnetic, not paramagnetic. With M.O. bonding theory, 2p- orbital bonding interaction would put two single electrons in a 2p- antibonding orbital, with **O** to **O** covalent bonding and (liquid oxygen) paramagnetism, as is the actual case, and which cannot be explained by the Lewis bonding theory].

Oxygen does not form ring or long chain structures. Sulphur, on the other hand, exists in (non-metallic) S_8 ring and (metallic) S_8 chain structures. Also, selenium exists as a (non-metallic) Se_8 ring structure and a (metallic) Se_8 chain structure.

The peroxides of the elements of Groups 1 and 2 are ionic compounds. The peroxides of zinc, mercury, cadmium, and silver are stable compounds, which have extensive, but varying degrees of covalent bonding. Peroxides in alkaline solutions readily release oxygen. On the other hand sulphuric acid is used to stabilize hydrogen peroxide.

Crystal structure of the Chalcogens (the Oxygen Group). For this Group, the atomic "nearest neighbor to the next nearest neighbor" (in the crystal structure) ratio increases with atomic number. This tendency reflects the trend to metallic properties with increasing atomic mass: O_2, ratio = 1.56; Se, ratio = 1.48; and Technetium, Te, ratio = 1.2. Note technetium is a metal which does not exist naturally. It is formed in radioactive reactions.

The "nitrogen group," Group 15, elements and compounds have well-known characteristics. Nitrogen is diatomic in all phases. Phosphorous exists as a finite molecule (white P) and as a macromolecule (red P). Arsenic and antimony exist as finite (non-metallic) molecules, e.g. As_4, Sb_4, but also as metallic (chain) forms, e.g. As_∞. Sb_∞). Bismuth exists only in the metallic form, as an infinite array of atoms. Arsenic is a human carcinogen. In the nitrogen Group, the "nearest neighbor to the next nearest neighbor" (in the lattice structure) ratio increases with atomic number. The ratio for (non-metallic) phosphorus 1.76; and, at the higher molecular weight end, the ratio for bismuth is 1.12. Bismuth is metallic.

The "carbon group," Group 14, elements and their characteristics are widely known: Carbon exists as diamond, (layer-structured) graphite, and (C60/C70) Fullerenes. Silicon and germanium have "diamond lattice" structures. And tin (which exists in two, temperature-dependant phases) and lead are essentially metallic, but not exclusively so: "stannate" ($SnO_3^{--}.3H_2O$) and "plumbate" ($PbO_3^{--}.3H_2O$) anions exist.

Diamond has a hardness of "10" (maximally hard) on the Mohs Hardness (Scratch) Scale. [Gypsum talc, calcium phosphate hydrate, has a value of 1 (least hard). The mineral, apatite, $Ca_5(PO_4)_3$ (F,OH), which is a constituent of bone and teeth, is 5 on the Mohs hardness scale. Plastics typically have a rating of about two, and 'Thermosets" are higher. A human nail has a Mohs hardness rating of 2.5. A scratch, not a mark or a deposition, is the test criterion]. Boron nitride, BN, which has a diamond-like structure, reportedly, scratches a diamond and is "off the Mohs Scale." Diamond is harder than silicon. Silicon is harder than germanium (a rare element). That boron nitride is evidently harder than diamond, may be explained by the gradation in the shortness and strength of the respective, covalent bonds: **C-C**, 1.54 A^0. **Si-Si**, 2.34 A^0. **Ge-Ge**, 2.44 A^0. **B-N**, 1.45 A^0.

Further observations on the Periodic Table.
Some environmentally significant chemistries

The placement of each element within each Group strongly reflects the influence of relative electronegativity, oxidation state, and outer electronic configuration on the respective chemistries.

Relative electronegativity means the relative ability of an atom, in a molecule, to attract an electron to itself. "Relative" conveys the point that an electron donor may be similarly electronegative, in which case any union which occurs has little if any ionic character, and some other type of bond exists.

Electronic configuration refers to the arrangement of the outer atomic orbitals and electron filling. The various sub-shell orbitals are filled by electrons following: the "Aufbau" orbital occupancy order (mentioned later); Pauli's exclusion rule (two, opposite spin electrons per orbital); and Hund's rule (maximize single electrons per orbital, in filling the p, d, f sub-shells. Half-filled and fully-filled orbitals provide extra-ordinary stability to an ion, element, or molecular complex).

The Alkali Metals Group 1 (Li, Na, K, etc.) occupy the first (left most) PT Group. The elements are characteristically soft, lustrous when cut, and highly reactive. They are the most electropositive of all the elements—or stated another way, the least electronegative of all the elements. The singly positively charged ion (cations) are coordinately bonded to a surrounding shell of water molecules. With this Group, the binary compounds formed with all the other elements are polar. Some small degree of coordinate bonding occurs in elemental vapor and in some solid molecular complexes; e.g. gaseous sodium, as Na_2, and rubidium complexes.

The alkali metals are too reactive to be stable by themselves in most media. Also, their reactivity (electro-positivity) increases in Group descending order. For example, lithium reacts only slowly with water, sodium (out of its oil containment) reacts vigorously with water, but potassium instantly explodes in water.

In the case of Group 1, Lithium is different from the other members in several other ways. Lithium hydride, LiH, is stable at 900 degrees Centigrade, whereas NaH decomposes at about 350 degrees. The difference is explained by lithium having a relatively far higher "ionic charge-to-ionic radius" ratio. In this regard, lithium resembles magnesium [Mg(II)] in salt formation and solubility.

Most of the metal salts (e.g. chloride, bromide, fluoride, phosphate, hydroxide) are soluble, but lithium with small anions (like fluoride) forms much less soluble salts: **LiF** is barely soluble (<3 gr/liter, 20 degrees Centigrade), while NaF is very soluble. On the other hand, lithium with a large anion (like chlorate) produces a more soluble salt, compared to the other elements in the Group. [The LiF bond is very strong due to the small radii of both the ions and a high electronegativity difference. The extent of lithium water coordination is greater than for sodium. This increased coordination causes an overall weaker bond between the lithium and the chlorate ions].

The Group 1 metals form reactive organic compounds, e.g. Li-alkyls. [Lithium forms many reactive organo metallic compounds: 2 Li + butylbromide (in ether) → $CH_3(CH_2)_2$ CH_2-Li (n-butyl lithium) + LiBr].

The **Alkaline Earth Metals, Group 2** (beryllium, magnesium, calcium, strontium, barium, radium) are relatively highly electropositive and chemically reactive. Their first ionization potential values are low, as are their second ionization potentials. They yield stable, doubly-charged ions, e.g. Ca^{2+}.

Most of the binary compounds, e.g. $CaCl_2$, of the Group 2 elements are ionic, but covalent type bonding also exists in molecular complexes, for example, the Ca^{+2} EDTA complex has both types of bonds. [EDTA: ethylene diamine tetra acetic acid].

Some common Group 2 element binary compounds are covalently bonded. For example, BeS, which is structurally similar to ZnS, a **zinc blende** mineral structure.

Beryllium. Beryllium is used extensively in manufacturing ceramics, X-ray tubes, and high strength-high conductance alloys. It is also a by-product of coal burning. It is hazardous and exposure may result in skin lesions, and pulmonary disease, including chronic beryllium disease. This disease is characterized by weakness, fatigue, non-productive cough, and possible pulmonary edema.

Beryllium is unique among Group 2. Its "charge-to-ionic radius" value is much larger than the rest of the Group. Beryllium forms a hydroxide, which, like magnesium hydroxide, is easily precipitated from solution. All the other alkaline earth hydroxides are appreciably water soluble. Beryllium bonds with carbon in different ways and ratios, to yield numerous, simple compounds, like beryllium carbide, $BeCH_3$, and compounds which are polymeric and/or have a bridge structure, e.g. crystalline $(BeCl_2)n$.

The Group 2 elements, except for radium, are widely distributed in soils and are present in sea water. Calcium, strontium, barium and radium have essentially divalent (ionic) chemistries. Radium is the most electropositive metal of Group 2. The isotopes of radium are radioactive. ^{226}Ra has a half-life of 1600 years.

Strontium chemistry resembles that of barium, essentially as O.N. +2 compounds. Strontium is a continuing world-wide public health concern. Strontium can displace calcium in the body. It has a long-lived radioactive isotope, strontium-90. This isotope is now widely disseminated, following several major nuclear plant incidents. Reportedly, in the period 1950 to 1970, Russian nuclear facility accidents resulted in the release of large quantities of strontium-90 and other radio-active elements, which were not only deposited in regional rivers and soils, but were transported in air across countries and oceans. Other countries also have had serious nuclear accidents. Strontium-90 soil and air contamination is well-monitored for public protection.

Barium chemistry is essentially O.N +2. It is poisonous, but occupational overexposure is rare. Inhalation of barium compounds as dusts has caused occupational injury involving the cardiovascular system, the pulmonary system, and the central nervous system. Barium compounds are used extensively as a rodenticide, a pesticide, paint pigments, plastic stabilizers, rubber mold lubricants, and as stabilizer additive for some magnesium alloys.

Groups 2 through 11. These Groups contain elements which can be considered *en bloc*. Their electronic configuration includes d- orbital filling to one degree or another. Some of the more environmentally problematic elements in this "block"are summarily described in this section and in other sections (see "Notes on the Transition Series").

Group 6 includes chromium and molybdenum. **Chromium (Cr).** [Ar core]$3d^5$ $4s^1$. Note the 3d-orbital filling to the half-filled point, before the 4s- orbital starts to fill. The 4s- orbital is also half-filled. Half-filling of confers extra-stability, due to relatively lessened nuclear shielding. Chromium is paramagnetic.

Chromium is used in making stainless steels, in welding rods for stainless steels, in chromate salts production, and in chrome plating. Chromium salts are colored. A 'wet chemistry' test for Cr is the blue color of unstable Cr(v), formed by acidified hydrogen peroxide.

Chromium compounds pose environmental and occupational concerns. Over-exposure to airborne chromium-containing particulate, regardless of the Cr oxidation state, may cause occupational nasal/sinus problems, neurological effects (weakness, dizziness), respiratory disease, depression of macrophage count and phagocyte activity, and birthing complications. Chrome plating workers and chromium chemical workers can have significantly (i.e. two orders of magnitude) higher chromium exposures than the general population. Also, long-term work in the vicinity of poorly ventilated chrome plating baths poses an unacceptable level of occupational cancer risk.

Chromium compounds exist in three main oxidation states: +2, +3, +6. The preferred chromium oxidation state is +3. [Chromium is a member of the "transition elements," so named because of the multiplicity of exhibited oxidation states. Other common transition elements of environmental importance are vanadium, iron, cobalt, and nickel]. Chromium(VI) — Cr +6, hexavalent chromium, chromate, polychromate — is a designated human carcinogen, as well as being a dermatic sensitizer. Chromium(VI) is more easily absorbed by the body than is chromium(III). In the body Cr(VI) converts to Cr(III), which readily enters the blood.

The current EPA risk level limit for Cr(VI) is 0.5×10^{-5} mg/day. All potential exposures to chromium-bearing particulate must be minimized, using all feasible engineering and administrative controls. Attention needs to be given to personal hygiene, work habits, and maximal separation from sources.

The chemistries of chromium and the other transition metals are influenced by how the d-orbitals (or f-orbitals in later transition series) are filled. Chromium chemistry may be summarized as follows:

O.N. +6: STRONGLY OXIDIZING STATE. CrO_3 (used in chrome plating and in anodizing aluminum). Chromates and polychromates, e.g. $Cr_2O_7^{2-}$ (orange dichromate). No "CrF_6."

+5: Hypo-chlorates exist in strongly alkaline media. CrF_5.

+4: Ba_2CrO_4. K_2CrF_6 (And mixed Cr oxidation state compounds).

+3: PREFERRED OXIDATION STATE. Stable Cr(III) ions, including F, Cl, Br, I. Cr_2O_3. Many complexes, e.g. $(NH_4)_3Cr(CNS)_6$.

+2: STRONGLY REDUCING STATE. Chromous acetate. CrO. Very few salts exist.

+1: Some Cr(I) complexes, i.e. Cr(I) dypyridine.

Zero: Cr $(benzene)_2$ — a *sandwich* compound [See fig.10, page 28].

Group 9 includes cobalt, which is of significant occupational health concern. Cobalt is used to braze tungsten carbide to steel, and in making cutting tools and drill stock. It forms an intense blue color when fused in a glass. The color is characteristic of ancient Chinese ceramics, e.g., bowls.

Cobalt: Co. [Ar core] $3D^7,4S^2$. Cobalt particulate and simple cobalt compounds are toxic, with the target organs being the kidneys and liver. Cases of reported industrial poisoning include three clinical manifestations: allergic dermatitis at the site of contact or friction, involving fine dust from cobalt-cemented metal working tools and from pottery working (which is demonstrable by skin patch testing); reversible pulmonary reactions, from working with cobalt-cemented tungsten carbide tools; and progressive lung disease, from chronic exposure to Cobalt dusts. Cobalt(II) compounds have also have been implicated in thyroid and heart diseases and in increased circulating red blood cells from over-production by bone marrow (polycythemia).

Cobalt exists in hexagonal close packed and cubic close packed forms. Elemental cobalt is also used extensively in manufacturing special purpose alloys, such as superior performance drill stock alloy. It exhibits two stable oxidation states: +2 ("ous" salts), +3 ("ic" salts) and forms numerous complexes, which are commonly tetrahedral in structure. No simple +1 compounds exist as solids or as simple ions in water. Cobalt major chemistry is summarized as follows:

O.N. +3: Simple Co(III) compounds are not stable.
Halides at this O.N. are only stable as complex structures (e.g. complexes with ammonia). A mixed Co(III), Co(II) oxide exists: cobalto-cobaltic oxide, Co_3O_4. Cobalt(III) complexes are stable. Numerous complexes, e.g. $[Co(NO_2)_6]^{3-}$ — hexanitrocobaltate(III). Note the six NO_2 radicals total six negative charges, which are offset by the three Co positive charges.

+2: Simple compounds of Co(II) are very stable, e.g. oxide, sulphide. Co on burning →CdO. $Co(OH)_2$, very low solubility. Co(II) complexes are unstable. Co(II)-Co(I) complexes exist.

Group 12. This Group includes zinc, cadmium and mercury.

Zinc, cadmium and mercury are metals with $d^{10}s^2$ ground state electronic configurations. The first and second ionization potentials for each element are, respectively, 9 -10 eV, and 17-18 eV. Their third ionization potentials are very high, 35-40 eV.

It might be expected from ionization data that the M^{+1} cation would exist for *all* three of these elements. **No simple M^{+1} ion exists for zinc.** Simple and complexed M^{+2} ions exist for zinc, cadmium and mercury.

The elements of Group 12 show a strong tendency to covalent bonding as M^{+2}. Zinc also forms a peroxide, ZnO_2 (Zn, formal O.N. 4), via hydrogen peroxide on zinc oxide, at minus 10 degrees Centigrade.

Zinc is used as a sacrificial cathode (a Redox mechanism) in the *cathodic protection* of the steel-hulls of ships and as a protective coating for steel Zinc chloride (melt, used in various metal joining fluxes) is an electrical conductor, unlike mercury chloride, which is a non-conductor. Zinc is amphoteric (reactive with both acids and alkalies). Zinc reacts with alkali to form a zincate: ZnO_2^{2-}.

Zinc is non-poisonous. Numerous zinc-containing enzymes have been identified in humans and many other species. The roles of some of the zinc enzymes are not completely understood. On the other hand, overexposure to zinc fume, as often occurs when zinc-protected steel is welded or gas torch-burned, may result in metal fume fever, which resembles influenza. The problem is self-limiting, however. It lasts only for two or three days after the onset of the signs.

Zinc, like cadmium, in complexes, shows "6- and 4-Coordination." Zinc also shows "5-Coordination," as in the trigonal bipyramid Zn(II) complexes. See fig. 3, page 6.

Cadmium (Cd): [Kr core] $4d^{10}5s^2$.

Cadmium is found in small quantities in the (CdS) ore Greenokite and in zinc, copper, and lead (sulphide) ores, from which it is smelted. Cadmium is used in numerous alloys, including (low-friction) bearing alloys and silver solders, in electro-plating (and hot dipping) steel, as a preservative, and in battery-making, and in making green phosphors used in television screens. It is also used in some fungicidal, insecticidal and nematodicidal preparations.

Cadmium is a designated human cancer agent. Cadmium particulate is a strong respiratory tract irritant. Acute over-exposure, from inhaled Cd dust, or Cd hot work or grinding, may cause metal fume fever. This causes flu-like symptoms, which develop within about a day, after onset following the initial, medically significant exposure. Cadmium is found in cigarette smoke. Heavy smokers show elevated blood cadmium.

Cadmium industry workers need to consistently practice good personal hygiene. Employers need to employ *administrative* (required washing, separate work, clothes-changing, and eating areas, etc.) As well as engineered controls for safeguarding employees. Hot work and grinding or blasting over cadmium-coated steel needs to be stringently regulated and only permitted as a last resort, when appropriate personal protection equipment and other safeguards are is required. A job safety analysis and industrial hygiene monitoring are essential. As used in other medically significant toxic metal/substance exposures, *medical* surveillance of the workers, including periodic blood analysis, is generally appropriate.

The main oxidation states of cadmium are summarized below.

O.N. +2: Salts are usually colorless and highly poisonous. CdO. CdS. $Cd(OH)_2$, a strong base. Cd (II) halides are soluble in water. $K_2Cu(CN)_4$. Auto-halide complexes exist (e.g. $CdCl_3^-$ in strong Cd-halide solutions. $CdCl_4^-$ in conc. HCl). With ammonia, Cd (II) forms (inorganic) amines: $[Cd(NH_3)_4]^{++}$.

+1: None.

Zero: Cd and Cd complexes. Cd exhibits sixfold coordination in some complexes.

Mercury (Hg): [Xe core] $4F^{14}5D^{10}6S^2$.

Mercury is dangerous when handled improperly. It is a highly toxic, major environmental pollutant. Elemental mercury is sufficiently volatile at room temperature to cause potentially seriously hazardous airborne exposures. Historically (pre-1960's) occupational mercury exposure caused "felters' (mad hatter) disease" — distal neuropathy in the wool felt industry, as well as the poisoning of workers in thermometer-manufacturing and in other operations where open mercury containers were present. These workers often exhibited the *blue gum line* sign of mercury poisoning. Nowadays, mercury poses a low-frequency occupational risk, but a significant environmental risk, which originates mostly from industrial sources, including power generators and waste treatment plants. Some Hg contaminant sources are natural.

In December, 2003, the Administration (U.S. EPA) proposed a major, comprehensive program to maximally limit mercury releases from power plants. These plants would have up to 15 years to install new technology aimed solely at reducing mercury pollution. In addition, measures were proposed for using advanced technology to achieve major reductions in soot-forming chemicals from smoke-stacks. Also, most mercury battery types, and also mercury biocides and other products, have been voluntarily or mandatorily phased out, or are subject to stringent waste disposal rules applied by the US. EPA and the States.

Mercury released into the environment can lead to bio-accumulation of organo-mercury compounds (e.g $(CH_3)_2Hg$ and CH_3Hg^+). In water this results from microbial action on elemental or mercuric mercury. Hg(II) is readily methylated, biologically and chemically. Organo-mercury bio-accumulation causes the regular consumption of tuna and bottom feeding fish to be a potential health risk. [In our regional bio-monitoring work we have seen several cases of employees with elevated blood mercury, which were ultimately traced to eating canned tuna].

Mercury in dentistry. A current health concern, to some individuals at least, is mercury amalgam used in dentistry. In recent years, claims have been made that a long-term, public health risk exists from mercury vaporization and leaching, albeit at low rates, from tooth amalgam. The *occurrence* of such leaching is supported by chemical testing, as well as mercury-isotopic monitoring of mercury in the body. The claimed *consequences*, however, are contentious. Arguments abound. The opponents of mercury amalgam dentistry assert that: (a) mercury, in the amalgam filling, vaporizes and disseminates into the brain, the liver, and into other human tissues, and this places minors and pregnant people at special risk; and (b) non-metallic, cost-effective materials are available and should be used. The proponents of mercury amalgam dentistry are the Boards of Dentistry and the dental supply houses. They argue the long-term absence of poisoning cases; the demonstrated general safety of mercury amalgam; and the absence of broad-application, cost-effective, alternative materials. At this time, the decision on accepting mercury amalgam dentistry is a personal choice and mercury amalgam usage in this country is seen as not likely to quickly change.

Mercury chemistry

Mercury itself is a liquid which is not affected by air. Mercury forms two series of compounds: O.N. +1, O.N. +2. Covalent bonding with mercury is common, e.g. the halides. The common names terms of the two oxidation states are: Hg(I), *mercurous*, compounds, and Hg(II), *mercuric*, compounds.

Univalent mercury halides show little tendency to form complexes. Mercurous oxychlorides exist.

Divalent mercury has a strong tendency for Hg(II) complex formation, e.g. $HgCl_2.2NH_3$.
Simple Hg(II) compounds exist, e.g. HgO, HgS. They are not very stable.
Hg(II) compounds are reduced to elemental mercury on heating. Also, they are readily "complexed."
All the Hg(II) halides are known. HgF_2 is water soluble. The other Hg(II) halides are insoluble.

Mercury chemistry is summarized as follows:

O.N. +2: Unstable O.N. ["- ic" compounds]. All reduce to Hg(I) on heating.
Only + 2 compounds yield stable "ammines" with ammonia.
HgO (black oxide) is known, which decomposes on heating to HgO.
HgS (cinnabar) exists naturally. It is made directly by the intimate mixing of the elements.
HgX_2 (all halides) are stable. They are formed by direct reaction.
Hg(II) has a marked tendency to form molecular complexes.

+1: Stable preferred O.N. ["-ous" compounds]. No stable complexes of Hg(I).
Hg_2O via direct burning in air. A bivalent Hg-Hg complex exists, e.g. Hg_2^{2+}.
Hg_2X_2 (all halogens) known, but only Hg_2F_2 is water soluble.
Estimated by standard iodometry. [Excess IO_3^- followed by filtration and titration of excess KIO_3, by standardized thiosulphate, using KI as the indicator].
Hg(I) is used to titrate Fe(III), with thiosulphite as the indicator for Fe(III). Cl^- and NO_3^- do not interfere, which makes the titration very useful.

