

## ***INORGANIC CHEMISTRY /SECOND YEAR***

### **RADIOACTIVITY**

The atom is the basic constituent of all matter and is one of the smallest units into which matter can be divided. Each atom is composed of a tiny central core of particles, or nucleus, surrounded by a cloud of negatively charged particles called electrons. Most atoms in the physical world are stable, meaning that they are not radioactive. However, some atoms possess excess energy, which causes them to be physically unstable. In order to become stable, an atom rids itself of this extra energy by casting it off in the form of charged particles or electromagnetic waves, known as radiation.

Of the nuclei found on Earth, the vast majority is stable. This is so because almost all short-lived radioactive nuclei have decayed during the history of the Earth. There are approximately 270 stable isotopes and 50 naturally occurring radioisotopes (radioactive isotopes). Thousands of other radioisotopes have been made in the laboratory.

Radioactive decay will change one nucleus to another if the product nucleus has a greater nuclear binding energy than the initial decaying nucleus. The difference in binding energy (comparing the before and after states) determines which decays are energetically possible and which are not. The excess binding energy appears as kinetic energy or rest mass energy of the decay products.

Nuclear decay processes must satisfy several conservation laws, meaning that the value of the conserved quantity after the decay, taking into account all the decay products, must equal the same quantity evaluated for the nucleus before the decay. Conserved quantities include total energy (including mass), electric charge, linear and angular momentum, number of nucleons, and lepton number (sum of the number of electrons, neutrinos, positrons and antineutrinos—with antiparticles counting as -1).

The probability that a particular nucleus will undergo radioactive decay during a fixed length of time does not depend on the age of the nucleus or how it was created.

Although the exact lifetime of one particular nucleus cannot be predicted, the mean (or average) lifetime of a sample containing many nuclei of the same isotope can be predicted and measured. A convenient way of determining the lifetime of an isotope is to

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measure how long it takes for one-half of the nuclei in a sample to decay—this quantity is called the half-life,  $t_{1/2}$ . Of the original nuclei that did not decay, half will decay if we wait another half-life, leaving one-quarter of the original sample after a total time of two half-lives. After three half-lives, one-eighth of the original sample will remain and so on. Measured half-lives vary from tiny fractions of seconds to billions of years, depending on the isotope.

### **NOMENCLATURE**

Radioactive elements (also called radionuclides) are referred to by a name followed by a number, e.g., cesium-137. The number following the name of the element is called the mass of the element and is equal to the total number of particles contained in the nucleus of the atom. Another way to specify the identity of cesium-137 is by writing it as Cs-137, where 'Cs' is the chemical symbol for cesium as it appears in the standard Periodic Table of the Elements.

### **COMMON TYPES OF RADIATION**

The three most important types of radiation are :

#### **1- ALPHA**

An alpha particle is identical in makeup to the nucleus of a helium atom, consisting of two neutrons and two protons. Alpha particles have a positive charge and have little or no penetrating power in matter. They are easily stopped by materials such as paper and have a range in air of only an inch or so. Naturally occurring radioactive elements such as uranium and radon daughters emit alpha radiation.

In alpha decay, the nucleus emits a  ${}^4\text{He}$  nucleus, an alpha particle. Alpha decay occurs most often in massive nuclei that have too large a proton to neutron ratio. An alpha particle, with its two protons and two neutrons, is a very stable configuration of particles. Alpha radiation reduces the ratio of protons to neutrons in the parent nucleus, bringing it to a more stable configuration. Nuclei, which are more massive than lead, frequently decay by this method.



In alpha decay, the atomic number changes, so the original (or parent) atoms and the decay-product (or daughter) atoms are

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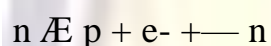
different elements and therefore have different chemical properties.

Because this energy must be shared between these two particles, and because the alpha particle and daughter nucleus must have equal and opposite momenta, the emitted alpha particle and recoiling nucleus will each have a well-defined energy after the decay. Because of its smaller mass, most of the kinetic energy goes to the alpha particle.