Zero: A large number of alkyl and aryl mercury compounds: RHgX and R_2Hg (e.g. dimethyl mercury, which is stable in water and bio-accumulates up to human consumption of contaminated fish).
Elemental mercury at room temperature is unaffected by the halogens in the absence of air.
Mercury amalgam.

Group 13 covers the elements Boron, Aluminum, Galium, Indium and Thallium.

Boron, B, has the ground state electronic configuration: $1s^2$, $2s^2$, $2p^1$. Boron is *not* similar to its Group member aluminum, since boron has essentially covalent chemistry (aluminum forms ionic compounds). The respective (three) ionization potentials of boron are too high to show ionic bond character, even after energy compensation by the relevant ionic hydration and lattice energies. No simple, B^+, B^{2+}, B^{3+} ionic compounds exist. Boron with nitrogen forms **borazon**, a stable *inorganic aromatic* compound.

Borides are known for most of the elements. They are generally hard, refractory, and chemically inert. They exist in numerous stoichiometries and geometric arrangements.

The main oxide of boron's is B_2O_3. Also, BO exists. **Boric acid,** $B(OH)_3$, ensues from B_2O_3 hydrolysis.

Borates exist as cyclic compounds and infinite chains. **Boron tri-halides** exist for all the halogens.

Boron hydrides exist and are known as boranes, but BH_3 exists only transitorily as an un-adducted molecule. Various borohydride ions exist, e.g. BH_4^-, BH_3CN^-, and $BH_3.NMe_3$.

Boron valency. Boron is almost always trivalent, because of orbital hybrization and the low energy needed for this to occur: [He core] $2s^2 2p^1 \Rightarrow$[He core] $2s^1\ sp_x^1,\ 2p_y^1\ (SP^2)$. This outer electron ($SP^2$) configuration confers a planar structure, with 120 degree separation of bonds, on the trivalent, uncharged molecule. The B atom in BF_3 is electron-deficient (i.e. two electrons short of an outer electron octet in an SP^3 configuration (which can accept a pair of electrons). Thus, BF_3 is a Lewis acid. It forms numerous adducts, e.g. BF_3.MEA (methyl ethyl amine). Moreover, the boron ion radius is small. The two last points account for much of boron chemistry. For example, the ion BF_4^- does not arise unless the associated cation is a large ion, like Ca^{++} (but not Li^+ or Na^+).

Boron industrial use. Boron compounds are used throughout industry. The element itself is used in metallurgy in making very hard alloys. Boric acid is used in fireproofing fibrous materials and wood. It is also used and sold as an topical antiseptic. Other uses include manufacturing glasses, soldering fluxes, ceramic enamels, and cleaning compounds. Boron trifluoride, BF_3, being a Lewis acid, is used as a catalyst and as a reactant in many organic reactions. For example, with a Grinyard reagent (RMgBr), BF_3 may form: BF_2R, BFR_2 and BR_3.

Boron compounds are local irritants (eyes, skin, nasal pasages). Boric acid or borax applied to broken skin may cause severe systemic poisoning (nausea, pain, vomiting, weakness). Industrial injuries have been associated with localized contact and poor occupational hygiene. Occupational boron poisoning is rare. Accidental or deliberate ingestion of boric acid, reportedly, has resulted in severe kidney injury and gastro-intestinal disturbances and a myriad of other symptoms and signs of systemic poisoning.

Group 14 includes **tin** (Sn) and **lead** (Pb). The Group mainly exhibits O.N. 2 and (more stable) O.N. 4 chemistry. The O.N. +2 state is reducing.

Tin. The chemistry of tin which is of major environmental importance concerns organo-tin compounds. These compounds have the general formula of $RSnX_{(4-n)}$. The tin oxidation state in these compounds can be +2 or +4. At least one covalent carbon-to-tin bond arises. The R radical can be alkyl or aryl. The (valence balancing) anions are numerous. They include: hydride, hydroxide, iodide, chloride, fluoride. oxide, acetate, mercapto-acetate, benzoate, laurate, and oleate. A large number of organo-tin compounds are used in vinyl polymer manufacturing (as stabilizer), in lubricants (as stabilizer), in shipbuilding (as a hull anti-fouling paint), and in numerous rubber product manufacturing processes.

The toxicity of the organo-tin compounds vary from isomer to isomer. Skin lesions caused by these agents, especially tributyltin acetate, heal slowly. Severe skin lesions may ensue from limited contact with tributyl tin compounds. Paint sprayers, chemical process workers and other workers who may be significantly exposed to any organo-tin compound ought to participate in a medical program.

Alkyl and aryl tin compounds exhibit mono-, di-, tri-, and tetra- (R) tin compound formation. More than 40 organo-tin compounds have been identified as U.S. industrial chemicals. Tetra-alkyl and aryl tin compounds are used extensively as wood preservatives. Tri-alkyl tin compounds, e.g. tributyltin fluoride, are used as biocides in shipbuilding. Dibutyl- and dioctyl- tin salts are used in PVC manufacturing.

Lead. [Xe core] $4F^{14}5D^{10}6S^{2}6P^{2}$. Until the late 1960's lead was used extensively in industry and in public works, sometimes with few environmental controls. It was used universally in potable water distribution (except in 'chemically soft' water[11] districts and where dissolved oxygen is high), in gasoline as an "anti-knock" compound (tetra-ethyl lead), in metal preservative paints (red lead oxide), and in electrical and structural solders (but not in water pipe solder).

Lead oxides and salts (but not the very soluble nitrate) are essentially insoluble in neutral water (lead has an appreciable solubility in highly acidic water) and have no significant vapor pressure. The hydroxide and the sulphate, however, are lowly water soluble (<200 ppm) at room temperature. Lead in soil, while it is nonmigratory, is the current dominant public exposure/environmental pollution concern. Except for a few situations, the common, earlier uses of lead have been discontinued, mainly as a result of EPA's efforts in banning or otherwise severely restricting lead use. Also, OSHA imposed stringent worker protection regulations many years ago. The OSHA Lead standard also brought occupational lead exposures under far better control than existed prior to the mid 1970's.

Lead Toxicity. Human lead toxicity involves: adverse effects on red blood cell synthesis, via inhibition of enzymes (notably, aminoleavulinic acid synthetase, and ferrochelase) which mediate heme synthesis; neurobehavioral effects; nerve damage; kidney disease; and impaired human reproduction and fetal development. Also, genotoxicity and cancer-initiation related to lead exposure are concerns.

The current lead concerns, in regard to occupational and public health exposure, are centered on exposure to (a) workers in lead reclamation, smelting, coating, bridge renovation, battery manufacturing operations, and (b) children under 5 years, who live near lead-contaminated soil or in lead paint-contaminated homes.

Occupational lead exposure and Medical surveillance. Medical surveillance is appropriate for workers who may experience ongoing, medically significant lead exposures on the job.[12]

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11. Soft water is water with about 20 parts per million or less of Ca^{++} or Mg++. At about 100 parts per million of either cation, the water is ranked "hard." Hard potable water is beneficial to health and also forms a hard, protective coating on the inside of water pipes, unlike soft water, but hard water also causes an insoluble scum with ordinary (anionic) soaps.
12. In this regard, the following personal experience in monitoring blood lead and zinc protoporphyrin, ZPP, for several hundred welders and burners in shipbuilding over several years, is offered. With ongoing lead exposure, in hot work close to or over lead paint on steel, a worker who had an initial 10-15 mg/100 gram whole blood lead level, would, after several weeks, incur a rapid blood lead level increase, quickly at first, then more slowly, until a plateau is reached after about twelve weeks. For such a worker, regular blood monitoring would show a linear blood lead rise over about 24 weeks, from about 10 to about 50 micrograms /100 grams (rbc). Upon cessation of these particular operational exposures, the blood lead would decrease, but rather less quickly than it arose. Those blood lead levels which were close to the upper permissible limit (50 mg/100 gram whole blood) would take about about half a year to return to the initial (unexposed) level, without medical intervention. [Seriously elevated blood lead may be remedied expeditiously using a medical chelating agent, such as ethylene diamine tetra-acetic acid, EDTA]. Reduction of blood ZPP, over a similar time frame, in similar circumstances, was seen to be erratic, which leads one to opine that ZPP, which, reportedly, has value as a quick screen for public lead exposure, is of little industrial value, and in industry at least, blood lead monitoring is the "gold standard" for assessing lead intoxication.

Main chemistry of lead. The chemistry of lead is typical of its Group (14). Lead chemistry is very similar to tin chemistry. The preferred oxidation number for lead is +2. Concentrated strong acids attack lead, but weak dilute acids are without effect.

Lead has five oxides, including mixed Pb oxidation number oxides (red lead, Pb_3O_4).

Lead dioxide, PbO_2 is a strong oxidizing agent and is amphoteric. With concentrated HCl, it forms a complex, $H_2\{PbCl_6\}$. With concentrated sodium hydroxide, it forms a "plumbate" salt, $\{PbO_3.3H_2O\}^{2-}$.

Lead organo-compounds are numerous. Tetra-ethyl lead, TEL, was used extensively prior to the 1970's to increase the octane rating of petroleum. EPA banned TEL round that time.

The main oxidation states and compound classes of lead are summarized below.

O.N. +4: Amphoteric Oxides. Covalent, unstable halides. Salts with oxy-acids. PbF_4, $PbCL_4$ (unstable). (Very unstable) hydride (PbH_4). The oxide PbO_2. The plumbate anion (PbO_3^{2-}).

+2: PbO. PbX_2 (all halides are stable). Lone pair of electrons on the lead atom. Also Nitrate. Sulphate. Carbonate. And Basic carbonate: $\{2PbCO_3.Pb(OH)_2\}$.

Group 15 includes N, P, and As (and Sb and Bi, which are not discussed).

The Group 15 elements, except for nitrogen, show a wide range of chemical behavior.

Nitrogen forms very large numbers of compounds (many organic) due in part to its ground state $2p^3$ outer electrons (all unpaired). It is very electronegative, only oxygen and fluorine are more electronegative. Nitrogen forms multiple bonds (N:::N) and is non-metallic in its chemistry, unlike the remainder of the Group.

Nitrogen Chemistry includes:

- **Nitrides**, as salt-like nitrides, e.g. Li_3N — the three electrons from the Li atoms complete the nitrogen octet. Ionic nitrides of Mg, Ca, Ba, Sr, Zn, Cd, and Th exist. Non-ionic nitrides exist with **B, S, and P**.
- Transition metal nitrides exist. They are similar to the carbides and borides, in that they are hard and have high melting points. Their composition are not always stoichiometric. Many have the nitrogen atoms residing within a metal atomic matrix.

- **Numerous oxides** (N_2O_5, NO_2, N_2O_3, NO, and N_2O), some of which are stable, some of which are oxidizing, and some of which are reducing. The oxides are acidic. NO_2 has a single electron ($^{\bullet}$) in an outer orbital, which accounts for its well-known brown color: $^{\bullet}N(=O)_2$.

- **Nitrogen oxides** cause environmental pollution concerns associated with: (a) acid rain, and acidified waters and soils; and (b) peroxyacyl nitrates (PAN's), which are strong irritants (oxidants), formed by NOx reacting with vapors in air and ozone under ultraviolet radiation. PAN's are a significant part of the oxidant-smog related, severe respiratory impairment and irritation problems seen in some major cities.

- **Highly reactive halogen nitrates**, e.g. $ClONO_2$. $FONO_2$.

- **Numerous oxy-acids**, e.g. nitric, nitrous, and hyponitrous acid.

- **Numerous oxides**, e.g. **nitrous oxide, N_2O,** and NO and NO_2, and several others. N_2O forms on heating ammonium nitrate, and in air-fuel combustion processes. **Nitric oxide, NO,** is formed by oxidation of nitrogen compounds, especially, ammonia. Nitric oxide readily oxidizes to **nitrogen dioxide, NO_2** — the brown, gaseous component of smog. Nitrogen dioxide in air, at above about five parts per million, with a short-term exposure, is irritating to the eyes and respiratory tract. Oxides of nitrogen contribute to acid rain, which has been discussed elsewhere. Nitrate (NO_3^-) fertilizer "run-off" (often in conjunction with phosphate "run-off") is a major cause of water pollution. [All nitrates are water soluble].

- NCl_3 is an explosive liquid.

- **Ammonia,** NH_3. Ammonia has a lone pair of electrons on the nitrogen atom. This causes ammonia to act as a base. Also, ammonia is extensively hydrogen bonded, much more so than its **P** or **As** counterparts. The oxidation of ammonia in air leads to nitrogen gas, but with platinum catalyst, nitric oxide, NO, is formed. With NaOCl, ammonia forms highly poisonous hydrazine, N_2H_4, an unstable, powerful reducing agent (stabilized by the addition of HCl), which is used as a oxygen-scavaging agent, in hot water boiler maintenance as well as a component of rocket fuel. The solvation chemistry of ammonia is similar to water. For example, liquid ammonia is a strong solvent and it reacts with zinc to form $Zn(NH_2)_2$, cf. zinc with OH-, yielding $Zn(OH)_2$. Ammonia forms "amines" with metals, e.g, lead amine.

Nitrate/nitrite contamination of water

1. Nitrate seepage and run-off into rivers and wells are significant public health concerns because:

   (a). Many communities and individual households rely solely on wells for their drinking water.

   (b). Nitrate/nitrite in potable water poses an especially high health risk to very young (six months old or less) babies ("*blue baby syndrome*") and other high risk people.

   (c). Nitrate in the body is reduced to nitrite. Nitrite is capable of: (i) combining with hemoglobin, causing a reduction in normal blood oxygen-carrying capacity; and (ii) reacting with amines, in digested foods, to form carcinogenic *nitroso-amine* compounds.

2. Private household wells should be periodically tested for nitrate/nitrite (and other contaminants). A positive nitrate/nitrite test result of one part per million or greater requires implementing a correction.

3. Water with a nitrate/nitrite level of 10 parts per million should never be used for drinking. Inexpensive test kits for these anions (and other water pollutants, including e-coli bacteria) are commercially available.

4. Ion exchange resin systems are effective in treating a household well-water supply. Numerous, broad-range" ion exchange (including *mixed bed*) types of water purification systems are commercial available for attachment to individual residential water supply systems.

5. Simply boiling nitrate-contaminated potable water is ineffective and should not be used as a remedy for nitrate/nitrite contamination.

Phosphorus, P. [Ne core]$3s^2 3p^3$ (and empty 3d-orbitals of low energy available for hybridization).

P exists as (a) white meta stable form (highly reactive, in 2 allotropes: Phosphorus, white 1 and Phosphorus, white 2, in P_4 cyclical atomic arrangements) and (b) Phosphorus red: a fairly reactive, but stable macromolecule. Red phosphorus is much safer to handle than white phosphorus and it does not spontaneously flame. It was used in making matches, but it has been replaced by sulphur. **P** chemistry is very extensive and may involve (a) covalent bonding with other elements, (b) pentavalent and trivalent stable oxidation states, and (c) hybridization of **P** 3d orbitals to some extent, e.g. in forming compounds like $P(OR)_5$ and $(phenyl)_5P$.

Phosphorus, like nitrogen, shows a good amount of covalence in its chemistry, but arsenic and antimony and bismuth have considerable cationic chemistries. The outer electronic structure of P is $2s^2,3p^3$. The As, Sb, and Bi elements have filled d-orbitals, with their respective 's^2p^3' configurations. Depending on the number of bonds made with other elements, numerous geometries of phosphorus compounds arise. For example, PH_3 (also AsH_3) is pyramidal. $P(O)(OH))_3$ is tetragonal. PF_5 (also AsF_5) is trigonal bypyramidal. The anion PF_6^- is octagonal (see fig.3), as are some corresponding Sb and Bi complexes. It resembles sulphur (adjacent Group 16) more than nitrogen in its chemistry. It forms numerous polyacids, similar to sulphur polyacids, but it does not form stable PH_4^+ salts (the exception is $PH_4^+I^-$, cf. NH_4^+).

White phosphorus (P_4, tetrahedral structure, two phases) is extremely poisonous. It is stored under water, which prevents it from burning spontaneously. It burns and deep into the skin on contact. Once on the skin, burning rapidly occurs. Extensive P burns are difficult to treat and can lead to systemic P poisoning, which may be fatal. Reportedly, prolonged water irrigation is the only effective treatment for an actual **P** burn. Chemical first treatment can enhance phosphorus absorption via the skin. [Reported history of suicidal ingestion, indicates that white phosphorus oxidizes to oxy-phosphorus acids in the body. These acids if ingested can severely damage the liver (fatty degeneration), when jaundice occurs within one or two days after ingestion. Skin and eye contact, however, account for almost all reported occupational injuries involving phosphorus]. Personal hygiene, changes of clothing, coveralls, and eye protection are required when phosphorus acids and their salts are used. Also, one must wash these materials off the skin immediately when it occurs. White phosphorus is used as rat poison, as pesticides, and in incendiary anti-personnel, and "fireball"munitions. Pellets of aluminum phosphide, treated with acid, liberates phospine (PH_3), a highly toxic gas. This reaction is the basis of a grain fumigation process, whose occupational history includes phosphine-related deaths.

One major environmental concern with phosphorus is "land phosphate run-off" entering waterways. This may result in algal growth and reduced oxygen content of water.

Direct reaction of phosphorus with metals yields one or more of four main types of compounds:

1. Volatile compounds (with Se, for example).

2. Extensively ionic compounds (with electropositive elements), e.g. Na_3P, Ca_3P_2, which hydrolyze to phosphine, PH_3 (a stable, but reducing gas; ammonia in comparison is not ordinarily reducing).

3. Covalent complex molecules, many of which are polymeric, e.g. P_4S_{10}.

4. Solids with metallic character.

Pentavalent and trivalent halides and mixed halides exist. Oxy-halides exist. Numerous salts, with P in different oxidation states exist: phosphates, phosphites, phosphides, and hypophosphites. Numerous phosphorus oxides and oxyacids exist as tautomers, in both the P(III) and the P(IV) states. Polymeric phosphates exist, like the mineral *apatite*, $Ca_5(PO_4)_3$, which is a main component of bone and teeth.

Pentavalent phosphorus oxyacids exist, including ortho-, pyro-, and meta phosphoric acids. The pyro- and meta-acids/salts convert on boiling in water to orthophosphoric forms, e.g. Na_3PO_4.

Phosphoric acid, H_3PO_4, is tri-acidic. Three H+ ions can be liberated stepwise, as follows:

$H_3PO_4 \Leftrightarrow H_2PO_4^- + H^+$. pKa = 0 (a strong acid, which, with NaOH, yields trisodium phosphate).

$H_2PO_4^- \Leftrightarrow HPO_4^{--} + H^+$. pKa = 7.2

$HPO_4^{--} \Leftrightarrow PO_4^{3-} + H^+$. pKa = 12.3

P has an extensive N chemistry, with N atoms in lieu of oxygen atoms in the analogous oxides. For example, H_3PN_4, cf. H_3PO_4. Also, $(PNX_2)n$ compounds exist, where X= F, Cl, Br, but not iodine. N to N double and triple bonds, exist in cyclical trimeric and tetrameric (ring) forms, which are stable, e.g. the *phosphononitrilic* compounds.

P has an extensive (covalent) S chemistry, with S atoms in lieu of oxygen atoms in the analogous oxides, e.g. P_2S_5, P_4S_{10} and P_2S_3, cf. the corresponding P oxides.

Phosphorus has a vast organo-phosphorus chemistry. It is based in large part on H_3PO, i.e. R_3PO and PCl_3 (phosphorus trichloride). Many organo phosphorus compounds are derived from PCl_3 or from PCl_3-based intermediates. For example, PCl_3, in a basic solvent blend, like triethylamine in ether, reacts with alkyl alcohols (ROH), to form $P(OR)_3$, tri-alkoxy phosphite. PCl_3 is a precursor for many highly toxic compounds, including organo-phopshorus insecticides, e.g. diazonon, malathion, and Sarin. [See page 28. Sarin is a liquid warfare nerve agent. It can be made in five simple chemical steps. Purification and containerization are the highest hazard steps in its synthesis]. These substances are toxic via cholinesterase-inhibition and subsequent interruption of neural-muscular activities.

P reacts with numerous reagents, to form important organic and inorganic compounds It readily reacts with many transition metals, e.g. Fe, to form interstitial compounds, like Fe_2P.

P also exists in negative oxidation states, for example P_2H_4 (P, O.N - 2) and PH_3 (P, O.N. -3).

Arsenic (As):[Ar core] $3D^{10}4P^3$.

Arsenic has two allotropes: yellow and grey, both of which readily oxidize to As(III): As_2O_3. Arsenates and arsenites are used as insecticides, herbicides, larvicides and pesticides. Arsenic trichloride is used as the starting reagent for "arsenical" drugs. Numerous organo-arsenic compounds exist, e.g. $As_2(CH_3)_2$, cacodyl. People who live near copper, lead or zinc smelters may be subjected to continuing airborne exposures above the average population's exposure.

Arsenic is a human carcinogen (skin, lung) and a powerful poison for humans, animals and plants. Also, the systemic, non-genotoxic, adverse effects of arsenic are well known. They include: red blood cell destruction (hemolysis); headache; shivering; stomach pain; blood-stained vomitus; and pulmonary edema.

Chronic exposure also results in many of the same signs and symptoms. A tolerance for arsenic intoxication can be build up over time. However, arsenic dosage is accumulative, due to the slow rate of elimination via urine. People with kidney disease or enemia are at elevated risk from exposure to arsenic, regardless of its chemical state.

When potential occupational arsenic exposures arise, medical surveillance is needed. It should: commence as a pre-job placement examination; continue over the time when potential significant exposures exist; and be completed at the exit/retirement. Occupational exposures are likely to be significant in such operations as: (arsenic-bearing) ore smelting and metal refining; metal pickling; arsenic impregnation of wood, and gallium arsenide alloy manufacture or use, in industries making lasers and satellite solid state sensors.

Arsenic in water. No amount of arsenic in potable water is acceptable. Continuous intake of arsenic-contaminated water in parts of Africa has caused major human problems, including numerous cases of fatalities from arsenic induced skin cancer.

Arsenic chemistry is extensively covered in every text on inorganic chemistry. A summary of its main oxidation states follows:

O.N. +5: [PREFERRED O.N.]
Oxides: As_2O_5, As_4O_{10}
Acidic H_3AsO_4, AsF_5
$Ca_3(AsO_4)_2$ — which is used as a pesticide and a wood preservative.

+3: [REDUCING]
As_2O_3, As_2O_6. The As(III) oxides are easily oxidized. Also, they are amphoteric. With HCl, they yield $AsCl_3$. With NaOH, they yield $NaAsO_2$ (arsenite).
All the trihalides (AsX_3) are known, and they are easily hydrolyzed.

Zero: Organo complexes, e.g. cacodyl, $[(CH_3)_2As]_2$

-3: Arsine gas (AsH_3). [Arsine generation from a sample is a quick very sensitive 'wet chemistry' (early 1800's, Marsh) test for arsenic on foodstuffs in water, in wood, etc. The sample is reduced by pure zinc and hydrochloric acid, the resulting AsH_3 is passed though a heated glass tube, and a black arsenic mirror deposits on the cool surfaces. Sb is an interference, but it is differentiated from arsenic by being soluble in sodium hypochlorite, NaOCl].

Group 16 includes **oxygen and sulphur**. As a whole the Group is consistent in the way the elements behave, except that, as in other Groups, the first member, oxygen, differs considerably from the rest of the Group. Oxygen is predominantly divalent in its chemistry. Water is extensively and strongly hydrogen bonded. Sulphur, on the other hand, (a) shows higher valencies, e.g. +4, +6, and (b) is not so significantly hydrogen bonded. However, sulphuric acid exhibits hydrogen bonding, as shown by its electrical conductivity. Hydrogen sulphide is weakly hydrogen bonded. It is *gaseous* at NTP, cf. water.

Oxygen forms many peroxides some of which are stable (but very reactive oxidants) and are commercially important. It also forms superoxides ($O_2 + 1e \rightarrow O_2^-$) with some metals.

The peroxides of the elements of Groups 1 and 2 are ionic, while the peroxides of zinc, mercury, cadmium, and silver are stable and involve extensive, but varying degrees of covalent bonding.

Oxygen, unlike sulphur, does not form ring or long chain structures. [Sulphur exists in (non-metallic) S_8 ring and S_8 chain structures. Also, selenium exists as a (non-metallic) Se_8 ring structure, as well as a (metallic) Se_8 chain structure].

Ozone may be readily recognized by its characteristic sharp, irritating odor, at sub-parts per million concentrations. It is a reactive, but fairly stable (metastable) gas of major environmental importance re: (a) the risk of severe respiratory distress (which, in the case of ground -level ozone, is serious in several cities here and abroad) and (b) depletion of the stratospheric (e.g. 10 - 30 miles high) ozone layer, via interaction with carbon-halogen compounds, e.g. $CFCl_3$ and other halides.

$CCl_2F_2 + hv \rightarrow CClF_2 + Cl$. $Cl + O_3 \rightarrow ClO + O_2$. $ClO + O \rightarrow Cl + O_2$, Net reaction:.$O + O_3 \rightarrow 2O_2$.

Depletion of stratospheric ozone increases UV radiation. Increased UV radiation poses risks of skin cancer, inheritable conditions, such as Cockayne's syndrome (dwarfism and skeletal defects), as well as ecological damage and changes in regard to fish and crops.

In environmental chemistry, photochemical oxidants refers collectively to ozone, NO_2 and peroxyacyl nitrates (PANs). The term **total oxidant** is often used in this regard. PANs are formed by photochemical degradation of hydrocarbons (of gasoline origin), which involves "peroxy" radicals. These radicals unite with nitrogen oxides. In urban areas, where photochemical oxidants is a major problem, one often 'sees' a daily pattern of (diurnal) total oxidant, with the highest concentrations occurring around midday. The factors of the actual pattern of photochemical oxidant pollution seen are topography, sunlight intensity, and vehicular traffic.

Elevated levels of ground-level ozone and PANs create moderate to severe risks of respiratory distress, impaired respiratory function, inflammation of and damage to the lungs, and aggravation of asthma. Long-term, moderate or high overexposure may lead to permanent lung injury in some individuals. The people most at risk from elevated ground-level ozone are active children, people with asthma, bronchitis or emphysema, or an impaired immune system, or who regularly, intensely exercise outdoors, or who have an unusual ozone susceptibility (the reason for which may not be clear). Injury may be medically seen as a shedding of damaged cells in the lungs, as a significantly altered spirometry, or a change in a medical X ray. People in urban areas would be wise to avoid outdoor activities and strenuous exercise on bad air days.

Hydrogen peroxide, H_2O_2, is widely used as a disinfectant and as a component of numerous commercial products. Decomposition is relatively faster in alkaline solution.

Peroxides and Peroxyacids. Numerous peroxides and peroxy acids exist, especially with the elements of Groups 1 and 2, but also with zinc, mercury, cadmium and silver. Peroxide solutions decompose on heating with the liberation of oxygen.

Sulphur. The chemistry of sulphur is extensive. It includes oxides, oxyacids, halides, oxyhalides, and oxyhalogen acids. Sulphur exists in several oxidation states, notably, but not limited to: O.N. **+6** (SO_3, H_2SO_4, $H_2S_2O_7$, SF_6, SOF_4); O.N. **+4** (SO_2, H_2SO_3, $H_2S_2O_5$, SF_4, HSO_2F); and O.N. **-1** (e.g H_2S).

The oxides of sulphur (as well as the HS- ion) are important environmentally. The oxides contribute to the problems of acid rain and reduced respirable air quality. Sulphur dioxide is stable. It exists in the preferred oxidation state of + 4. It is an angular, inter-molecularly bonded, polar molecule, which has its relatively high boiling point (-10 degrees Celsius).

Sulphur dioxide can react with chlorine (and fluorine) without a change in oxidation state to form thionyl chloride (or fluoride). Sulphur dioxide is reduced by hydrogen sulphide. With ozone, it is oxidized to sulphur trioxide.

Peroxy-sulphuric acids exist and are highly reactive, e.g. Caro's acid, H_2SO_5. Peroxydisulphuric acid, $H_2S_2O_8.SO_3$, is a powerful oxidizing agent. It can be stabilized (by boron), as a polymeric compound (e.g. "Sulpham," $(SO_3)_3$, which is used in sulphonation reactions). Numerous stable salts exist of sulphur- oxy acids, with two or more sulphur atoms in the molecule. Oleum, which is polymeric, is an example. Also, some sulphur oxyacids (as solutions or salts) are reducing agents, e.g. $H_2S_2O_3$.

Group 17. The halogens as a group are the most electronegative of all the Groups. The order of decreasing electronegativity is F > Cl > Br > I. Iodine to a limited extent shows metallic properties.

Fluorine is significantly different from the other halogens. Fluorine has the highest electron affinity of all the elements. The small size of the fluoride ion (1.35 A^0), compared to the other group ions (Cl^-, 1.8 A^0; I^-, 2.2 A^0), accounts in large part for the molecular and structural differences between fluorides and the other halides. The very small size of the fluoride ion makes it easy to "pack" many F ions around a central atom/ion (maximal central atom coordination). Fluorine raise a respective anion to its highest oxidation number. It increases the acidity of groups like -COOH and $-SO_3H$ in certain conjugated or closely substituted molecules (e g. CF_3COOH). It also increases the efficacy of certain pharmaceutical products when it is made part of the molecule and it is a constituent of several pesticidal compounds.

Fluorine is exclusively monovalent. Silver fluoride is very soluble, but silver chloride is insoluble. Fluorine excites higher oxidation states of less electronegative elements, which the other halogens do not, for example sulphur hexafluoride is stable, but sulphur hexachloride does not exist.

With Fe(II) or Fe(III), fluorine yields an octahedral complex, cf. chorine. Chlorine does not form an octahedral complex. Perchloric acid exists (formally Cl, O.N. 7), but no"perfluoric" acid exists. Di-iodine pentoxide (I_2O_5) exists, but a corresponding fluorine oxide does not exist. Iodates and bromates exist naturally, but 'fluorates" do not exist. Hydrogen fluoride (bpt.19.5^0 C) is extensively hydrogen bonded, but the other hydrogen halides are not comparably hydrogen bonded (hydrogen chloride is a gas).

The bond character of the HX ('haloacids') changes with the series: HF, 47%; HCl, 17%; HBr, 11 %; and HI, 5% [per L. Pauling' data]. The hydrogen bond length seen in (hydrogen bonded) HF is the shortest (strongest) of these bonds. Unlike the other binary acids of Group17, HF is designated a weak acid, because the H-F bond is so strong. HF, nevertheless, is corrosive and toxic, but so are many weak acids.

HF gas and its aqueous solution and salts are used in the production of fluorides, fluoro-plastics, catalysts for paraffin alkylation (petroleum industry), as well as in glass-etching processes, numerous industrial cleaning products, and in the synthesis of numerous organic chemicals. Where and whenever HF (or any acid or base for that matter) is occupationally used, (1) the operation should be subjected to a job safety analysis, (2) personnel protective equipment must be used, to protect against both inhalation and eye and skin-contact hazards, (3) and an emergency eye-wash, a shower facility, prompt first aid, and medical treatment need to be promptly available.

Public exposure to HF and fluorides (apart from exposure to fluoridated water and proximity to fluorine/fluoride-using industrial plants) is minimal, with the possible exception of exposure incurred in an accident or release.

Halogen chemistry may be "condensed" (as much as seems possible) as follows:

1. The halogen elements all have an outer orbital of "p^5." For example, **F**, $1s^2$, $2s^2$, $2p^5$ and **I**, [....] $5p^5$.

2. With increasing element atomic weight within the Group, one sees:

   (a). **Electronegativity** decreases, e.g. **F** electronegativity = 4, and **I** = 2.8.

   (b). **Bond length** increases.

   (c). **Ionization potential** decreases, e.g. **F** =17.4 eV, and **I** =10.4 eV.

   (d). **Ion radius** increases, e.g. F^- = 1.3 Angstrom, and I^- = 2.2 Angstrom.

3. Chlorine, like bromine and iodine, exhibits many oxidation states.

   O.N. +7: $HCLO_4$. ClO_3F. Perchlorates.

   +6: ClO_3.

   +5: $HClO_3$

   +4: CLO_2

   +3: $HCLO_2$. Also I_2Cl_6 (s), via the reaction: 2 **ICl** + 2 Cl_2 (g).

   +1: Cl_2O. Also ICl, via chlorine gas on solid iodine crystals.

   -1: The preferred oxidation number for all the halogens. Simple Halides.

4. Bromine and iodine are similar in their chemistries to chlorine, except that no Br +7 or I +6 exists. [Brominated diphenyls/diphenyl oxides are ubiquitous flame-retardants of environmental concern].

5. Iodine in the presence of moisture reacts rapidly with aluminum, and manganese.

Notes on Coordination Complexes

The first organometallic, $Zn(CH_3)_2$, was made in the 1850's, but much of the important chemical research and commercial (plastics, polymers, catalysts) development on these kinds of compounds started in the 1950's, beginning with $FeCO_5$ and followed by a numerous complexes of the first, second and third transition elements. Organometallic compounds involve: (a) the transition metals in various oxidation states, which are generally lowly positive or zero; and (b) a host of neutral or charged molecular entities (ligands), including reactive alkyl carbonyl systems; alkynes; and allyl groups. The latter "complexes" may exist in *uncommon* molecular structural forms: sandwich, half-sandwich, anti-sandwich, triple sandwich, and other shapes. Such structures constitute an expanding, major field of chemistry in regard to catalysts for the petrochemical and the plastics industries.

Molecular compounds often do not behave as might be expected from their composition. For example, cobalt is poisonous and cyanide is poisonous, but both cobalt and cyanide are a major part of vitamin B12, which can be safely ingested in relatively large amounts. Another illustration of the point is the reaction of $FeCN_3$ (ferric cyanide, systematic name, Fe(III) tri-cyanide) with excess potassium cyanide, to form the stable *complex* $K_3Fe(CN)_6$. This compound responds negatively to the colorimetric Fe(III) thiocyanate test. Clearly some compounds have some bonds which are special. They are called *molecular complexes.* They are indeed molecular compounds. The associated "inner" bonds are strong "auxiliary bonds."

In molecular complexes two kinds of valency (or types of bonding) operate and atoms or ions arrange themselves around a central atom in different arrangements. The complex is written in as special way. In the potassium-iron-cyanide case, for example, the complex is written: $K^{+}_{3}[Fe(CN)_6]^{3-}$. It is noted that numerous mixed iron oxide — Fe(II) and (Fe(III) — complexes exist.

The term "coordination number" signifies the number of the specially-bonded atoms or molecules around the coordinated atom. In potassium iron(III) cyanide, the complex has a coordination number of six. There are six "CN" ligands around the central iron atom. 6-coordination is very common. Also, it is spatially described as an octahedron: the six bonds are directed towards the four corners and the two apices of an octahedron.

Other coordination numbers occur with other complexes, although not as frequently as for the octahedron arrangement. The nickel cyanide complex ion, $[Ni(II)(CN)_4]^{2-}$, is a planar structure. Platinum also yields 4-coordination compounds, which can exist in two geometries: sp^3 tetrahedra, and dsp^2 square planar.

8-coordination type complexes exist.

Some general "rules" apply to complex formation, these include: (1). Complex formation is promoted by small ionic radii and high charge for the central atom; and (2). Subshell d-orbitals must be available for hydridization, in order to form strong covalent bonds. The relationship between orbital hybridization, coordination number, and shape was established by L. Pauling. See Table 11.

HYBRIDIZATION / COORDINATION		SPATIAL ARRANGEMENT
d^2sp^3	6 -COORDINATION	OCTAGONAL
d^3s	4-COORDINATION	TETRAHEDRAL
p^3s	4-COORDINATION	TETRAHEDRAL
dsp^2	4-COORDINATION	CO-PLANAR (CORNERS OF A SQUARE)

Table 11. Orbital hybridization, coordination, and spatial arrangement

The entity around the central atom (the ligand) in a complex may be a mono-molecule or radical, or it may be "polydentate." [Polydentate ligands are chelating agents which attach to the central atom at two or more places]. As expected, complexes with a mix of mono-ligands or with polydentate ligands exist, which may be optically active ("cis' and "trans" forms). Some common polydentates are acetyl acetone (a β-diketone), glycine, NH_2CH_2COOH, and ethyl diamine tetra acetic acid (EDTA). Many complexes are pH-sensitive. Many complexes show unexpected chemical and physical properties, including deep colors in different pH solutions. Many charged ions of unstable nature (in principle valence-bonded compounds), e.g. Cu^{+}, upon being "complexed" become stable. Indeed, reversal of (O.N.) stability usually occurs with complexation. [Electrode potential values are different with different ligands]. Complexation (chelation) is used industrially to purify elements and to facilitate chemical processes. For example, in silver plating CN^{-} is added to the plating solution to complex (and so increase the solubility of) Ag^{+} cation.

Molecular complexes and complexing agents are used in medicine. Disodium Fe(II) hexacyanonitro, (common name, sodium nitroprusside) is used, in conjunction with monitoring of plasma cyanide, in treating severe systemic hypertension.

Ethylene diamine tetra acetic acid, EDTA, is used in lead detoxification and in treating nail fungal infection (topically applied preparation[13]).

Notes on the Transition Elements

The transition elements are traditionally described as "elements with partially filled d- or f- orbitals." A broader definition is "transition elements are those elements or ionized elements which have partially filled d- or f- orbitals." On the latter basis, most of the known elements are transition elements.

Several series of transition elements exist. The "first transition series elements,"or "partially filled 3d-block" elements, in the narrow definition, are: Sc, z =29: [krypton] $4s^2$, $3d^1$, followed by Ti, V, CR, Mn, Fe, Co, Ni, and Cu.

A second transition series exists, which covers the 4d- sub-shells, with partial electron filling: yttrium ($4d^1$) followed by: Zr, Nb, Mo, Tc, Ru, Rh, Pd (and Ag, if one includes the ion Ag^+). This block, however, is less important environmentally than is the first transition elements. The Lanthanides (all of which have very similar chemistries) and the Actinides (all of which have very similar chemistries), respectively, comprise the "second" and the "third" transition series.

The first transition elements, starting with element 21 (scandium with outer electron orbitals [argon]$3s^2$, $2p^6$, $4s^2$, $3d^1$), have many properties in common: they are metals with hardness, high boiling point, electrical conduction, alloy formation, etc. The elements in this "block" are all industrially important.

Commonly known transition elements, which have similar properties, are shown in Table12.

Group 8	Group 9	Group 10	Observation
D^6S^2	D^7S^2	D^8S^2	← the filling of the outer orbitals.
26 Fe	27 Co	28 Ni	Many of the first transition series elements are environmentally important, with the exception of the high priced elements.
44 Ru	45 Rh	46 Pd	
76 Os	77 Ir	78 Pt	

Table 12. Some common Transition Elements

The chemistries of transition elements and complexes are beyond discussion here, except to mention that:

(a). Traditionally, certain molecular compounds are named complexes. The distinction is arbitrary and unnecessary, but it is too ingrained in the literature to be strongly argued against. To illustrate this point: nickel sulphide, NiS, is a compound, but nickel carbonyl, $Ni(CO)_4$, is a Ni(0) complex; and SF_6 is a compound, but the anion SF_7^- is a complex; and so forth.

(b). Certain compounds and ions exist or behave in ways that might not ordinarily be expected, e.g. $Ni(CO)_4$ and various, so-called "sandwich"complexes (e.g. pentadienyl and other kinds of molecular complexes), which are important petrochemical products (e.g. petroleum "antiknock" agents).

13. *Penlac* ® utilizes EDTA to complex Fe(III) and Al(III) ions, which otherwise would be utilized by the fungi in cellular detoxification—the removal of toxic peroxide radicals from their cells.

(b). Certain compounds and ions exist or behave in ways that might not ordinarily be expected, e.g. $Ni(CO)_4$ and various, so-called "sandwich"complexes (e.g. pentadienyl and other kinds of molecular complexes), which are important petrochemical products (e.g. petroleum "antiknock" agents).

(c). Ions or groups surrounding a central atom in a 'complex' are termed"ligands." Ligands, depending on their composition, exert weak or strong forces on a coordinated atom or ion. This may affect the sequence of d-orbital filling by electrons.

(d). In some instances paramagnetism[13] is exhibited. In non-linear complex molecules (e.g. Cu(II)), the d orbitals may be distorted by a ligand, and some orbitals of relatively lower energies may be created (which is named the "Jahn -Teller Effect").

(e). In general, the complex coordination number is in the range of two to nine, with two, four and six being very common coordination numbers. The coordination number relates to molecular complex structure. For example, 2-coordination relates to either a linear (e.g. CO_2) or a bent (e.g. H_2O) shape (molecular resonance possibility and the presence of one or more lone pairs of electrons are also shape factors). 4-coordination relates to either a tetrahedron or a square planar shape. More than one coordination number may be manifested simultaneously by a complex, especially when little difference exists in the relative stability of alternative arrangements. For example, cobalt(II)-water complexes, exist, which are *tetrahedral* (4-coordination) and *octahedral* (6-coordination). [Coordination number, in context with complexes (but also applicable to generic compounds), means the number of ligands (ions or groups) immediately around the central atom].

(f). The elements shown in Table 9 are similar to each other, but gradations exist in melting point, specific gravity, atomic radius, and oxidation states. Most of these elements are essential to life.

(g). They show variable valence (note OsO_4). Compounds are often colored and non-stoichiometrical.

(h). They form many stable complexes with inorganic and organic compounds/radicals. The complexes may involve mixed oxidation states of the same metal, e.g. ferrous ferricyanide, $Fe_3[Fe(CN)_6]_2$.

(i). Some complexes have M(0) oxidation number, e.g. cobalt carbonyl $Co_2(CO)_8$. Many of the transition elements *(in a particular state, with d^1 to d^9 configuration)* yield complexes which have variable paramagnetism, depending on the ligand. [The "*Spectrochemical Series*" effect].

(j). Copper fluoride has a bond dissociation (positive) energy comparable to lithium chloride (respectively, 728, and 640 KJ/mol), despite copper's greater atomic weight. The reason is that copper has d-electrons, and the d-orbital makes a poor 'electron shield' around the nucleus.

(k) Complexes, with a common central atom in the same oxidation state, can have different properties.

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13. Paramagnetism is the property of being drawn into a magnetic field due to one or more unpaired electrons in an orbital. [Diamagnetism is the opposite case]. Paramagnetism is measured using an instrument called a **GOUY** balance. Many transition metal salts or complexes are paramagnetic due to unpaired d-orbital electrons. Chromium [$3d^5,4s^2$ with 5 unpaired electrons, $3d^5$] is the ultimate example of paramagnetism. The total number of unpaired electrons in the orbitals can be quantified in terms of magnetic moment, expressed in Bohr magneton units. The reason for transition metals exhibiting different levels of paramagnetism is that a ligand (in the case of an octahedral complex, but possibly not in the case of a tetrahedral complex) may be strong enough a force field to cause an energy split in the degenerate orbitals, with maximal electron pairing. CN- is one such ligand.

Some notes on radioactive isotopes

Radioactive isotope decay entails an (unstable) atomic nucleus (the ***parent***) transforming spontaneously into a stable isotope of the same element (same atomic mass), or (ii) an isotope of another element —and either product is known as a ***daughter***. Radioactivity only involves the nucleus. He orbiting electrons have no part in the process (except for intra-electron capture).

In radioactive isotope decay:

1. At any one time the sum total of the parent and daughter atoms equals the number of (parent) atoms at the very start of the decay—which provides the basis of radiometric dating.

2. The parent nucleus undergoes one or more of three, radioactive processes.

   (A). A proton may become a neutron, by **capturing** a beta (β) particle. [A β particle is an electron].

   (B). A neutron may become a proton, by the **emission** of a beta particle.

   (C). A heavy particle, comprising 2 protons and 2 neutrons, called an alpha (α) particle, may be emitted from an radioactive particle.

3. Gamma radiation, from the breaking up of an unstable nucleus; can be emitted. The occurrence of gamma radiation does not change the atomic mass *or* the atomic number.