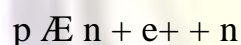
### **2- BETA**

Beta radiation is composed of particles that are identical to electrons. As a result, beta particles have a negative charge. Beta radiation is slightly more penetrating than alpha but may be stopped by materials such as aluminum foil and Lucite panels. They have a range in air of several feet. Naturally occurring radioactive elements such as potassium-40 (K-40) emit beta radiation.

Beta particles are electrons or positrons (electrons with positive electric charge, or antielectrons). Beta decay occurs when, in a nucleus with too many protons or too many neutrons, one of the protons or neutrons is transformed into the other. In beta minus decay, a neutron decays into a proton, an electron, and an antineutrino:



In beta plus decay, a proton decays into a neutron, a positron, and a neutrino:



Both reactions occur because in different regions of the Chart of the Nuclides, one or the other will move the product closer to the region of stability. These particular reactions take place because conservation laws are obeyed. Electric charge conservation requires that if an electrically neutral neutron becomes a positively charged proton, an electrically negative particle (in this case, an electron) must also be produced. Similarly, conservation of lepton number requires that if a neutron (lepton number = 0) decays into a proton (lepton number = 0) and an electron (lepton number = 1), a particle with a lepton number of -1 (in this case an antineutrino) must also be produced. The leptons emitted in beta decay did not



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exist in the nucleus before the decay—they are created at the instant of the decay.

To the best of our knowledge, an isolated proton, a hydrogen nucleus with or without an electron, does not decay. However within a nucleus, the beta decay process can change a proton to a neutron. An isolated neutron is unstable and will decay with a half-life of 10.5 minutes. A neutron in a nucleus will decay if a more stable nucleus results; the half-life of the decay depends on the isotope. If it leads to a more stable nucleus, a proton in a nucleus may capture an electron from the atom (electron capture), and change into a neutron and a neutrino.

Proton decay, neutron decay, and electron capture are three ways in which protons can be changed into neutrons or vice-versa; in each decay there is a change in the atomic number, so that the parent and daughter atoms are different elements. In all three processes, the number  $A$  of nucleons remains the same, while both proton number,  $Z$ , and neutron number,  $N$ , increase or decrease by 1.

### **3 - GAMMA**

Gamma radiation is a form of electromagnetic radiation, like radio waves or visible light, but with a much shorter wavelength. It is more penetrating than alpha or beta radiation, capable of passing through dense materials such as concrete. X-rays are similar to gamma radiation.

In gamma decay, a nucleus changes from a higher energy state to a lower energy state through the emission of electromagnetic radiation (photons). The number of protons (and neutrons) in the nucleus does not change in this process, so the parent and daughter atoms are the same chemical element. In the gamma decay of a nucleus, the emitted photon and recoiling nucleus each have a well-defined energy after the decay. The characteristic energy is divided between only two particles.

### **Units of Radioactivity**

The number of decays per second, or activity, from a sample of radioactive nuclei is measured in becquerel (Bq), after Henri Becquerel. One decay per second equals one becquerel.

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An older unit is the curie, named after Pierre and Marie Curie. One curie is approximately the activity of 1 gram of radium and equals (exactly)  $3.7 \times 10^{10}$  becquerel.

The activity depends only on the number of decays per second, not on the type of decay, the energy of the decay products, or the biological effects of the radiation

### **HALF-LIFE (symbol $t_{1/2}$ )**

In radioactivity the interval of time required for one-half of the atomic nuclei of a radioactive sample to decay (change spontaneously into other nuclear species by emitting particles and energy), or, equivalently, the time interval required for the number of disintegrations per second of a radioactive material to decrease by one-half.