4. β particle *capture* and β particle *emission* (decay) may occur together in definite proportions. For example, ^{40}K (one of three natural isotopes of potassium) undergoes two different processes: β particle capture (to yield the daughter ^{40}argon, via a proton becoming a neutron after impact with the β particle, with an atomic number decrease of 1); and β particle decay (to yield the daughter ^{40}calcium, via a neutron emitting a β particle, and becoming a proton, with an increase of 1 in the atomic number). With ^{40}K, the ratio of the decay schemes and respective daughters produced is always 0.88 to 0.12, the latter value is for the beta particle capture process and argon-40. This distribution of daughters is independent of the environment — one reason why ^{40}potassium/^{40}argon - radiometric dating is so useful for examining volcanic rock and many other minerals.

5. The half-lives of the radioactive isotopes used in radiometric dating (carbon-14, with β particle decay and nitrogen-14 as the daughter; potassium-40; uranium isotopes 232, 235, and 238; and rubidium-87, with β decay and strontium-87 daughter), and their decay schemes are well established.

6. The three isotopic decay processes that are mentioned in 2 above can be summarized as follows:

   - **The two beta (β) particle-related processes**: Either one of these two processes involves *an alteration* (as a "1" gain or as a "1" loss) to the respective mass number (Z), but with *no change of* the atomic mass (atomic weight).

   - **The emission of an alpha (α) particle from the nucleus**: The alpha particle comprises 2 protons and two neutrons. Upon its emission, the nucleus undergoes a *mass number reduction of 2*, and an *atomic mass reduction of 4.*

7. **The mathematics of radioactivity decay** was established, in the early 1900's, as a first order differential equation. It equates to: $N = N_0 e^{-kt}$, where N is the amount of the sample remaining after time "t" and N_0 is the initial amount at t = zero. This reduces to: $\ln N = -kt + \ln N_0$. By plotting ln N against time, one obtains the value of kt. By rearranging this equation, an equation for calculating half-life, $T_{½}$, can be established. The latter equation reduces to: $T_{½} = 0.693/k$. [$T_{½}$ values of radioisotopes of interest, together with information on the respective daughter products and the decay schemes are provided in physical-chemical textbooks]. Finally, the decimal fraction of a radioactive substance remaining after the passage of a number (n) of $T_{½}$-periods is $(½)^n$.

§B. Comments on inorganic nomenclature

Information about the composition, structure and properties of inorganic compounds is forthcoming from some common names of compounds, but the common names, except for a few well-established ones, are often difficult to characterize chemically.

The (cation) names of many common inorganic compounds typically end in "ous" and "ic," which frequently do little in the way of rationally identifying compounds. Useful information is more likely to be provided by the corresponding systematic names. An example of the inutility of some common names is seen in the case of the many oxides and oxyacids of nitrogen, phosphorus, sulphur, chromium, and chlorine. A simple illustration of the point is — sulphuric acid for H_2SO_4, but perchloric acid for $HCLO_4$.

Historically, the elements' symbols have been are based on latin names, e.g., Na for natrium, for sodium; Fe for ferrum, for iron; Cu for cuprum, for copper, and so on. Inorganic *compound* names are English words, except for a few, like "stannates' and "ferrates."

Conventionally, the relatively positively charged constituents of inorganic compounds are cations, and the relatively negative constituents are anions and the order of naming is, first, the cation followed by the anion, e.g. Na^+Cl^-, sodium chloride. In a binary compound (one cation and one anion), the cation is usually mon-atomic (uncombined), while the anion may be mon-atomic (which carries an "ide" ending) or it may be polyatomic, which can be a little disconcerting to name, e.g. $Co(NO_2)_6^{3-}$ — hexanitrocobaltate(III).

Some common names of (inorganic binary compound) mon-atomic anions are as follows: H^-, hydride; F^-, fluoride; Cl^-, chloride; S^{2-}, sulphide; Se^{2-}, selenide; As^{3-}, arsenide, and so on — note the "ide" ending. Some common names of polyatomic anions, which also have "ide" endings, are: I_3^- (tri-iodide); O_2^{2-} (peroxide); and N_3^- (nitride).

Clearly, common chemical names do not provide much information on the number of atoms in each cation or anion, or on the oxidation states of the elements comprising the molecule, and they are inconsistent across chemically analogous, inorganic compounds (i.e. H_2SO_4 is *sulphuric acid*, but the similar acid $HClO_4$ is *perchloric acid*).

Modern systematic naming, based on a "coordination" principle and generally accepted rules, facilitate the unambiguous description of many if not most of all of the inorganic compounds (organic chemistry has its own system). However, even some of the systematic names are awkward sounding, or otherwise they are not used when the respective common names are well known and embedded in the chemical literature.

A discussion of the relevant naming systems and rules is beyond the scope of this presentation, except to mention that:

(a). One way of systematically naming inorganic compounds is the Stock Notation process. This is based on oxidation state and a defined approach. It provides a far greater logical association between name and formula than does the use of common names.

(b). Some common names have the same "ic" ending, but quite different formula. Using the Stock Notation, for example, $FeCl_3$ (ferric chloride) would be written as iron(III) chloride, and $CuCl_2$ (cuprous chloride) would be written as copper(II) chloride.

(c). With the Stock Notation (which is generally approved) the cation (e.g. Fe^{3+}) is named first, as the element name, followed by the (bracketed) cation oxidation state, followed by the cation name, with the appropriate ending, e.g. for Cl^-, chloride.

(d). The Stock Notation is not used for a compound when its common name is unambiguous.

(e). With some of the more complex inorganic molecules, the number of atoms of each element in is signified by the systematic name. For example, with the Stock Notation, Cl_2O_7 is "dichlorine heptoxide" and Fe_3O_4 (a mixed iron O.N. compound) is "tri-iron tetroxide." These and other systematic names are not currently in wide use in the English chemical literature. Common-place names are allowed and still used for binary compounds which may have polyatomic cations and/or anions. For example, SiH_4, silicon(IV) tetrahydride, is "silane."

(f). The Stock Notation is especially useful for "handling" anions, with polyatomic ligands, which would be difficult to trivially name. For example, $[Co(NO_2)_6]^{3-}$: hexanitrocobaltate(III).

(g). Various anion-ligand arrangements with an "ide," "ite," or "ate" ending, can be systematically named without sounding similarly awkward. For example an anion-ligand arrangement might have a name ending such as: $\mathbf{F}^-$ fluoro (not fluoride); $\mathbf{Br}^-$ bromo (not bromide); and $\mathbf{OH}^-$ hydoxo.

(h). Various molecular arrangements with neutral ligands ("radicals"), such as CO or NO, have names with an "yl" ending. For example, the neutral ligand CO is "carbonyl" and the neutral ligand NO is "nitrosyl."

(i). The "old" names for some ions, such as "ammonium" for NH_4^+ and "pyridinium" (for the cation of pyridine) are perfectly adequate because of their widespread familiarity.

(j). Some complexes with cationic radicals have name endings which are the same as those of the corresponding neutral complexes, e.g. NO_2+ is "nitrosyl," and VO^{2+} is "vanadyl" ("vanadyl" is also used the neutral VO radical).

(k). The common names of compounds comprising elements which show stable (or unstable) multi-oxidation states, such as the various phosphorus-based and boron-based oxy-acids, are often confounding, nevertheless they remain in wide use. One has to resort to a chemical text to make sense of the names of some fairly common names of compounds.

(l). The common, but still used names of compounds of elements which show (stable or unstable) multi-oxidation states, contain archaic prefixes as "hypo," "per," "peroxy," "ortho," meta," "para," "thio," and some other prefixes. When used to name compounds of elements in different PT Groups, such common terminology may not clearly convey a chemical meaning.

(m). Hypo- implies a lower oxidation state; per- implies a higher oxidation state (re: the preferred O.N.); and ortho-, meta-, and para- (which are prefixes of oxy-acids and other inorganic compounds) imply that the relevant element exists in the same oxidation state, but with a different bound-water content or molecular structure.

(n). The difficulty is shown by the following: H_3BO_3 is orthoboric acid (or monoboric acid); $(HBO_2)n$ represents polymeric boric acids, e.g. $(HBO_2)_3$ is trimetaboric acid and $H_4B_2O_4$ is hypoboric acid. H_3PO_4 is orthophosphoric acid, and $H_4P_2O_7$ is pyro- (or di-) phosphoric acid. $H_5P_4O_{10}$ is triphosphoric acid. These phosphorus oxy-acids also exist as tautomers (same composition, different atomic arrangement around the central atom), which further complicates nomenclature.

As a closing comment, a greater use of the systematic names of chemicals might make understanding inorganic chemistry generally simpler.

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Basic Chemical Principles and Facts for Safety, Health and Environmental Management (SHEM) Managers and Environmental Protection Professionals

Part Two: Aspects of Relevant Organic Chemistry and Related information

Science to Protect Health and Environment.
Using science to make a difference in the EPA Regions

N.A. Beddows

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Much of the data and information are from are from the Handbook of Chemistry and Physics, 1992. Organic Chemistry (Vol. 1, 7th ed.), LL. Finar; and numerous journals, papers presented on internet chemistry sites, and personal chemical notes.

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Disclaimer

This material and the information provided is not presented as, or implied to be representative of the policy or position of any agency or group with which the writer is associated.

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Part Two: Aspects of Relevant Organic Chemistry and Related information

N. A. Beddows

SHEM Managers, environmental protection professionals, chemical plant accident investigators and attorneys review technical documents and reports which are replete with technical information on chemicals, processes, and occupational health and environmental issues. For this a basic knowledge of organic chemistry is needed. It is also needed to optimally support EPA programs, including inspections of industrial, chemical and pharmaceutical plants, and plant accident analyses.

This Part is an aid to attaining and maintaining a knowledge of organic chemistry which is pertinent to occupational safety and health and environmental protection.

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Author's note. This Part is complemented by two other Parts (inorganic chemistry and physical chemistry). Each one is intended primarily for classroom use (which provides for detailed explanations). Much of the material, however, is suitable for individual reading. Each Part covers basic principles and selected chemistries of environmental, ecological, or occupational safety importance. Information is provided in one or more Parts on chemical nomenclature, physical and chemical properties, toxicology, chemical reaction types, and sampling and analysis methodology.

This (organic chemistry)Part comprises three sections:

1. ***General information and comments.*** *This section includes: background information; physical and chemical properties; aromaticity and stability; chemical reaction types, and aspects of toxicity.*

2. ***Classes of chemicals, functional groups, forms, and related information.*** *Included in this section are organic chemical classes, such as the alkyl-, the aryl-, and the halogenated- compounds; common functional groups; heterogeneous compounds (e.g., carbon compounds with oxygen, sulphur, nitrogen, phosphorus and metals); enantiomers and other chemical conformations; and chemical reactions and mechanisms.*

3. ***Selected substances and related information.*** *This section includes information on: flammable and/or toxic substances; common environmental contaminants; and dioxin-like compounds (aryl hydrocarbon receptor ligands), such as the polybrominated diphenyls, the polybrominated diphenyl oxides, and the polychlorinated dioxins and furanes.*

1. GENERAL INFORMATION AND COMMENTS.

A. General Information

*(1). **Purpose, scope and material organization.** This material is primarily intended to provide an understanding of organic chemical classes, functional groups, respective reactions and properties, and occupational safety and environmental contamination risks. It is intended primarily for use in a classroom setting (which affords needed discussion opportunities), but it is suitable for individual "refresher" training and self-instruction. The scope and the organization of this material reflect the needs of the intended audience. The material is not a teaching agenda for basic organic chemistry. Organic chemicals which pose major environmental, ecological or occupational risks are discussed generally in terms of chemical classes. Information is provided on: straight chain, branched chain and ring compounds; phenolic, carboxylic acid, ketonic, amino, and other functional groups; special interest compounds, including freon(s) and halogenated diphenyls and diphenyl oxides (plasticizers and flame retardants); and sampling and analysis methodology.*

*(2). **Detoxification of foreign substances in the body.** A number (nine in all) of synthetic or conjugation type reactions, catalyzed by liver enzymes mostly, are involved in getting rid of foreign chemical substances in the body. They are very effective except when: (a) the substance is converted to a more toxic metabolite (e.g., acridine oxidized to a more potent carcinogen acridone); (b) the detoxification process is overwhelmed by either the toxicant uptake (when specific organ damage or bio-accumulation may occur), or is too slow to prevent (fatty tissue) absorption of the substance; and (c) the substance is taken up by bone or by an organ (e.g., the thyroid). Lead and strontium 90, and radioactive iodine, respectively, are archetypical substances in this regard. The bio-transformation processes may occur successively or concomitantly. Also, a substance may be eliminated chemically unchanged.*

AN EXPLANATION OF HUMAN CHEMICAL DEFENSES. Three basic types exist, each of which is enzymatically regulated in the liver:

***Conjugation reactions** such as a reaction resulting in (urine-eliminated) **glucuronates**, ('-$OC_6H_9O_6$' either as an ether type of glucuronide of a hydroxyl group(but not a sugar -OH), or as an ester type glucuronide of an aliphatic/aromatic -C(O)OH compound), or as an **ethereal sulphate** (-OSO_3H, as formed with phenol). In addition, **glycine conjugates** (-$NHCH_2COOH$) are formed (with numerous phenols, carboxylic acids, and aliphatic alcohols).*

***Chemical reactions** most of which involve one or more of the following reactions: oxidation (and sulphur-based reactions like the conversion of cyanide and nitriles to thiocyanates, RCN →RCNS); reduction; methylation (addition of CH_3-); acylation (addition of CH_3CO- to amines and amino acids); dehalogenation (of chlorinated compounds); and hydroxylation (of esters and labile hydrogen). The reaction products may or may not be water-soluble. Water soluble products are mostly eliminated in urine. Some non-soluble products are readily eliminated in expired breath or feces (on the other hand some are persistent in body fat).*

***Encapsulation or retention in fatty tissue** of some foreign substances occurs. Lead and strontium-90 deposit in bone. Radioactive iodine deposits in the thyroid. Dioxin-like substances and other stable, low-soluble compounds are absorbed by and retained in fatty tissue, sometimes for several years.*

(3). **Organic chemistry defined**. Organic chemistry is the chemistry of carbon. Organic chemicals are essentially covalently bonded. Compounds with carbon-to-carbon bonding are *homogeneous* compounds. Compounds formed with carbon bonds to another element are *heterogeneous* compounds. Single C-C bonds are weaker (and shorter) than double bonds, which in turn are weaker than triple C-C bonds. [Examples of naming organic compounds are given in this Part, but the general (IUPAC) naming rules are too extensive to be described]. Carbon is unique among the elements in the number of compounds it forms. Carbon forms millions of compounds with itself and with other elements, including, but not limited to, hydrogen, oxygen, sulphur, nitrogen, the halogens, and metals (for example magnesium in *Grinyard* reagents, which serve as intermediates in the synthesis of numerous classes of compounds). The uniqueness of carbon is due to its ability to form three hybrid atomic orbital states from its six-electron atomic orbital ground state of $1s^2$, $2s^2$, $2p^2$. These hybrid states are designated sp, sp^2 and sp^3. Each state has a corresponding spatial arrangement and bonding capability. These three states, in turn, form molecular hybrid orbitals. The molecular hybridized orbitals underpin the hundreds of thousands of known organic chemicals. This particular property of carbon is termed "catenation." [Part One provides an explanation of orbitals and hybridization, and bond orders].

(4). **Organic chemical forms**. Different molecular forms (*conformations*, discussed later), of one kind or another, of a substance with a fixed chemical composition and molecular weight exist. Some forms are described herein. Also, different molecular configurations exist, some of which are also described. Different molecular configurations of a substance have different chemical, physical, and toxicity properties. Generalizations on chemical classes' activities and functional groups, however, must be limited. Molecular environments significantly alter the mechanisms and rates of chemical reactions. For example, one alkyl halide might have a branched chain chemical configuration and be resistant to hydrolysis by a strong base (Sn2 substitution reaction, described later), whereas a straight chain halide would be rapidly hydrolyzed in the that chemical environment. Another example of the point is the difference between phenol (PhOH) and ethanol (C_2H_5OH). The phenyl- (Ph) group attached to -OH creates a strongly acidic -OH moiety [In shorthand terms, for phenol: Ph-OH → PhO^- (phenolate radical) + $H^+_{(aq)}$. On the other hand, the ethyl- group (in ethanol) makes the -OH radical essentially neutral.

Note. The alcoholic -OH radical behaves like an acid in strongly basic conditions (e.g., sodium dissolved in a nondollar solvent, like dry ethanol). That is, the H atom in the alcoholic -OH radical becomes labile: C_2H_5OH → $C_2H_5O^-Na^+$, sodium ethoxylate. [Insight into reaction phenomena may be gained by reading the section on *substitution*, *addition*, *elimination*, and *rearrangement* reactions].

(5). **Acute human health effects**. Acute human health effects from acute overexposure are well established for most commercial chemicals, but sub-clinical human health effects (including genotoxic effects) associated with chronic, low level exposures, are often far from clear. Human data are scant and animal data are scarce or compounded by factors of species, strain, sex and age. Also, no single health risk model is reliable. The totality of test data, modeling information, and biochemical observations, however, is persuasive in regard to plausible consequences of toxic exposures.

(6) **Toxicity models**. Animate and inanimate models exist for predicting toxicity. Inanimate models use a big variety of determinants, including but no limited to: molecular structure, conformation and configuration; octanol coefficient; molecular planarity; aromaticity; electronegativity; exposure; environmental chemical persistence; and affinity (of a ligand) for human cell receptors.

(7). **Variable chemical class toxicity**. Some members of a chemical class (or a collection of environmentally important similar groups, like the PCB's) exist in numerous forms; they exist as congeners, which may number in the hundreds per chemical class. Not all of the congeners of a class are equally toxic, or persistent, or water-soluble, or fat-soluble, or acutely toxic or genotoxic. One congener may pose a potential serious risk of cancer, immunotoxicity, etc., while another may pose little risk. [Most of the congeners of major environmental contaminants have not been characterized].

(8). **Toxicity testing**. Acute toxicity tests and genotoxicity tests of air-, water-, or soil-borne contaminants are quite different. An ecological impact assessment may involve testing an extract of airborne particulate, soil, or contaminated water on one or more species of fish, frogs, midge larvae, etc. Whereas a genotoxicity test will use an extract of a 'few milligrams per liter' concentration in some kind of 'mutation-reversal' test, e.g., the Ames test (which is surprisingly negative for benzene), the 1980's vintage Mutatox™ test, and the newer *CALUX*® assay (which can be used to evaluate dioxin-like compounds). Batteries of tests are used in assessing acute toxicity or genotoxicity. Some tests in a battery of tests in a particular instance may give anomalous results. [Different mechanisms may occur].

(9). **Genotoxicity.** Genotoxicity means the substance reacts with DNA. The genotoxicant may interfere with reproduction, cause hormonal imbalances, or promote/cause tumor development. The biochemical mechanisms involved are not the same for each effect. Moreover, a particular effect may be caused by compounds from different chemical classes.

(10). **Common organic environmental contaminants**. Well-known carbon compounds of every day, occupational and environmental significance include: carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), benzene (C_6H_6), carbon disulphide (CS_2), the "carbon chlorides," such as carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$), and fluorocarbon compounds (C-F bonds, freons). Compounds with common functional groups: aldehydes (formaldehyde); ketones (acetone); aliphatic hydrocarbons (propane); aromatic hydrocarbons (ortho-, meta-, para- xylenes); halogenated hydrocarbons (vinyl chloride, used in making PVC plastic); carbamate-type *(Sevin)* and organo-phosphorus type (Malathion) pesticides; and numerous dioxin-like, polyhalogenated, multiple ring compounds.

(11). **Excessive risk compounds**. Numerous lists of *excessive risk* compounds exist. Rather than trying to memorize such lists, or the properties of a specific compound one should use high-quality, material safety data sheets (MSDS's) prepared by industrial hygienists, safety engineers, or other authoritative personnel.

(12). **Some major environmental contaminants**. Major environmental contaminants include: azaarenes (acridine), and polyhalogenated aromatic ring compounds (halogenated diphenyls and diphenyl oxides, and compounds with multiple fused benzenoid ring compounds (benzαpyrene).

(13). Compounds may have acute toxicities which do not go correlate well with their respective genotoxicities (different factors apply to each end-point). Also, the respective metabolites, created by microorganisms in water and soil, may 'switch' positions in their 'toxicity vs. genotoxicity ' patterns. Carcinogenic acridine is more acutely toxic (in the *midge larvae* test) than is the metabolite acridone, but acridone is more genotoxic than acridine (in the *Mutatox*™ genotoxicity test).

(14). **Common use of compounds of concern.** Many compounds of major concern are used in (or are bi-products of) the chemical industries, agriculture, and papermaking. These compounds may damage the central nervous system, cardiovascular system, kidneys, or liver. Also, low chronic exposures may aggravate a pre-existing condition (chemical sensitivity, asthma, contact dermatitis, or impaired lung, liver or kidney function) and the damage may not always be immediately evident.

(15). **Occupational and public (chronic) exposures.** Occupational exposure relates to 18-65 year old, generally healthy workers who work 2000 hours a year for 40 years in industrial and in other kinds of workplaces. On the other hand, public (chronic) exposure relates to the youngest, the oldest, and the in-between people, 7 day, 24 hour/day chemical insults, and the respective lifetimes.

(16). **Chemical exposure changes.** Occupational and public exposures to noxious chemicals have declined drastically since the late 1960's. This is due in large part to OSHA and EPA enforcing their rules and standards. However, serious health and safety risks to industrial workers are still significant. Also, public health and environmental and ecological chemical risks still exist regionally and locally.

(17). **Changing safety limits.** Since the 1980's many public and occupational safety and health standard limits have been made more stringent. However, a case may still be made for additional limit reductions and in some cases outright bans on use. More stringent regulation on a substance may be justified when newer types of tests indicate the substance affects mammalian DNA. [It is noted that narcosis was the basis for setting exposure limits on some substances which are now recognized to be genotoxic].

(18). **Current limits.** About 450 substances have assigned occupational permissible exposure limits. These exist as: (a) time weighted averages (TWA's); (b) short-term ceiling limits; (c) short-term exposure limits (STELS); or (d) an immediately dangerous to life or health (IDLH) limit. An even greater number of substances show up on hazardous chemical lists in federal regulations (some overlapping occurs between the lists established under different federal programs).

(19). **No safety limit assignment.** Some known mutagenic and/or carcinogenic compounds do not have federally- or internationally- established exposure limit values. However, most of them have respective "standards" of one kind or another (guides, foodstuff contaminant limits, etc.). Chemical manufacturers provide health, safety and environmental exposure limits/recommendations.

(20). **General health and safety and environmental protection guidance.** Numerous safety, health, and environmental protection guidelines and standards exist. They include federal OSHA regulations (CFR Title 29), EPA regulations (CFR. Title 40) and DOT Hazardous Materials regulations (CFR. Title 49). Periodically, these guidelines are changed to reflect current knowledge and concerns.

(21). **Newer limits.** Acute, one-time, airborne exposure limits based on post mid 1980's reviews of all the available toxicological data exist for about two dozen dangerous (inorganic and organic) substances. These are the Acute Exposure Guideline Levels, AEGL's. These guides were first issued in the late 1980's by the National Academy of Science. Development of AEGL limits is ongoing.

(22). **AEGls.** AEGls are acute, one time, airborne exposure limits. They exist in three categories, each of which reflects a (stated) endpoint (to an exposure concentration of 10 minutes to 8 hours duration).

(23). **AEGL classes.** Three AEGL's classes (with different endpoints) exist: AEGL 3— fatality; AEGL 2— appropriate escape/unprotected entry; and AEGL 1—onset of severe sensory or non-sensory, but reversible effects.

(24). **Key AEGL's.** The AEGL 3 and AEGL 2 level limits are especially important to agencies involved in preparedness for high hazard chemical releases: DOD, DOE, COAST GUARD, EPA, and FEMA.

(25). **AEGL 3.** This limit relates concentration to duration of exposure, in terms of the risk of fatality or an increasing likelihood of death from a continuing burden on the respiratory system.

(26). **AEGL 3 does not apply to carcinogenic substances which are not extremely toxic.** AEGL 3 level limit applies only in a case of one-time, short term, airborne exposure to a highly toxic substance.

(27). **AEGL 2.** This limit applies to an airborne concentration of a toxic chemical with a (stated) duration of exposure, and impairment of generally safe escape, or a potential for serious injury with an unprotected entry into a previously contaminated space.

(28). **AEGL 1.** AEGL 1 is the point at which a 'concentration-time' circumstance creates the risk of incurring a "notable discomfort."

(29). **Dominant risk factor.** In some acute chemical exposure risk situations, the concentration of the substance, not the duration of exposure, may dominate the risk. In other circumstances, concentration and duration of exposure may contribute about equally to imminent serious risk. Only rarely is duration of exposure the dominant factor. In reality, data are too scant to currently support the use of the 'dominant risk factor' principle in setting standards.

(30). **Safety limit issue.** 'Threshold of safety' is a perennial health issue on some substances. However, a threshold limit must be applied as a practical necessity in many cases. A threshold limit is not, however, a fine line of division with respect to safety. Also, with a carcinogen, applying a threshold limit is generally objected to; the absence of an observable adverse human health effect does not mean that a potential for a future serious illness does not exist. On a separate matter, many limits were set before current tests for assessing sub-clinical effects existed. [The results from using newer tests have changed how chemical risks are viewed. Such tests include: (a) the sheep red blood cell (SRBC) test for predicting immunotoxicity and DNA damage; (b) the Micronuclear, MN, test; (c) the mammalian cell genotoxicity test; (d) the chromosomal aberration, CA, test; (e) the sister-chromatid exchange, SCE, test; and (f) the lymphocytes impact test for mutagenicity and carcinogenicity.

(31). **Need for familiarity with environmental risk evaluation.** Safety and health specialists and many environmental protection professionals are knowledgeable about human health standard limits and their biological underpinnings. They need to be familiar, if they are not already, with how environmental and ecological chemical risks are evaluated. This is needed to support many of the programs of the federal and state environmental protection agencies.

Note. **Human health risk assessments are predicated on tests made on primates, dogs, mice, microbes (i.e., microbial mutagenicity tests), and occasionally humans, in regard to organ function, skin and/or eye irritation, elevated liver and/or kidney enzymes, thyroid chemistry, thyroid size changes, and several other factors. On the other hand, quite different tests are used to assess environmental and ecological risks associated with public expósures to organic chemicals (environmental contaminants). The latter assessments typically comprise a battery of procedures which may include:**

- **Mineralization/degradation tests, coupled with carbon dioxide evolution measurements over three or more months, as well as specific chemical analyses. These tests provide information on chemical persistence, in various media and in various circumstances.**
- **Bio-accumulation tests, and, separately, toxicity studies on fish, carp, flounder, and rainbow trout.**
- **%lethal response-concentration tests, such as the '50% lethality response (LC50) -15day-soil worm' test.**
- **Midge larvae toxicity tests.**
- **Daphnia magna life cycle tests, used to determine "no observed effect" or "low observed effect" concentration, and other, similar parameters.**
- **Long-term sediment toxicity (LC50) tests, employing various organisms.**
- **Seedling emergence tests (cucumber, onion, etc.) Re: a "21-day, no observed adverse effect."**

(32). **High-risk environment contaminants**. Many of the higher molecular weight, halogenated organic compounds are environmentally persistent, high-risk chemicals. There are literally hundreds of congeners per substance, of these kinds of chemicals. The halogenated (chlorinated/brominated) diphenyls and diphenyl oxides, and their early metabolites ('diols') are high risk environment contaminants, of which large numbers of congeners exist.

(33). **Accumulation and persistence of high molecular weight, halogenated organic compounds in the body**. High molecular weight, halogenated organic compounds, once in the human body, accumulate in fatty tissue. To some degree they undergo a variety of bio-conversions in the body which aid in their elimination. However, some of these chemicals are retained in fatty tissues for many years.

Note. **Body chemical overburden with dioxin-like substances are now a wide-spread problem, and the reported half-lives in the body of some dioxin-like substances are 5-10 years. Most polychlorinated compounds have very much shorter half-lives in fatty tissue.**

(34). **Public standards issues**. Public skepticism over safety claims and exposure limits is commonplace, especially if they are not based on findings from newer (sub-clinical) toxicity tests. Health standard limits may be a significant public issue for some years to come.

B. Qualitative chemical observations and inferences

(1). **Color** is of little value in classifying or identifying an organic chemical or a functional group. A few exceptions exist. [A prussian blue color is confirmatory in the Lassaigne test for nitrogen in a compound, and a blue glass bead formed in the borax fusion test confirms cobalt].

Many pure compounds, including most liquid and solid phenols, carboxylic acids, polyhydric alcohols, esters, and halogenated aliphatic and aromatic compounds, are colorless. However, they become colored on aging (oxidization). Some nitro compounds and poly-keto compounds are deep yellow. Many quinones are highly colored (yellow-orange)

(2). **Peroxidation-induced color.** A yellow color may be seen in chemicals which are susceptible to peroxidation. Such chemicals are colorless when freshly supplied, but upon aging in the presence of air (peroxidization) become colored and potentially shock-sensitive (explosive). Ether, diethyl ether, diisopropyl ether, dioxane, tetrahydrofuran, acrylic acid, and butadiene form explosive peroxides. Many other ethers and unsaturated compounds are peroxide-formers.

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Note. A test for peroxidation (which should only be used on relatively new material), is to add a (water) solution of potassium iodide to the substance with gentle mixing; the formation of a yellow-brown color within about 10 to 15 minutes is positive, but a false positive may occur. Obtain safety professional help before handling/disposing of a suspected peroxidized substance.

(3). **Odor,** unlike color, can be a useful guide to identifying certain chemical classes and chemical substances. Distinctive odors are noticed with halogenated compounds. These include chloroform, hexachloroethane, aniline, acetamide, formaldehyde, acetic acid, and low molecular weight acids and esters (amyl acetate). Amines have a "fishy" odor. Aromatic side-chain amines, like benzylamine, are liquids with unpleasant 'oily' odors. [Smell memory can be useful in identifying released substances. Most odorous substances have characteristic smells and can be detected at a level of few parts per million, in air or water].

(4). **Smell (odor) is not a general acceptable criterion of safety. It cannot be used to assess risk.** Many toxic substances (and asphyxiating or toxic atmospheres) have no adequate hazard-alerting odor. Their odor (or taste) thresholds are too near their respective immediately dangerous to life or health, IDLH, concentrations, to adequately warn of danger. Exceptions exist, and in some fixed chemical process operations, odor can be a useful safety alert. For this purpose, however, the odor (or taste) must be well recognized, and the detection threshold concentration must be about two orders of magnitude lower than the respective IDLH limit.

(5). **Smell ability is absent** in a small percentage of the general population, as are smell memory and taste memory. Also in some cases (e.g., H_2S) the smell sense can be lost temporarily.

(6). **Halogenated (but not fluorinated) chemicals on burning in the presence of copper produce a green colored flame.** [A green flame on heating a substance on copper wire is the basis of the classical Beilstein halogen test.]

(7). **Organic substances on burning** may generate a sooty flame, a clear flame or an ash, depending on the class and molecular composition. Flame appearance and ash can indicate chemical class.

(8). **Sooty flames** are seen with burning aromatic compounds, some unsaturated compounds, most saturated organic compounds which have five or more carbon atoms per molecule, and many chlorinated hydrocarbons, e.g., chloroform.

(9). **Clear flames** occur with burning, low molecular weight, saturated aliphatic compounds.

(10) **Ammonia** occurs with burning nitrogenous compounds.

(11). **Sulphide odor or sulphur dioxide odor** occur with burning sulphur-containing compounds.

(12). **Solubility**. The solubility of a gas, liquid, or solid in polar solvent, or in an apolar solvent (e.g., octanol), depends on the solute and the solvent. The solubility rule is "like dissolves like."

(13). **Polar solvents** include water, and water- alcohol combinations. Non- aqueous systems can be polar (e.g., liquid ammonia). **Apolar solvents** include the lower molecular weight esters, nitriles, and phenols.

(14). **Most low molecular weight, polar organic compounds are water soluble.** Compounds with fewer than five carbon atoms per molecule and some degree of polarity are generally miscible with water. Water readily dissolves many lower molecular weight alcohols, aldehydes, ketones, and (some) esters, amines and phenols. The lower aliphatic acids in water are acidic (pH about 5). The lower amines are alkaline in water (pH about 10). The lower alcohols are neutral in water.

(15). **Water solubility generally increases with increasing temperature**. The lower molecular weight aromatic acids, including citric acid, benzoic acid and salicyclic acid, are appreciably water soluble. Their hot solutions tend to crystallize on cooling.

(16). **pH may affect solubility**. Alkalinity increases the water solubility of most organic acids. Acidity increases the water solubility of the lower molecular weight amines.

(17). **Many alkanes/alkenes/alkynes, and halogenated organic compounds are not appreciably water soluble**. However, they are soluble enough be cause serious environmental problems. These kinds of substances are very soluble in apolar solvents: hexane, toluene, etc. Many of the common mutagenic and carcinogenic organic compounds are only sparingly water soluble (i.e., a few milligrams/liter). Exceptions exist: nitrosamines and amines are appreciably water soluble.

(18). **Octanol** is one of several solvents which readily dissolve higher molecular weight, uncharged, non-polar, organic compounds. It is used in the "octanol coefficient" test. This test numerically describes the distribution of a chemical in a two-phase (octanol-water) mixture. It is an indicator of the potential environmental transport of a compound. It also indicates a potential for chemical bioconcentration in animals.

(19). **Environmentally persistent chlorinated/brominated compounds with high octanol coefficient values (e.g., 10^5)**. Compounds of this kind tend to bio-concentrate in fish and animals, and travel through the food chain to humans. They are ligands for cellular aryl hydrocarbon receptors, ahR's.

Note. The octanol coefficient is central to inanimate (computerized) models for predicting the genotoxicity of a substance which has an affinity for cellular aryl hydrocarbon receptors, ahR's. The human ahR receptor is part of the pathways for the synthesis of (or adverse effect on) proteins involved in immunotoxicity, cancer promotion, endocrinal imbalance and/or human reproduction problems. Other 'ahR' aspects include transport of the ahR-ligand to the cell nucleus, and subsequent binding to DNA.

(20). **Fish bio-concentration factor** (BCF). This factor is determined in laboratory tests using carp and other fish. A "BCF" of 10^3 or greater is a mark of potential bio-accumulation.

(21). **Vapor pressure.** Many occupationally and environmentally problematic chemicals (e.g., the carbonyl compounds (aldehydes, ketones) and the halogenated hydrocarbons) have values of vapor pressure at standard temperature which exceed that of water. Also, their boiling points are below the normal boiling point of water.

(22). The boiling points of organic compounds are affected by the "bulkiness" of their molecular structures. Branching lowers 'compactness' and lowers boiling point (via reduction of weak intra-bonding).

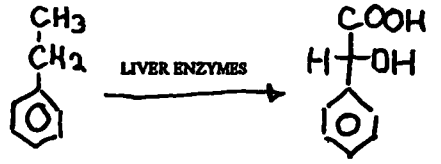
(22). **Boiling points of aromatic hydrocarbons.** Toluene and the higher molecular compounds in this class (but not benzene) have boiling points well above that of water. Chlorobenzene and the ortho-, meta-, and para- chlorotoluenes have boiling points much higher than that of water.

(23). Methylene dichloride, trichloroethylene, methyl chloride, n-butyl chloride, and many other simple organic halides have boiling points below that of water. The bromide analogs of the above compounds have boiling points which are generally 50% or more higher than their corresponding chlorides. The esters of carboxylic acids and alcohols which each have three or fewer carbons in the respective molecules (e.g., ethyl propionate) have boiling points lower than water.

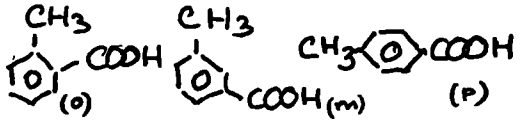
(24). **Specific gravity.** The specific gravities of most non-halogenated organic compounds with five or fewer carbon atoms per molecule, and the specific gravities of many higher molecular weight, simple, non-substituted organic compounds, are equal to or less than the specific gravity of water, which is 1 gr/cc. The latter kinds of compounds, however, when they contain a nitro- group, are denser than water, e.g. paranitrotoluene, S.G. = 1.12; and ortho- and meta- nitrotoluenes, S.G's = 1.16. [Compounds containing multiple "nitro" ($-NO_2$) radicals are notoriously explosive, cf. trinitrotoluene, TNT].

(25). **Post chemical release (or post biological uptake) detection.** Oftentimes a test for an organic chemical known to be in soil or in the body will be negative; generally, chemical and/or enzymatic degradation and bio-conversion account for the discrepancy.

ETHYL BENZENE EXCRETED IN URINE AS PHENYL GLYCOLIC ACID



ORTHO, META, AND PARA TOLUIC ACIDS



Note. In humans, inhaled ethyl benzene is excreted in urine as phenyl glycolic acid, rather than as unchanged ethyl benzene. This metabolite can be measured spectroscopically and is used to assess ethyl benzene exposure. Likewise, the o-, m-, and p- xylenes are metabolized in the body to ortho-, meta-, and para-toluic acids. These acids are subsequently conjugated by glycine. The xylenes are also enzymatically converted to the corresponding xylenols. All these metabolites are excreted in the urine.

C. Other Matters

At this juncture we will make a detour and briefly comment on several matters of major interest to safety and health professionals. This will include information on homeland security (chemical) issues and some common organic chemical classes and functional groups.

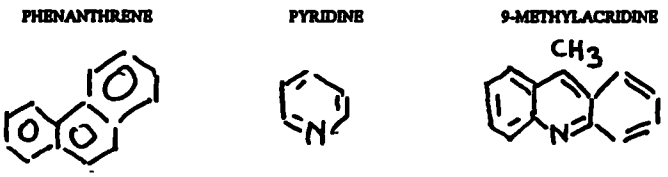
(1). **Lists of high risk chemicals.** A large number of regulatory lists pertain to both inorganic and organic chemicals which are "high risk." Rather than attempting to memorize lists and risks, it is better to read the applicable material safety data sheets and the rules for the proper use, transport, and disposal of chemicals.

(2). **Acute exposure standards.** Fractional (e.g., one hundredth or one-tenth) IDLH values are sometimes used as one-time, acute, short term exposure limits, to avert lethality or irreparable health damage in emergencies outside of general workplaces. (The IDLH limits originated with NIOSH with workplaces in mind). There is little scientific substantiation for such use. On the other hand, the relevant Academy of Sciences' AEGL 3 level limits (see page 5), which cover inorganic and organic substances, are supported by recent risk assessments made by experts.

(3). **Chemical classes. Functional groups. Chemical forms.**

(a) *Chemical class* (or family). Organic compounds often can be placed unambiguously in one class (esters, ethers, etc.) of compounds, but sometimes a compound can be rightly placed in more than one class. [Some common classes are described later. Many drugs are *chemical unions* of common classes of (C3 - C8) homo-and heterogeneous ring structures and molecular chains].

HOMO-AND HETEROGENEOUS RING STRUCTURES



(b) **Functional groups**. An organic chemical of any class may have, within its main structure or attached to this structure, a chemical entity which generally has a unique mode of reactivity. This entity is termed a functional group. [Functional groups are described later].

(c) **Forms**. Entities with a common fixed molecular composition and molecular weight may exist as forms of one kind or another. Certain forms (e.g., isomers) have different chemical or physical properties (boiling point, etc.), and some forms (enantioners, diastereoisomers) have the same physical properties, except they rotate polarized light differently (they also differ in their biological utility).

NOTES

Note 1: DISTINCTIONS BETWEEN CHEMICAL CLASS, FUNCTIONAL GROUP, AND FORMS.

Distinctions are difficult to verbalize. 3-D molecular models, bond projection drawings and drawings of arrangements of atoms or groups are used to show distinctions. Consider paranitrophenol. This chemical may be regarded either as a phenol, or as a "nitro" type of compound. [Distinctions between forms are best looked at separately].

PARANITROPHENOL

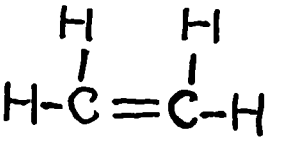
Note 2: 3-D MOLECULE REPRESENTATION ON A FLAT PAPER SURFACE.

As a preface to looking at chemical classes and forms, an explanation is needed of the two common methods used (shown in the sketches below). Variations of the two methods are sometimes employed.

(A). **The Fisher projection method.** Fisher projections are very useful for showing spatial dispositions of different parts of a simple molecule. Simple lines represent bonds and directions. **Horizontal lines represent bonds projecting forward** (out of the paper's plane). **Vertical lines represent bonds which project backward** (behind away from the plane of the paper).

FISHER PROJECTION METHOD.

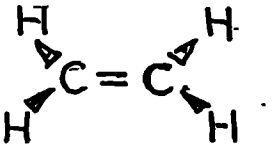
(2-butene)



(B). **The Wedge projection method (and The Newman variation).** These projections consist of elongated triangular shapes, which are either all black-filled or line-filled to represent spatial arrangements. The all-black filled shapes represent bonds projecting forward, out of the paper's plane. The line-filled shapes represent bonds projecting backwards How these two molecular projection schemes appear are shown in the following sketch. Wedge projections are sometimes drawn as a rectangular shape rather than as a wedge shape.

WEDGE PROJECTION METHOD

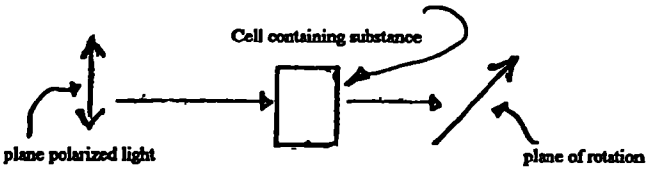
(2-butene)



A variation of the Wedge projection method involves looking along the C-C axis of the projection to "see" the various possible molecular conformations (i.e., the angular torsion, with sinusoidal changes in energy, over180 degrees of rotation, around a C-C single bond). This variation is named the "Newman projection." [This projection provides little useful information on molecular volumetric shape. Solid models or computer representations are used for this purpose].

Note 3: OPTICAL ACTIVITY.

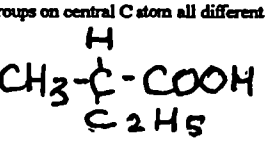
OPTICAL ACTIVITY ILLUSTRATION



Optical activity needs to be briefly explained before we discuss some molecular "forms" (conformations), and some reactions, especially, the reaction known as the "Sn2 substitution reaction". [Sn2 substitution, described later, characteristically involves a molecular inversion (called the Walden inversion), accompanied by reversal in optical rotation activity, see sketch].

COMPOUND WITH A CHIRAL CENTER

Groups on central C atom all different



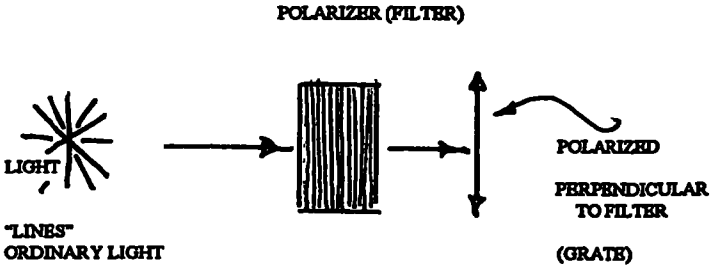
Certain compounds with one or more chiral centers (i.e., a carbon atom to which are attached four different subgroups or radicals; the carbon atom itself should not be called 'chiral carbon') in a monochromatic beam of plane polarized light, rotate the beam to the left or to the right. These compounds are said to be optically active. Lactic acid is an example. A left-rotating form of such a compound is "leavo" (l), and the right-rotating form is "dextro" (d).

The d and l forms may be inter-converted by appropriate chemical reactions. Also, a 50:50 molar mixture of the forms (called a racemate or racemic mixture), and a similar mix within a well-defined crystalline addition compound, called a recemic compound, is mutually cancelling. A racematic mixture does not cause polarized light plane rotation.

The extent of rotation of a defined monochromatic light (typically the D line of the sodium spectrum) depends on the substance itself (the respective constant) and the substance's concentration and the light path length. The substance's specific rotation constant [α] (left or right rotation of equal magnitude) is determined under fixed parameters (temperature, concentration, path length, light wavelength). It is usually reported as $[\alpha]_D^{20}$, where the "$_D$"= the D-line of sodium spectrum, and "^{20}" means 20 degrees Celsius.

A polarimeter is used to measure polarized light plane rotation and the monochromatic light used is normally the D line of the sodium spectra. Light polarization and the polarimeter device are shown schematically opposite.

POLARIMETER SCHEMATIC



It is also noted that a particular d form (also denoted by +) or an l form (also denoted by -) of a compound may be especially important commercially. For pesticidal enantiomers, only one form of the pair (enantiomers, discussed later) is specifically biologically active, but both forms are generally toxic. Being able to manufacture only the biologically active form is highly desirable because use quantities (of a racemate) could be cut by in half and the human risk could be similarly reduced. On a separate aspect, the direction of optical rotation is not correlated with the actual absolute configuration of the molecule. Absolute configuration is an entirely different aspect which is replete with conventions and rules (these are outside the scope of this presentation).

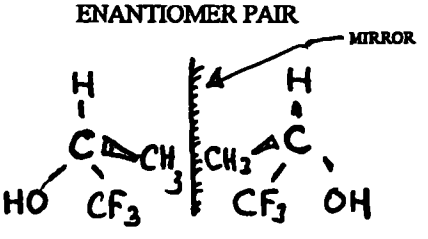
[Chemical forms continued]

(4). **Enantiomers**. Compounds that have identical molecular composition and molecular weight, may exist in different forms (*conformations which arise without the breaking and reforming of chemical bonds*). These forms generally have identical properties, except for (a) optical activity (*plane polarized light rotation direction*), and (b) interaction with other *chiral* compounds.

Note. The term "chiral" (gr) means "handiness" and can be illustrated by an analogy to ones hand viewed in a mirror. As an aid to understanding *enianoimorphorism*, consider your left hand (using a mirror and a conventional pair of gloves). You will notice that you cannot see an imaginary plane (*plane of symmetry*) "running" through the hand, neither can you find a symmetrical center-point (*center of symmetry*). Also, and most importantly in topical context, the hand and its mirror image cannot be superimposed. Furthermore, only one of the regular pair of gloves will fit the one hand. The analogy is this: the hand is the equivalent of a chemical with a chiral center, as is the glove which fits the one hand.

Enantiomers are chiral chemicals with non-superimposable mirror image forms. With enantiomorphism there are only two stereo isomers for each set.

ENANTIOMER PAIR



Note. Other *superimposable*, polarized light plane rotating, molecular mirror image entities exist. They are known as diasterioisomers. For example, +2-butanol and -2-butanol, which have the formula $CH_3CH_2CH(OH)CH_3$ are diasterioisomers. [See "diasterioisomers".]

Enantiomers are extremely important to the drug and pesticide industries. Generally, only one member of an enantiomer pair is specifically biologically active. On the other hand, each member may be very toxic. [The body utilizes one form or another of some classes of chiral molecules, to the general exclusion of the alternate form. Thus, all of the amino acids used in the body are "leavo," while all of the sugars used by the body are "dextro"].

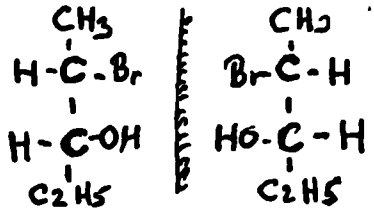
Other aspects of enantiomorphism (chirality) exist which are outside the scope of this presentation, except to mention that thousands of "starting block" enantiomers are now commercially available for synthesizing pharmaceutical and pesticidal products. [There is a strong interest in the selective development of pesticides, since they offer maximal effectiveness with the least overall toxicity risk]

(5). Diastereoisomers

Diasteriosomers have different properties, but a common empirical formula. Characteristically, diasteriosomers have two (or more) stereogenic carbon atoms per molecule. A diasteriosomer can cause polarized light plane rotation. Also, a diastereoisomer *is* super-imposable on its mirror image. 2-bromopropanoic acid is an example of a diastereoisomer.

DIASTEREOISOMERS

(NOTE TWO CHIRAL CENTERS/MOLECULE)



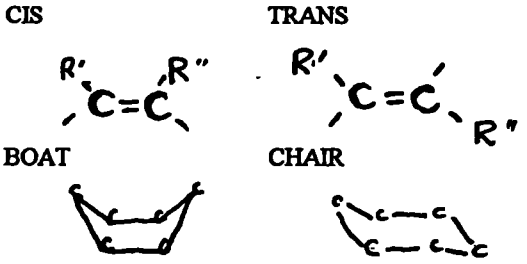
Enantiomer images are non-superimposable. Diastereoisomers have superimposable mirror images.

(6). **Tautomers.** Some molecular structures (configurations) change form by undergoing a proton shift (see illustration). This shift is facilitated by the mutual proximity of active chemical moieties. Individual tautomers are formed according to their chemical environment and their relative abundance can be affected by the solvent system which is used. Tautomers have different properties (boiling points, acidity, etc.).

(7). **Other forms.** Absolute and Relative configurations. A spatial arrangement of a chiral compound can be described, according to certain arbitrary rules. Mere knowledge of a compound's polarized light rotation capability is of no use for this purpose. [Polarimetry *is* the basis for "describing" the *relative* configuration of a chiral substance]. The best and most used rules for identifying the *absolute* configuration of a chiral substance are known as the **"Cahn-Ingold-Prelog"** system. This system used a letter designation (R and S) to identify a configuration. Absolute and relative configurations are explained in standard chemistry texts.

Cis and trans configurations
Boat and chair configurations.

The general forms are shown schematically opposite.



DETOUR: (1) MOLECULAR SHAPE FACTORS AND (2) FREE RADICALS

1. **MOLECULE SHAPE** [Molecular shape depends on molecular conformation and configuration]

The three-dimensional shape of a molecule, in particular, the shape of the outermost part of the continuous surface called the "steric boundary" (which excludes the inner "crannies" that are inaccessible to external contacting surfaces). The steric boundary and the molecular physical dimensions and planarity, and other properties, regulate binding to other molecules (e.g., cellular receptors). The other factors may include: the immediate chemical environment, functional groups, labile hydrogen (which can enter into hydrogen bonding with the contacting surface of another moiety), electronic charge, thermodynamic properties and cell membrane transport. For example, the very toxic (chlorinated dioxin) TCDD, "dioxin," is a ligand for aryl hydrocarbon receptors in human cells (and similar receptors in other species). TCDD has a strong affinity for ah receptors, due to its molecular planarity and dimensions (reported to be about 14 x 12 x 5 Angstroms), and other factors.

The overall solid shape and volume of a molecule are affected by: (a) its configuration (the structural arrangement of the molecular 'parts,' which may be ascertained from crystal structure X-ray analysis and from stereo-specific chemical reactions), and (b) its conformation (the spatial arrangement of the molecular 'parts' — conformations can interchange with each other without breaking and reforming strong bonds).

2. **FREE RADICALS**

Free radicals are derived from chemical homogenous decomposition, by ultraviolet light, heat, and other sources of energy: RX —> R· + X· [X=a halide, typically]. Many commercially important, large scale polymerization chemicals and processes are "free radical." These processes use massive quantities of monomers which are highly flammable and/or highly toxic. Also, free radicals are involved in many addition type chemical reactions (with and without polymerization). In industrial polymerizations, free radicals are generated from relatively stable compounds by the action of heat or ultraviolet irradiation (and pressure). These free radicals initiate a cascade of secondary free radicals within unsaturated structures, and this results in polymerization. Many of the monomers used in this process pose ongoing chemical accident risks of major proportions.

Free radicals are molecules with an odd, unpaired electron. They exhibit paramagnetism (which can be studied by paramagnetic resonance spectroscopy, PRS). Generally, free radicals are unstable and short-lived, and they are fast-acting with unsaturated compounds, via radical addition across double bonds. But not all free radicals are short-lived. Some, like the triphenylmethane free radical ($ph_3C^{\cdot}$), are stabilized by resonance energy (delocalization of the lone electron). Also, some may be "cold-trapped" within a high polymer matrix (as may be demonstrated by PRS). Apart from their involvment in producing high polymers, free radicals arise in environmental pollution, in cigarette smoking, in pesticidal and herbicidal actions, and in human metabolism.

THE TRIPHENYLMETHANE FREE RADICAL, PH_3C·

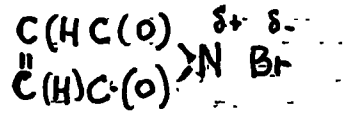
The generation of some free radicals in humans may be beneficial (viricidal/bactericidal; free radical formation and subsequent reaction with the cellular components of microbes underlie the pharmacological action of many anti-microbial drugs), but by and large they are harmful to living cells. Free radical cellular damage in humans, reportedly, is cumulative on aging. The antioxidants, vitamins C and E, protect against free radical-induced cellular damage. They break the associated radical chain reactions, and prevent the free radical oxidation of lipids (which otherwise might produce substances which clog arteries). Vitamin C and E mega-dosing, however, can cause serious liver and/or kidney injury.

Free radical-based, industrial high polymer production processes. Many large-scale polymerization processes, involving unsaturated (i e., double bond) chemicals, like vinyl chloride, CH_2=CHCl, involve free radical initiation and a highly efficient propagation of other (induced) free radicals. The latter free radicals then proceed to add to double bonds within molecular chains. The "vinyls" are made in this way, using high temperature–high pressure processes.

It is noted that non-polymerization, free radical reactions occur (e.g., chlorine addition across double bonds) and, non-free radical commercial polymerization processes exist (e.g., the condensation reaction in making nylon).

Several compounds are widely employed as free radical sources (initiators) in important organic syntheses and *high polymer* manufacturing processes. Two initiators are benzoylperoxide (which is used to "cure"— crosslink— mixtures of unsaturated polyester resins and styrene, to make thermoset polyester plastics) and n-bromosuccinimide (which is used to brominate aromatic ring structures, to make such compounds as polybrominated diphenyl oxides, which are plasticizers and flame retardants). Free radical reactions are not interminable; collisions between free radicals and electrophilic reactants ultimately terminate free radical generation and stop the reaction. [In plastic polymer manufacturing, this free radical termination step must not occur until well after hundreds of subsequent free radical inductions have occurred].

N-BROMOSUCCINIMIDE

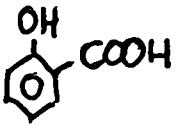


BENZOYLPEROXIDE

END OF DETOUR

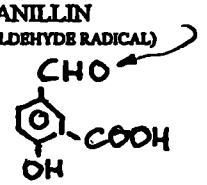
(8). **Aromatic compounds** (annulenes). Aromatic compounds are compounds which have a planar ring structure, and molecular orbital arrangements which allow for (delocalized) pi-electron clouds above and below the planar ring of conjugated single and double bonds. Many aromatic compounds exist in plants and foodstuffs, including caffeine, salicyclic acid, vanillin (vanilla). Five- and eight- member rings can be aromatic, as well as the well-known, 6- member (benzenoid) ring.

SALICYLIC ACID



BENZENE

VANILLIN
(ALDEHYDE RADICAL)

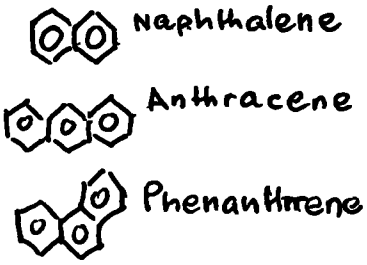


Aromaticity relates to: (i) a propensity for *substitution* chemical reaction, rather than an *addition* reaction; and, (ii) a relatively high chemical stability (known as *resonance energy stability*). The resonance energy of an aromatic compound is less than that which exists in the comparably unsaturated (i.e., double-bonded), non-ring compound. Benzene is the archetypical aromatic compound. [Its 'shorthand' representation is a **circle within a hexagon**, as shown above]. Benzene has three double bonds, but its heat of hydrogenation, Δ_{Hh}, from the addition of hydrogen atoms to the three double bonds, is about 40% less than "three times the corresponding heat of hydrogenation" of cyclohexadiene (a non-aromatic cyclo-hexene, with one double bond). This net energy difference is the *benzene stabilizing energy*. The effect is called the "resonance effect" or the "mesomeric effect." The six (benzene) hydrogen atoms are energetically equal and the three double bonds are conjugated with three single bonds. These double do not chemically react like double bonds in a non-aromatic compound. For example, bromine water is decolorized upon addition to a solution of a straight or branched *chain* compound with multiple double bonds (a "polyene"), but is not decolorized upon mixing with benzene. The reason is that there is an added stability with aromaticity because the electrons involved in the carbon bonds are delocalized (in pi bonds) around and above and below the planar ring(s) — a phenomenon termed "resonance." The benzene aromatic structure may be thought of as a structure existing of two or more *canonical* (Kekule) forms, but not as an actual mixture of such forms.

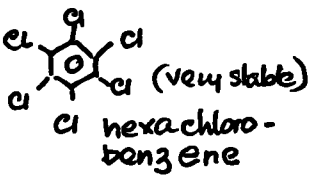
Note. In the body benzene is converted to phenol which is subsequently eliminated via urine as a conjugate of hippuric acid: $C_6H_5C(O)N(H)CH_2COOH$.

(9). **Polyaromatic hydrocarbons (PAH's), and halogenated aromatic hydrocarbons (HAH's).** These are environmentally ubiquitous, generally persistent environmentally, and potentially mutagenic, carcinogenic, and/or pseudo-endocrinal. They are fused ring compounds based on benzenoid rings and benzene ring analogs (ring containing atoms other than carbon, i.e., O, N, P).

PAH's



HAH's



(See page 30)

PAH's are resonance energy stabilized, like benzene.

Not all mutagenic PAH's, or their early metabolites, test positive in every mutagenicity test.

The most toxic carcinogens among the PAH/HAH's are benz(α)pyrene, and the chlorinated PAH, 2,3,3,8- tetrachlorodibenzo-p-dioxin (TCDD). Reportedly, these two compounds and some of their early metabolites —diols, (and others 'dioxin alikes') activate *aryl hydrocarbon receptors* in human cells. [They are referred to as 'ahR ligands']. They affect protein synthesis. They are associated with tumor promotion, immunotoxicity, interference with cell growth, and alteration of endocrinal 'balances' and skin-contact allergy. These kinds of substances accumulate in the body. However, they are metabolized to some degree and at different rates by monoxygenases and other enzymes in the body. The products of their metabolism include diols and epoxides. These are ultimately eliminated in urine, as thioglutamates and other conjugated entities. These kinds of substances form adducts with DNA. [Their biological activity may be gene-dependant; some test strains of mice are resistant to PAH-induced cancers].

(10). **Common PAH/HAH's.** Two-, three-, or four- fused ring PAH's are well-known and exist naturally. HAH's are produced in chemical and thermal processes, including waste and fuel incineration, metals manufacturing, chlorine-bleaching processes (e.g., paper mills) and chlorophenol manufacturing. In general, their high stability is not equi-proportional with respect to the increased number of benzenoid rings in the molecule. This is shown by their respective molar heats of hydrogenation and comparison to the respective straight chain, olefinic compounds.

(11). **Environmental persistence.**

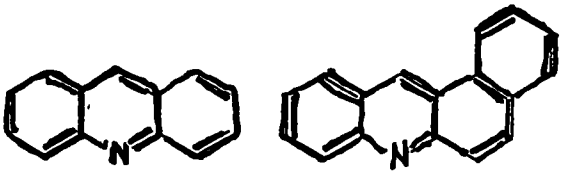
The PAH/HAH's and their congeners are environmentally persistent. Concentration affects persistence, possibly due in part to concentration-dependant microbial toxicity.

Note. In the body, PAH's and HAH's are chemically converted by specific liver enzymes, which aids in their elimination. However, the past and current production of HAH's in the industrial countries has created public chemical (body) burdens which are too high for the body to effectively detoxify and eliminate them, and being lipophilic, they accumulate (and persist) in the fatty tissues. [Over the last 75 years, industrial chemistry and public demand for pesticides, plastics, paper products and other materials, which are associated with the generation of dioxin-like chemicals, has 'outrun' biochemical knowledge of the day and possibly has exceeded due caution.]

Some PAH/HAH's are degraded in water and sludge, to the point of mineralization, by soil bacteria, e.g., *Sphingomonas.*

Nitrogen-heterocyclic PAH's are similarly degraded.

SOME NITROGEN-HETEROCYCLIC PAH'S



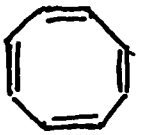
acridine benz[a]acridine

(12). **Some less-common aromatic compounds.** Many multiple-fused, planar ring structures, which contain either more than six carbon atoms in a ring (with conjugated bonds), or carbon and other atoms in a ring are aromatic.

LESS-COMMON AROMATIC COMPOUNDS

BENZYNE

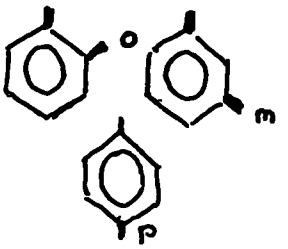
CYCLOOCTATETRACENE



(13). **Substitution reactions and aromatic compounds.** A typical substitution reaction with an aromatic compound is shown in the following sketch. Substitution reactions, rather than addition reactions, are typical of aromatic chemicals.

(14). **Ortho, meta, and para positions on the benzenoid ring.** With mono-substituted benzene and similar molecules, ring positions are designated as *ortho*, *meta*, or *para*. The scheme is shown opposite.

ORTHO, META, AND PARA POSITIONS ON THE BENZENOID RING



Note. The o, m, p positions are occupied preferentially by different "attacking" moieties, and in accordance with the nature of any existing substituent.

Moreover, halogen-occupied o-, m-, p- positions are not equally degraded by microorganisms which cause reductive dehalogenation.

Several kinds of soil bacteria selectively dechlorinate (substituted benzene compounds), at the *ortho* position.

(15). **Halogenated hydrocarbons are major pollutants.** Virtually all of the common halogenated solvents which were/are used as cleaning agents have caused major persistent pollution of ground water including aquifers and potable well water.

(16). **Some well known or common classes of organic chemicals.** [Scope limits discussing 'classes'].

CLASS / GROUP	KEY PARTS/ MOLECULE	SUBSTITUTION (S)	ADDITION (A)	REMARKS
ALKANES	C-C; C-H	✓ of H by Cl etc.	of HX, X= halide, etc	No Pi bonds; sigma only
ALKENES	C to C triple bond	✓	✓	SP2 hybrids, and Pi bonds Addition to C=C is significantly different than addition to C=O
ALKYNES	C=C	✓	✓	SP hybrids; triple bonds
ALKYL HALIDES	H-C, C-X	✓	✓	S & E (elimination) reactions may compete in a given case
ALCOHOLS	H-C; C-O-H	✓	✓	✓ Oxidation; ✓ Elimination
ETHERS (including epoxides (e.g., the sterilant ethylene oxide), which exist as a bond-strained, three-member ring, of two C atoms and one O atom).	C-O-C	✓(of OR/alpha H)		Ethers are generally chemically unreactive (they form adducts), but epoxides, with their strained 3-member ring, are reactive.
ALDEHYDES	C-CH=O	✓ (H/alpha H)		✓ Oxidation
KETONES	C-CR=O	✓ (of alpha H)	✓	
CARBOXYLIC ACID	C-CO_2H	✓ (of H/OH)	✓ (to C=O)	
AMINES (1,2,3)	C-NH_2 (1) C-NHR (2) C-NR_2 (3)	✓ (of H) ✓ (of H)	✓ (to N for all 3)	✓ Oxidation of N
BENZENE RING	C_6H_6	✓ (of H)		Aromatic ring, Pi bonds, electron delocalization-stabilization

Note. In general, the alkanes and the ethers are generally unreactive, but the esters, carboxylic acids, and many others are reactive. Also, some chemical classes, like the purines, the pyrimidines (classes of components of DNA), and many others are essential to life. Several of the DNA "building block" classes are used to make important drugs. For example, derivatives of guanine (a purine) are used as anti-cancer drugs.

A. Alkanes

N- BUTANE *ISO(I)* BUTANE

The alkanes are hydrocarbons (i.e., only C and H atoms in the molecule), with the general formula C_nH_{2n+2}. They represent the largest practical source of manufactured energy.

$CH_3CH_2CH_2CH_3$, $(CH_3)_2CH_2CH_3$

The first member in the series is methane (structural formula, CH_4), the most abundant component of natural gas. The C - hybridization is sp^3. Hence all the alkane molecules have tetrahedral geometry. The next member is ethane. [Its *molecular* formula is C_2H_6; its *condensed* formula is CH_3-CH_3.]

After propane the series continues, but does so by allowing for branching structures (with branching at various levels). Butane, for example, exists as normal (n) butane, straight chain C_4H_{10}, and as isobutane $(CH_3)_2CH_2CH_3$. The two isomers have different physical properties. [Note. There is no isopropane, but the isopropyl radical exists.]

Note. Re: Alkane carbon numbering, and 'forms'.

The alkanes (explained later) underpin the naming of many common compounds. For the substituted alkanes (and the alkenes and alkynes), the rule for carbon atom numbering is: "The correct end to start the 'counting' is the one which gives the lowest sum from adding the numbers used to signify the substituted carbon atoms." Also, different forms exist with slightly different energy content: fully eclipsed, and fully staggered forms, in the extremes. The alkanes are generally chemically unreactive, except for combustion and room temperature halogenation under ultraviolet radiation (e.g., methane can be so chlorinated, to yield a mixture of partially and fully chlorinated products; also, propane is similarly chlorinated to n-propyl chloride and isopropyl chloride).

Some common alkyl groups are given below. IUPAC nomenclature rules apply.

PARENT ALKANE	ALKYL GROUP	FORMULA/STRUCTURE	REMARK
Methane	Methyl	CH_3- (Radical)	
Propane	*n*-propyl	$CH_3-CH_2-CH_2-$ "	"*n*" stands for "normal."
Propane	*iso*propyl	$(CH_3)_2CH-$ "	There is no isopropane, but the isopropyl radical exists.
n-butane	*n*-butyl	$CH_3-CH_2-CH_2-CH_2-$ "	
*iso*butane	*iso*butyl	$CH_3-CH(CH_3)-CH_2-$ "	
*n*butane	*sec*-butyl	$CH_3-CH(H)-CH(H)-CH_2-$ "	*Sec* is bbreviated to "*s*". The source is *n*butane.
*iso*butane	*Tert*-butyl	$(CH_3)_2C(H)CH_2-$ "	*Tert* may be abbreviated to "*t*". Note, *iso*butane, but *tert*butyl terminology.
*iso*pentane	*iso*pentyl (also called *iso*amyl)	$(CH_3)_2C-CH_2-CH_2$ "	
neopentane	neopentyl	$CH_3-C(CH_3)_2-CH_2-$ "	

B. Alkenes

The alkenes have the general formula C_nH_{2n}. For example, ethylene (correctly named 'ethene'; C_2H_2), and propylene ('propene'; C_3H_6) are unsaturated, substances of this general formal. They each have a double bond. They are very reactive and undergo numerous addition reactions.

BUTADIENE (a monomer with two = bonds, used in making rubbery polymers: ("DI" = two)

$CH_2=C(H)C(H)=CH_2$ (BUTADIENE)

C. Alkynes

The general alkyne formula is C_nH_{n-2}. The alkynes are very reactive and are strongly exothermic in burning, cf. acetylene metal cutting. They undergo innumerable addition reactions to their (characteristic) C to C triple bond(s).

ACETYLENE (note the triple C to C bond)

HC ≡ CH (triple bond between carbons)

D. Alcohols

Alcohols are aliphatic carbon compounds with one, two (diol), or three or more (polyol) -OH radicals directly attached to a carbon atom belonging to the parent molecular "skeleton." They may behave as a feeble acid in some circumstances. The higher molecular weight alcohols exist as isomers, e.g., primary and secondary alcohols (see the sketch). Primary alcohols upon appropriate oxidation yield aldehydes. Secondary alcohols similarly yield ketones. Also, alcohols with carboxylic acids yield esters, via *condensation*: the elimination of the elements of water: OH- from the alcohol, and H+ from the respective acid. [See 'esters']. *Intra molecular* hydrogen bonding occurs with some alcohols (as evidenced in infrared spectroscopy). Some alcohols are toxic. Methyl alcohol can cause blindness and glycol can cause kidney failure.

TYPICAL PRIMARY AND SECONDARY ALCOHOLS

PRIMARY	SECONDARY
CH_3CH_2OH	$C_6H_5\text{-}CH_2C^*(H)(OH)CH_3$
Ethanol	(Note the chiral center *) 1 phenyl-2-propanol

ALCOHOL - ORGANIC ACID REACTION (with elimination of water)

$CH_3CH_2OH + C_6H5COOH$ (BENZOIC ACID)

$\Rightarrow C_6H5COO\,CH_3CH_2 + H_2O$

E. Ketones

Ketones are reactive substances with a common >C=O constituent. Attached to the respective carbon (shown) can be simple, complex, alkyl, amyl, etc. The lower molecular weight ketones have a sharp odor and are highly flammable. They are used largely in industry as solvents.

KETONES

$CH_3C(O)C_2H_5$	$CH_3C(O)C_6H_5$
Methylethylketone	methyl phenylketone

F. Aldehydes

Aldehydes have as the functional group -C(H)=O. The group attached to the highly reactive functional carbon atom can be simple, complex, alkyl, aryl, etc. Formaldehyde is the simplest aldehyde. It is used in manufacturing urea formaldehyde and other resins, and as a bactericide (as paraformaldehyde, a cyclic trimer of formaldehyde).

ALDEHYDES

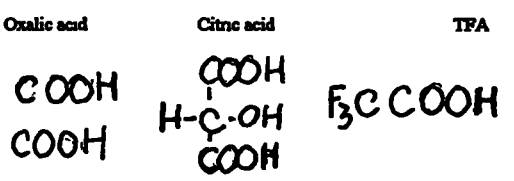
HC-C(H)O [Formaldehyde monomer]

C_6H_5CHO [Benzaldehyde]

G. Carboxylic acids

Carboxylic acids have the empirical formula R-COOH, where R can be one of a number of different structures, chains, and (aromatic or nonaromatic) rings. Many are present naturally in foodstuffs (vitamin A) and plants (oxalic acid). In most cases, these acids are weak acids, that is, they are not fully dissociated (pH ~ 5).

COMMON CARBOXYLIC ACIDS
& TRIFLUORACETIC (TFA) ACID



The higher (>C5) molecular acids are lowly water soluble. Halogen substituted, carboxylic acid is a strong acid; that is, it is virtually fully dissociated: -COOH → -C(O)O$^-$ + H$^+$. Trifluoroacetic acid, CF_3COOH, is the primary example. The proximate F atoms draw electrons away from the -OH part of the carboxylic acid group, and causes extensive ionization. The low molecular weight carboxylic acids pose no problem for compound naming, however, this is no the case when large molecules are involved, even though *some* such molecules (see the example shown opposite) have generally well-recognized trivial names. To remedy the naming problem for large molecules, rules have been set by IUPAC (International Union of Pure and Applied Chemistry).

FORMULA	COMMON NAME (ACID)	IUPAC NAME (ACID) ·
$CH_3(CH_2)_2$ COOH	BUTYRIC	BUTANOIC
CH_3 $(CH_2)_8$COOH	CAPRIC (NON-DESCRIPTIVE)	DECANOIC
$CH_3(CH_2)_{10}$COOH	LAURIC (NON-DESCRIPTIVE)	DODECANOIC
$CH_3(CH_2)_{16}$COOH	STERIC (NON-DESCRIPTIVE)	OCTADECANOIC

Note. The APACE ruling for naming carboxylic acids are:

1. Reference the total number of carbons is first referenced, e.g., butyric acid has four carbons.
2. Reference the carboxylic carbon as "C1" and continue to number the carbons in the direct chain.
3. Drop the 'e' from the parent alkane name and add 'ioc.' Thus, butane goes to 'butanoic.'
4. Name the parent and the remaining substituents. Thus CH_3-CH_2-C(O)OH is 'propanoic acid.'

Carboxylic acids yield innumerable derivatives, including anhydrides, acid chlorides, amides, and esters. Several carboxylic acid derivatives are shown opposite.

CARBOXYLIC ACID DERIVATIVES

(a) $2\ CH_3COOH \xrightarrow[(-H_2O)]{Ht + H^+} CH_3C(O)\text{-}O\text{-}C(O)CH_3$ (acetic anhydride)

(b) $CH_3COOH + NH_3 \longrightarrow CH_3CONH_2$ (mouse smell) (acetamide)

(AND MANY OTHERS)

(H). Esters

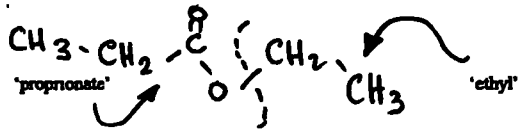
An ester is the product of the chemical union of an organic acid and an alcohol, via a condensation reaction involving the elimination of the elements of water. For example, CH_3COOH (acetic acid) + CH_3OH (methyl alcohol) ⇒ CH_3COOCH_3 (methyl acetate) + H_2O. Most esters have pleasant odors (e.g.. Ethyl propionate has a rum-like odor). Some can be detected in air at a few parts per billion, ppb (e.g., ethyl butyrate, odor threshold: one part per billion). Most esters have odor threshold values of less than a few thousand parts per billion. The odor threshold for ethyl formate is relatively high (150,000 ppb). Also, some esters have an oily or fatty odor, e.g., the esters of the fatty acids, like palmitic acid and myristic acid.

—

. Note. The IUPAC naming rules for esters are:

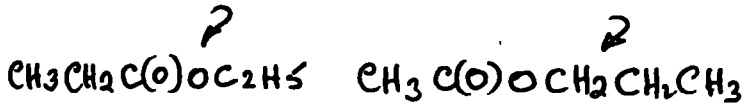
1. Name the 'R' group in the generic form -C(O) OR, as a side chain.
2. Name the acid portion (for example, $CH_3(CH_2)C(O)O$) by carbon number value, end with 'oate.'

ETHYL PROPIONATE



The ester formed from ethanol and propionic acid is named 'ethylpropionate,' while the ester formed from propyl alcohol and acetic acid is IUPAC-named 'propylethanolate.'

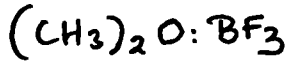
ETHYLPROPIONATE & PROPYLETHANOLATE



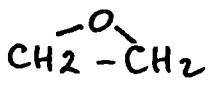
(I). Ethers

The ethers have the characteristic functional group >C=O, which is notably reactive in adduct formation. Ethers have some degree of hydrogen bonding (this accounts for the significant solubility of diethyl ether in water. The simplest ether is methyl ether: CH_3-O-CH_3. The two lone electron pair on the ether oxygen atom makes the functional group reactive in forming chemical adducts (e.g., the 1:1 ether-boron trifluoride coordination complex). Also, cleavage of the C-O bond can be affected by aqueous HI, via initial protonation of the ether oxygen atom. Moreover, ethers can be peroxidized easily (to form explosive peroxides). They are also highly flammable. For example, the flash point of dimethyl ether is minus -49 °C, well below that of 100% octane gasoline (-38 °C). Otherwise, the ethers in general are chemically unreactive. [A notable exception is the "epoxide' form. An epoxide may be also considered as a functional group in its own right. It is a three-member ring with a molecularly strained configuration. Epoxides are highly reactive with alkyl halides and other compounds, with consequent ring opening of the epoxide and *addition reaction* type products.]

ETHER-BORON TRIFLUORIDE COMPLEX



ETHYLENE OXIDE



Ethylene oxide is a widely used sterilant (gas) which attacks -NH groups in amino acids / proteins in microorganisms

Many other chemical classes exist.

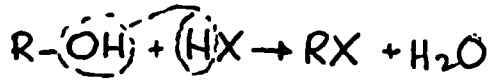
(15). **Some common functional groups.**

Functional (reactive) groups are entities which exist either inside or outside of the carbon-rich main structure of the ring or chain compound. The "class —functional group" distinction is arbitrary, but it is sensible for the purpose of looking at the derivatives formed by reaction of the functional group with other groups or classes of compounds.

Note. **A test for a functional group within the carbon skeleton of the molecule is the ability to continuously trace the respective carbon atoms in the drawing of the entire molecule.**

A. **The alcoholic OH.** Characteristically, the -OH behaves as a complete radical. Thus with HI (or HCl) the -OH of an alcohol, upon reaction (via a Sn1 or a Sn2 mechanism), leaves the alcohol, to be replaced by -I (iodide) or -Cl (chloride), to yield an "acid halide."

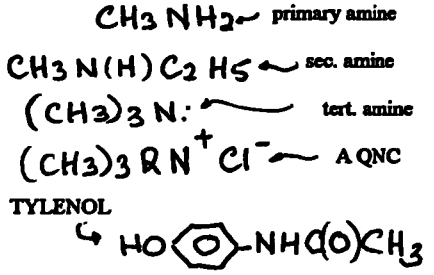
-OH BEHAVING AS A COMPLETE RADICAL



B. **The phenolic OH.** Characteristically, the Phenyl-OH dissociates and the compounds are acidic. Phenol destroys skin. It is strongly acidic because the phenolate, C_6H_5O-, ion is resonance stabilized.

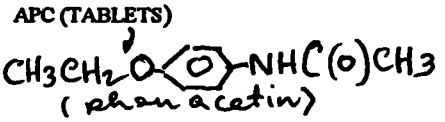
C. **The amino group, nitrosoamines, and amides.** These three classes can be grouped together. They are environmentally and/or chemically or biologically closely linked. Amines exist as three "kinds": **primary** amines (RNH_2); **secondary** amines (RRNH); **tertiary** amines (RRRN). All three kinds of amines are basic and form salts, e.g., RNH_2.HCl. Many foodstuffs and plants contain amines, some of which are very toxic. In the case of a tertiary amine, a "*quaternary ammonium* (or an 'analog,' e.g., 'pyridinium') *halide* ('X') can be formed: R,R,R,RN^+X^- (a *cationic* compound. The R's can be similar, different, aliphatic, or aromatic radicals). An amine can be *heterocyclic*, e.g., a ring structure with one or more nitrogen atoms.

AMINE TYPES AND QUATERNARY NITROGEN COMPOUND (QNC)



TYLENOL

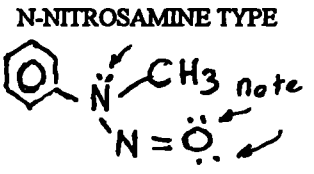
APC (TABLETS)



D. The nomenclature of amines is straightforward and similar to that of the carboxylic acids. For example, the '-oic' term in the acid is dropped and replaced by 'amine.' Many amines are of great medical significance. Tylenol and A.C. tablets are amines, as are CNS stimulants (amphetamines etc.) and depressants (e.g., the sleep aid barbital).

Nitrosamines are products of nitrous acid and amines. N-nitrosamines (see the sketch) are environmentally important (carcinogens).

N-NITROSAMINE TYPE



Note. In the environment (soil), but also in the human body, nitrates are reduced, by nitrate-reducing Enterobacteriaceae-type bacteria and other microbes, to nitrites. Also, nitrates and nitrites exist in foods and plants, as preservatives, but also naturally. Nitrites in the body react with amines in acidic media to form N-nitrosamines. Amines may arise from external sources and/or from ingested meats, meat pies, fish, etc. Reportedly, amines, nitrosoamines, and various stomach-residing microbes may be present at elevated quantities in individuals with reduced stomach acid production (e.g., gastroenterostomy patients).

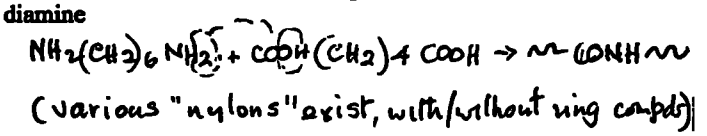
Amides result from the condensation of amines with organic acids, with elimination of water. They have the characteristic '-CONH-' group. Their nomenclature is simple and similar to that of carboxylic acid (drop the -ioc, add "amide").

AMINE-ACID REACTION, TO FORM AN AMIDE

Amides are used in manufacturing *'high polymer'* substances. Nylon (a polyamide high polymer) can be made by reacting a *polyamide* (hexamethylene diamine) with a *dicarboxylic acid* (adipic acid).

'NYLON' CHEMISTRY

hexamethylene diamine — adipic acid



Amides are the building blocks of proteins, which have peptide (amide) internal "links."

Numerous other functional groups are fairly common. For example, **peroxy** (-O-O); **vinyl** (-C(H)=CH_2); **mercapto** (thio, -S-H); **imino** (>C=N-H); **allyl** (-$C(H)_2$-C(H)=CH_2).

Each functional group has a characteristic chemistry which may be modified by the group to which it is attached.

E. Classes of (1) solvents, and (2) main reactions

(1). Classes of solvents.

The class of a solvent has a profound effect on a reaction type and reaction mechanism. The outcomes of reactants undergoing elimination, substitution, addition or rearrangement reactions (see page 27), in terms of *the product(s)'* chemical and physical properties, depend in large part on whether or not the solvent involved is (I) ***photic***, and, separately (ii) ***polar***. A **'protic'** compound is one which can donate a cation (i.e., H+) to a substrate. An **'aprotic'** compound cannot donate a cation to a substrate. **Polarity** refers to significant electro-negativity difference between the component elements of the compound (solvent). A list of some common *aprotic* and *protic* substances, expressed in terms of (rounded) P value follows.

APROTIC SOLVENT	DIELECTRIC POLARIZATION (P)	PROTIC SOLVENT	DIELECTRIC POLARIZATION (P)
HEXANE	1.9	ACETIC ACID	6.2
BENZENE	2.3	ETHANOL	24.3
DIETHYL ETHER	4.3	METHANOL	33.6
CHLOROFORM	4 8	FORMIC ACID	58
DIMETHYL FORMAMIDE (DMF)	38	WATER	80.4

Solvent polarity is measured as in terms of **dielectric polarization, P**. A non-polar solvent, like hexane, has a low P value; whereas a polar solvent, like water, has a high P value.

Solvents with high P values stabilize intermediate entities (e.g., an intermediate cation), which arise in a (Sn1) reaction. Conversely, a low P solvent favors an Sn2 substitution reaction, via solvation of a low energy state nucleophile, and consequential inversion of a molecular configuration (explained later).

In short, the reaction mechanism, the nature of the dominant product, and the respective rate of reaction depend on the solvent system, but other factors (e.g., molecular volume and bond strength) exist. Also, reactions are not necessarily exclusive; substitution and elimination reactions (see below) occur together, in reactions with alkyl halides and other substances.

(2). Chemical reactions.

Organic chemical reactions are broadly classified in **four classes**, some of which have more than one related underlying mechanism—which produce different products. Also, some reactions of one or more groups may occur simultaneously, but not generally at the same rate of reaction.

The four classes of chemical reaction are: ***Elimination*** (with **E1** and **E2** mechanisms). ***Substitution*** (with **Sn1** and **Sn2** mechanisms, which result in *different* reaction products). ***Addition*** (across a double/triple bond). ***Rearrangement*** (typically via a proton shift mechanism).

ELIMINATION (may occur via E1 & E2 mechanisms) $CH_3CH_2Br \Rightarrow CH_2{=}CH_2$	**SUBSTITUTION (may occur via Sn1 and/or Sn2 mechanism)** $CH_3Br + OH^- \Rightarrow CH_3OH + HBr$ **NOTE. AS A Sn2 REACTION (BIMOLECULAR), THE RATE OF REACTION IS = k[OH][CH_3Br]**
ADDITION $CH_2{=}CH_2 + HBr \Rightarrow CH_3CH_2Br$	**REARRANGEMENT (proton shift)** $(CH_3)_2C(OH)C(OH)(CH_3)_2$ **(Pinacol, an *enol*).** $\Rightarrow (CH_3)_3C(=O)CH_3$ **(Pinacolone, a *keto*).**

ELIMINATION REACTIONS (E1 AND E2 MECHANISMS)

Generally, with an alkyl halide the "central" carbon atom of the polarized molecule is electrophilic, and the halide component is nucleophilic, and therefore can be 'removed' by a Na+ ion. The organic halide, upon the elimination of the elements of hydrogen halide (e.g., HX, where X = Cl, Br), by reaction with a strong alkali, forms an unsaturated (double bond) compound, known as an alkene. The actual elimination process and the corresponding product(s) depend on the starting materials and the reaction mechanism involved.

In regard to *elimination* mechanisms, the mechanism can either involve the generation of one of two intermediates:

- **A charged ion.** This moiety is a 'carbanion.' It is stabilized by the water molecules which surround it.

  This particular elimination mechanism is referred to as the E1 PROCESS.

  Note. The E1 mechanism does not occur with primary halides, i.e., with RCH_2X. However, the E1 mechanism can occur with secondary and tertiary halides, and with *benzylic* or *allylic* structures.

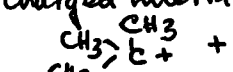
- **A transitional compound.** This moiety results from an incoming group or radical and an outgoing group or radical transitorily being loosely attached to a core structure. With an organic halide undergoing this kind of process, the net result is a transfer-in of a group from a reactant, and the simultaneous departure of the halide radical out from the transitional compound.

  This particular elimination mechanism is referred to as the E2 PROCESS.

E1 and E2 MECHANISMS

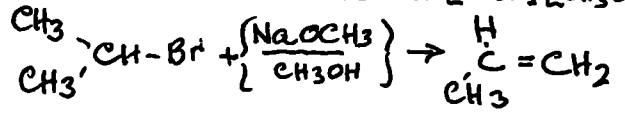
E1 MECHANISM (with secondary halides)

charged intermediate formed $(CH_3)_3I \rightarrow$



E2 MECHANISM (bimolecular reaction)

Rate = $K[R\text{-}Br][CH_3O^-]$



The E2 mechanism is strongly favored when a strong alkaline solution acts on a secondary (R_2CHX) or a tertiary (R_3CX) halide. Also, it is stereo specific.

In summary, for *elimination* processes:

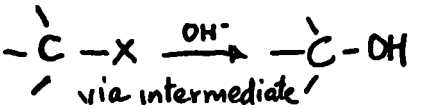
- Stereo chemistry differences arise with the two elimination processes involving organic halides.
- The E1 mechanism does not require a strong base.
- The E1 mechanism is not stereo specific (i.e., a chiral center configuration is not changed).
- The E1 mechanism may occur simultaneously with a Sn1 substitution reaction.
- The E2 mechanism only occurs when a strong base is present, also, it is stereo specific.

Note. **A double bond forms with HX elimination from alkyl halides (and other organic classes).** The anticipated bond location is determined by empirical rules. These rules were based initially on early experimental observations and now on theoretical *change- in-free-energy* considerations relating to the reactants, the products, and the intermediate entities or energy transition states which may occur in the processes. In general, the elimination of HX from an alkyl halide follows Zaittsev's rule: *the product (an alkene) which predominates is the more highly substituted alkene of the alternatives.* In the elimination of HX from 2-bromobutane, two products (2-butene and 1-butene) are formed, but the 2-butene form predominates. This is the more substituted "ene" form. Thus: $CH_3CH_2CH(Br)CH_3$ with sodium in alcohol forms: 80% $CH_3CH{=}CHCH_3$ (2-butene) and 20% $CH_3CH_2CH{=}CH_2$ (1-butene).

SUBSTITUTION REACTIONS AND ALKYL HALIDES: SN1 AND SN2 REACTIONS

Note the "code" used to describe (nucleophilic) substitution mechanisms:
S = substitution.
n = nucleophile (the entity which replaces the halide).
'1' or '2' = the respective 'molecularity' of the reaction. That is, '1' and '2' refer to the number of 'concentration' factors involved in the applicable rate law. [Substituents in an aromatic ring can affect the rate of a subsequent substitution-reaction].

Sn1 SUBSTITUTION MECHANISM
[No inversion at the chiral center].

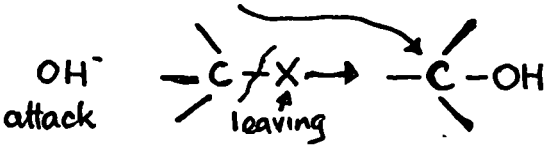


The Sn1 substitution, with alkyl halides, occurs in two steps and results in molecular inversion. The first step is *dissociation* (ionization) of the molecule. This results in the formation of a cationic intermediate, known as a *carbocation.* The carbanion is stabilized by hydrogen bonding with surrounding water molecules. *Carbonation* formation is the rate-limiting step in the process. Immediately upon formation, this intermediate reacts (a fast step) with the nucleophile (in this case OH-) to form an alcohol.

The Sn1 reaction does not result in a molecular inversion (i.e., a change of chiral center configuration and optical rotation reversal). Its mechanism involves the formation of a transient *intermediate* compound. This intermediate consists of the two simultaneous incoming and the outgoing groups, both of which are transitorily, partially bonded to the chemical nucleus.

The Sn2 reaction is most strongly favored by relatively non polar, aprotic solvent conditions. It involves molecular inversion, as may be demonstrated by reversal of plane polarized light rotation. The Sn2 reaction is a bimolecular reaction. [A Walden inversion which can be likened to an umbrella blowing inside out]. Molecular "bulkiness" can cause steric hindrance to a Sn2 mechanism. The Sn2 process rate of reaction depends both on the concentration of the substrate and on the concentration of the attacking nucleophile.

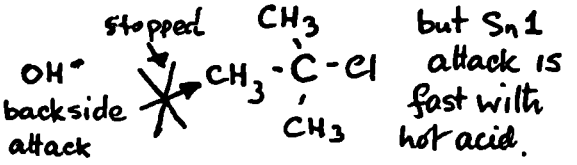
Sn2 MECHANISM
[Walden inversion at the chiral center].



Note. HYDROLYSIS OF A CHEMICAL & STERIC HINDRANCE.

Hydrolysis refers to the elements of water entering a molecule which generally results in a 'split' and the formation of two different molecules. It is visually at least the reverse of a condensation reaction. As an example, ethyl acetate (an ester), in a strong sodium hydroxide solution, 'splits' into ethyl alcohol and acetic acid (as sodium acetate). [The respective mechanism and the direction of attack by the OH radical are shown in the sketch]. This particular reaction is not inhibited by the (minimal) molecular volume of the methyl radical in the ester. The hydrolysis of an ester with an attached highly branched alkyl radical is different, and hydrolysis by sodium hydroxide tends to be slow. This is because in the Sn2 case, a 'backside -OH attack' occurs on the central carbon atom, with a subsequent Walden inversion, but this is hindered (obstructed) by an extensively branched structure around the central carbon atom in the ester. When (Sn2) steric hindrance occurs, hydrochloric acid-hydrolysis can be faster than alkaline hydrolysis.

STERIC HINDRANCE (of Sn2 hydrolysis)



ADDITION REACTION (ACROSS A DOUBLE BOND. ADDITION TO AN ALKENE)

This type of reaction is basically the opposite of the elimination type of reactions involving alkanes, it is mostly exothermic (i.e., a negative heat of reaction). It involves a change in carbon hybridization state (sp^2 to sp^3), breakage of the = bonds (comparatively less energy in this bond compared to the sum of the products energy content), and formation of two single bonds (H-C and halide to carbon, with comparatively more net energy in these bonds). For example, >C=C< + H-Br → CH_3-CH_2Br. The actual locations of the entities adding on (known as **regioselectivity**), in the case of an unsymmetrical alkene, is such that a preponderance of one possible product over another occurs. The situation is governed by rules, including the Markovnikov Rule (with a strong acid, HX, the acidic H+ adds to the carbon of the double bond that already has the greater number of H atoms), but exceptions exist. An example of the Markovnikov rule in action is the addition of HCl to 2-methyl-2 butene:

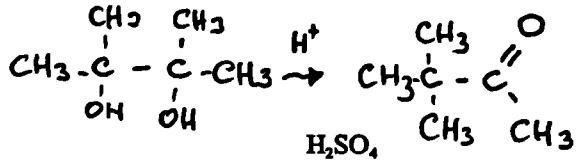
$(CH_3)_2C{=}CHCH_3 + HCl \rightarrow (CH_3)_2CH\text{-}CHClCH_3$ (But **not** $CH_3CH_2CH_2CH_2Cl$).
2-methyl-2-butene 2-chloro-3-methylbutane 2-chloro-2-methylbutane

Further discussion of *addition* reactions is beyond the scope of this presentation, except to say that the Markovnikoff rule was formulated before the reaction mechanistics and molecular complexes, which involve carbocation formation and pi bonding in a complex, were known. Also, an antimarkovnikoff product may ensue from an addition reaction. That is, in the type of example given, the X- (halide) goes to the most saturated of the two carbon atoms involved in the C=C bond.

REARRANGEMENTS

There are literally hundreds of rearrangement reactions and a comparable number of respective commercial chemical processes. Basically, this type of reaction involves a structural rearrangement, such as a shift of a methyl group or a hydrogen atom from one carbon atom in the affected molecule to a neighboring carbon atom. Various factors, such as molecular strain and enhanced stability of a carbocation intermediate involved, affect the outcome. Also, a saturated and unsaturated nucleophiles, and saturated and unsaturated electrophiles take part in such rearrangements.

THE PINACOL REARRANGEMENT



$(CH_3)_2C(OH)C(OH)(CH_3)_2 \xrightarrow{H_2SO_4} CH_3)_3C(=O)CH_3$
(an 'enol') (a'keto')

Many named reactions involving molecular rearrangements exist, and many of these are a variation on a mechanistic theme (such as when a Grinyard reagent is involved in the reaction). Some well-known, nucleophilic rearrangements include the *Neopenyl halide* rearrangement, the *Beckman* rearrangement,' and the *Curtius-Schmidt* rearrangement —all of which are described in standard texts. A rearrangement example is the "enol-keto" pinacol rearrangement. Acetone, $(CH_3)_2C{=}O$, on reacting with sodium in ethyl alcohol, is converted to pinacol $(CH_3)_2C(OH)C(OH)(CH_3)_2$ (an *enol*). Subsequent treatment of pinacol (which can be isolated) with concentrated sulphuric acid results in a molecular shift (a rearrangement), resulting in an additional methyl group on the end carbon (see the sketch). The product is pinacolone (a *keto*). This mechanism is well understood. It may be described as an intermediate sequence of protonation of the -OH radical, loss of the elements of water (one molecule), alkyl group migration, and de-protonation.

C. Special interest compounds and other matters.

Compounds of historical and recent interest to environmental protection professionals include peroxyacyl nitrates; halogenated organic compounds (solvents and refrigerants, pesticides, and plasticizers for commercially important thermoplastic *high polymers* and thermoset polymers); and organo-phosphorus compounds (cholinesterase-inhibiting pesticides and chemical warfare agents). Some of these are briefly commented on below. Also, some of the (halogenated) compounds are collectively discussed because they are (a) individually well documented in EPA technical publications, (b) environmentally persistent, (c) pose significant potential human health and environment risks, and/or (d) dioxin-like in toxicity to one degree or another. In short, they pose potential risks of cancer, immunotoxicity, reproduction interference, and other problems.

(1). **Peroxyacyl nitrates, PAN's.** PAN's are formed by the action of UV light on an air-pollution mixture of nitrogen oxides and petroleum vapors. They are classified as 'oxidant' together with ozone.

(2). **Short-chain halogenated hydrocarbons.** Industrial/commercial cleaning solvents are of a particular concern re: pollution of aquifers and wells.

SOME OLDER INDUSTRIAL CHLORINATED CLEANING SOLVENTS OF MAJOR CONCERN

carbon tetrachloride CCl_4 $CHCl_3$ trichloromethane

(3). **Freons.** The freons are a class of chlorine and/or flourine substituted alkanes (methane,ethane and propane). "Freon" refers to dichloro-difluoromethane (designated trade name R-12). It is destructive of the ozone layer (which protects earth against harmful UV light) R-12 has been largely replaced as a refrigerant by 1,1,1,2 tetrafluoroethane (R-135a), which unlike "freon" (R-12) is a hydrofluorocarbon (i.e., a class which contains hydrogen as well as one or more halogens).

SOME FREONS.

TRICHLOROFLUORMETHANE (R-11)
DICHLORDIFLUOROMETHANE (R-12)
CHLORODIFLUOROMETHANE (R-22)
1,2-DICHLORO-1,1,2,2-TETRAFLUOROMETHANE (R-114)
1,1,1,2,3,3,3-HEPTAFLUOROPROPANE (R-115)

(4). **Cholinesterase-inhibiting compounds, organo-phosphorus chemicals and carbamates.**

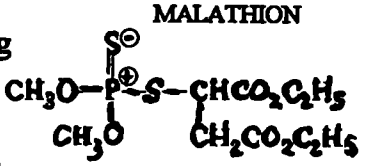
The neuromuscular junction in humans and other species utilizes *acetycholine*, $(CH_3)_3(CH_2)_2$-O-C(O)-CH_3, as a neurotransmitter. Acetylcholine, to function properly, must operate in a very rapid on-off hydrolytic mode, which is moderated by the enzyme *cholinesterase*. Certain organo-phosphurus compounds (and carbamate compounds, e.g., Sevin) very effectively block the action of cholinesterase. This blocking action is the toxic mechanism of certain pesticides (e.g., malathion, an 'op compound' and sevin, a 'carbamate') and chemical warfare agents (e.g., Sarin, an 'op compound'). Their respective structures are shown opposite. Their indivual effectiveness is "tailored" around molecular volumetric shape, and binding strength to Cholinesterase receptor(s) on the muscle cell membrane in the neuromuscular junction.

(a). **Organo-phosphorus compounds** used as pesticides include Malathion. Those used as warfare agents include Sarin.

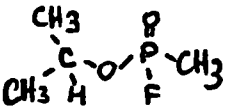
(b). **Carbamates** are widely used acetylcholionestase-inhibiting pesticides.

(5). **Polychlorinated benzenes. PCB's. Aldrin and Dieldrin. Dioxins. Halogenated furans - dioxin analogs. Polybrominated diphenyls. Polybrominated diphenyl oxides.**

MALATHION



SARIN

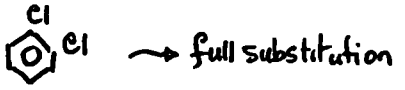


CARBARYL (Sevin®)

These compounds can be considered collectively for toxicity-genotoxicity risk discussion purposes. They are a diverse group of halogenated compounds with some chemical and physical properties in common. From a health risk-environmental risk perspective they are very similar. They are persistent, bio-accumulative, acutely and chronically toxic, and able to one degree or another to invoke adverse gene expressions which may affect tumor promotion, immunotoxicity, and hormonal imbalances.

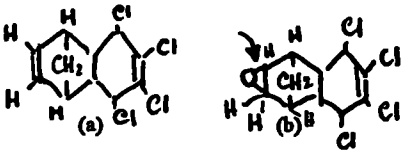
STRUCTURES OF SOME REFERENCED CLASSES

POLYCHLORINATED BENZENES.

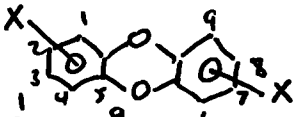


PCB'S.

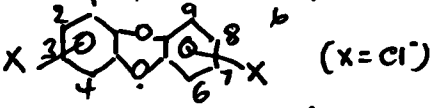
ALDRIN (a) AND (b) DIELDRIN epoxide



HALOGENATED DIOXINS (generic structure)



HALOGENATED FURANS (generic)



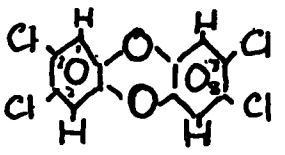
POLYBROMINATED DIPHENYLS. (generic)

DIOXIN is a general term for a family of highly environmentally persistent, chlorinated di-aromatic hydrocarbons which are unwanted byproducts of certain manufacturing processes and waste treatment operations. Many hundreds of congeners of various "dioxins" exist. Of this large number, currently only seventeen molecular 'dioxin' versions have a special environmental significance. These seventeen 'dioxins' comprise:

- **Seven compounds PolyChlorinated diBenzo-p-Dioxin. [PCDD's; *true dioxin structures*].**
- **Ten compounds PolyChlorinated diBenzoFuranes. [PCDF's; *dibenzofuranes*].**

Of these seventeen moieties (hereafter referred to as dioxins) the (true) dioxin **TCDD** (2,3,7,8-tetrachlorodibenzo-p-dioxin) has the highest toxicity rating. The toxicity rating of the 'dioxins' extends over four orders of magnitude. An equivalent ranking system must therefore be used, and it is termed the 'TCDD equivalence quantity' (TEQ).

TCDD

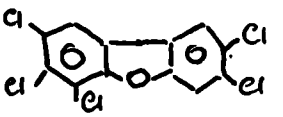


DIOXIN-LIKE SUBSTANCE	TEN	REMARKS
Todd. [2,3,7,8, tetrachlorodibezo-p-dioxin]	1	The TEQ reference substance (=1)
2,3,4,7,8 pentachlorodibenzofurane (PeCDF)	0.5	Five chlorine atoms/furane ring
1,2,3, 6,7,8 hexachlorodibenzodioxin. (HxCDD) 1,2,3, 7,8,9 hexachlorodibenzodioxin. (HeCDD)	0.1	The extra chlorine atoms/dioxin ring does not cause a greater TEQ than TCDD. Note the difference re: Cl placement on the rings. Most of the 17 key 'dioxins' have this TEQ value.
1,2,3,7,8,9 heptchoro-dibenxofurane and 1,2,3, 6,7,8 hexa chloro-dibenxofurane (HpCBF).	0.01	Several other key dioxin-like compounds have this TEQ value.
Octachlorodibenzofurane	0.0001	The 'dioxin' with the least TEQ value.

In summary and in context with the preceding:

- Cancer risk is not the sole factor in the experts' assignments of TEQ's. Others factors include chronic exposure and adverse health effects (immunotoxicity, hormonal imbalance).
- Dioxin-contaminated food intake, rather than breathing contaminated air, is the primary source of risk.
- The linkages between chronic exposure and immunotoxicity and less symptom-specific effects (hormonal imbalances, etc.) are not completely settled. However, in one instance at least a good correlation has been reliably reported on a regional basis (e.g., Baltic Sea Coast populations) between breast cancer and low birth-weight, and dioxin-contamination in regional fish-catches.
- The seventeen key 'dioxins' are not equally present in the environment or in foods (meat, fish, etc.).
- The greatest source of uptake for humans is food, and milk contamination is the biggest concern for babies. Dioxins are found in trace, but measurable quantities in human milk, various human foods and animal feedstock.
- The most common dioxin present in Baltic Sea herring, reportedly, is **(PCDF)**: 2,3,4,7,8-pentachlorodibenzofurane (TEQ = 0.5).

2,3,4,7,8-PENTACHLORODIBENZOFURANE



At this juncture, further discussion on dioxin-like compounds is outside the scope of this presentation, other than to remark that:

- TCDD is a designated (Class 1, human) cancer agent. It is a component of Agent Orange.
- TCDD and other dioxins are formed when chlorine-containing waste chemicals are incinerated under less than optimal conditions.

- Other reported major dioxin sources are wastes from: chlorine bleaching processes used in papermaking; commercial manufacturing operations which use chlorinated chemicals; and pesticide manufacturing.

- Automobile emissions are a major source of dioxin.

- Some current sources provide products which society in general now considers essential.

- Human dioxin exposures arise mostly from the intake of beef and other meats, fish, and milk and dairy products. These sources may contain up to a few parts per billion dioxin. Also, the dominant human source is often region-dependant.

- The safety consensus of the regulators appears to be that there is no known safe dioxin exposure level vis-a-vis cancer risk. However, a "tolerable daily uptake" limit is practicable. [Currently this kind of limit is used by the U.S. EPA and by the European Union (E.C.). However, there is a 'two order of magnitude' difference between the respective values. The U.S. EPA has the more stringent limit.]

- In the United States, reportedly, the human dioxin burden has decreased over the last twenty years. This is seen as a direct benefit of the bans and regulations of the U.S. EPA. [Reduced risks have also been claimed by the E.U.] Nevertheless, chronic exposures continue to be national and international concerns. [Reportedly, current, chronic dioxin uptakes, in the U.S. and the E.U. populations, are approximated to be several picograms per kilogram of body weight (one picogram = 10^{-12} gram).]

- Some dioxin-like chemicals are still used making flame resistant plastic cases, etc. for electrical equipment.

- As of 2001, many if not most of the dioxin-like substances are banned internationally, under the United Nations Environmental Programme. The banned substances include: pesticides (e.g., aldrin, dieldrin chlordane, DDT, hexachlorobenzene, toxaphene); (e.g., polychlorinated biphenyls); and manufacturing byproducts (e.g., PCDD's and PCDF's).

- No way is known to effectively reduce dioxin body burden and no antidotes are known. Diet control is the key to avoiding dioxin uptake.

- Reportedly, infants generally have the highest risk of chronic exposure to dioxin compounds.

- Numerous congeners exist of the brominated diphenyl type flame retardants. These congeners exhibit significant specific toxicity differences. Scientific information exists and is also emerging which make almost all of these kinds of substances at least very suspect in regard to potential genetic damage. At this time, proposals (and laws in some European countries) exist to ban the future use of some of the lower degree of halogenation-types, and to hold in abeyance decisions on the continuing use of the higher (i.e., "deca") halogenated substances.

- Certain substances may remain in use for a long time and are likely to be the subject of future arguments re: 'continued use with evident fire safety benefits' versus 'involuntary serious health risks.'

SOME POINTS ON ENVIRONMENTAL SAMPLING AND ANALYSIS

Note. *Field and laboratory workers are involved from time to time in collecting toxic materials and having them analyzed. Some general comments on the sampling and analysis of workplace and environmental contaminants, or chemicals or materials which may be involved in some way in chemical accidents, are offered here.*

- Almost all of the high precision analytical methodologies require (a) the use of particular sampling procedures and collection media, including collection filter material, and (b) operator skill.

- Before an evaluation of workplace/environmental contamination which will involve laboratory analysis is undertaken, in fact, at the evaluation planning stage, the involved laboratory staff needs to be consulted. The purpose for this is to determine (a) the correct sampling protocol and equipment to be used, (b) interferences and /or limitations which apply, and (c) other pertinent facts.

- Gas detector pump and an appropriate detector tubes. Various types are commercially available. Using this methodology, workplace gaseous and vapor contaminants can generally be qualified rapidly at the levels of concentration which relate to (OSHA) permissible exposure limits, with an accuracy of plus or minus 25%. Several manufacturers offer complete extensive kits (together with self-instruction type guidelines) for evaluating most the contaminants likely to be found in offices and workplaces.

- A portable gas chromatograph may be used to evaluate office environments, including off-gassing from fibrous furnishings. It affords a quick, inexpensive way of identifying common contaminants and quantifying them at the "few parts per billion in air" level, with high precision.

- Sampling and microbiological culturing ensembles (pumps and aseptic special agar-formula petri dishes), together with species identification and evaluation services, are available from several national commercial microbiological laboratories, for evaluating issues of mold and bacterial contamination in the workplace.

- Various methodologies are available for evaluating liquids, vapors and solids in various media. In general, the order of common use in industrial hygiene work and chemical accident investigation are: gas chromatography, atomic absorption spectroscopy (flame and flame-less); ultraviolet-, light-, or infrared-spectroscopy.

- Some methodologies are simple to operate. In addition to these common analytical methods, gravimetric analysis for known substances, x-ray analysis, mass spectroscopy (invariably used in conjunction with gas chromatography), and high pressure liquid chromatography (coupled with appropriate methodology for identification and evaluation) are used extensively for workplace evaluation. Also, in the laboratory, atomic absorption spectroscopy and atomic emission spectroscopy are used to evaluate metals in various media, and in environmental and/or industrial hygiene risk assessment work. These (field/ laboratory) methodologies and many others are described in standard chemistry texts.

- Infrared spectroscopy (which is nondestructive), basically, is applicable to analyzing compounds in which bond stretching, bond angle bending, and molecular polarization changes occur, when its molecules are excited by energy associated with the infrared spectrum (0.7 to 300 micrometers). It is most useful in identifying functional groups in a compound or material and in helping in the determination of molecular structure. [The spectral wavelength range is described in nanometers. One micrometer = 1000 nanometer.]

- Infrared is especially useful in helping to characterize compounds with polarized groups, e.g., O-H, N-H, C-H, S-H, C-NO_2, C-O, C-N, C-S, and C-Cl (F) (Br), or hydrocarbons with an asymmetrical, double bond (>C=C<) or with a triple bond.

- Infrared spectroscopy is **not** used for total structure determination.

- Ultraviolet spectroscopy, UV, (nondestructive methodology, 0.1-0.7 micrometer wavelength range) deals with the (measurable) absorption of ultraviolet, UV (and visible, Vis) radiation by molecules (which causes electron excitation). Saturated hydrocarbons (and alcohols) do not absorb in UV-Vis range and therefore they are good analytical solvents for use in UV spectroscopy.

- Chromophores are simple groups which adsorb in the (UV-Vis) radiation wavelength range, of which many exist. They include the following compounds/functional groups: acetylene, allene, cyano, nitro, phenyl, carbonyl, and disulphide (for which UV analysis is useful).

- Auxochromes are groups which are conjugate- bonded to chromophores, and which alter a chromophore's UV-Vis characteristic absorption wavelength(s).

- UV spectroscopy is used extensively in steroid analysis and vitamin analysis, and in checking the purity of these and other organic compounds, as well as in numerous organic chemical structural studies.

- Mass spectroscopy involves bombardment of the molecules of interest with an electron beam and measuring the resultant molecular damage, in terms of the molecular ions formed (which can be separated in a variable magnetic field and analyzed for their individual mass-charge value, via an ion collector, an amplifier and a spectrum graphic plotter). From analysis of the ensuing molecular fragments, determinations may be made of molecular weight and structure. Mass spectroscopy (a sample destructive procedure) is often used in conjunction with gas chromatography in environmental chemistry. Mass spectroscopy is routinely used in evaluating chemical pollution involving sulphur-, nitrogen-, and halide-substituted organic compounds, and petrochemicals and other hydrocarbon compounds, e.g., 1-chloro-2-nitrobenzene, n-hexadecane, pinenes (terpenes), and dioxin like substances.

- Mass spectroscopy *state of the art* equipment comprises: special detectors, and software for separating the spectra of overlapping compounds, and high speed—large volume gas chromatography with special sample injection devices and separation columns. This type of equipment is needed for identifying and evaluating dioxin-like compounds in earth materials, animate materials and foodstuffs. Advanced mass spectroscopy and skilled operators and analysts, and accredited laboratories are fully utilized; The (GC-MS) analysis of dioxin-like substances and other special interest compounds is costly.

- End -