Half-lives are characteristic properties of the various unstable atomic nuclei and the particular way in which they decay. Alpha and beta decay are generally slower processes than gamma decay. Half-lives for beta decay range upward from one-hundredth of a second and, for alpha decay, upward from about one one-millionth of a second. Half-lives for gamma decay may be too short to measure (around  $10^{-14}$  second), though a wide range of half-lives for gamma emission has been reported.

radioactive half-life refers to the amount of time it takes for half of the original isotope to decay. For example, if the half-life of a 50.0 gram sample is 3 years, then in 3 years only 25 grams would remain. During the next 3 years, 12.5 grams would remain and so on.

$$\ln \frac{N_t}{N_0} = -kt$$

$N_t$  = mass of radioactive material at time interval (t)

$N_0$  = mass of the original amount of radioactive material

k = decay constant

t = time interval ( $t_{1/2}$  for the half-life)

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question 1 : If the half-life of 100.0 grams of a radioactive isotope is 8 years, how many grams will remain in 32 years?

Answer:

To answer this question, there is no need to solve for the radioactive decay equation. If  $32 \div 8 = 4$ , then the material will go through 4 half-lives.

100.0g  $\xrightarrow{1^{st} \text{ half-life}}$  50.0g  $\xrightarrow{2^{nd} \text{ half-life}}$  25.0g  $\xrightarrow{3^{rd} \text{ half-life}}$  12.5g  $\xrightarrow{4^{th} \text{ half-life}}$   
6.25g

question 2 What is the decay constant for a radioactive isotope with a half-life of 22.5 hours?

Answer:

At first glance, it may seem that not enough information was provided to solve this problem. However, if the half-life value is given for time (t) then the value of  $\frac{N_t}{N_0} = \frac{1}{2}$  (because only half of the original material remains).

$$\ln \frac{N_t}{N_0} = -kt$$

$$\ln 0.5 = -k(22.5)$$

$$-.693 = -k(22.5)$$

$$k = 0.0308 \text{ hours}^{-1}$$

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### **ACID BASE CHEMISTRY**

#### **INTRODUCTION**

The terms *acid* and *base* have been used for several hundred years. Acids were substances that had a sour taste, were corrosive, and reacted with substances called bases. Substances that had a bitter taste, made skin slippery on contact, and reacted with acids were called bases. However, these simple definitions had to be refined as the chemical properties of acids and bases became better understood

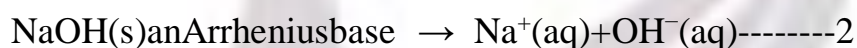
#### **Definitions of Acids and Bases**

We can define **acids** as substances that dissolve in water to produce  $H^+$  ions, whereas **bases** are defined as substances that dissolve in water to produce  $OH^-$  ions. In fact, this is only one possible set of definitions. Although the general properties of acids and bases have been known for more than a thousand years, the definitions of *acid* and *base* have changed dramatically as scientists have learned more about them. In ancient times, an acid was any substance that had a sour taste (e.g., vinegar or lemon juice), caused consistent color changes in dyes derived from plants (e.g., turning blue litmus paper red), reacted with certain metals to produce hydrogen gas and a solution of a salt containing a metal cation, and dissolved carbonate salts such as limestone ( $CaCO_3$ ) with the evolution of carbon dioxide. In contrast, a base was any substance that had a bitter taste, felt slippery to the touch, and caused color changes in plant dyes that differed diametrically from the changes caused by acids (e.g., turning red litmus paper blue). Although these definitions were useful, they were entirely descriptive

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### The Arrhenius Definition of Acids and Bases

The first person to define acids and bases in detail was the Swedish chemist Svante Arrhenius (1859–1927); Nobel Prize in Chemistry, 1903). According to the *Arrhenius definition*, an acid is a substance like hydrochloric acid that dissolves in water to produce  $H^+$  ions (protons), and a base is a substance like sodium hydroxide that dissolves in water to produce hydroxide ( $OH^-$ ) ions



According to Arrhenius, the characteristic properties of acids and bases are due exclusively to the presence of  $H^+$  and  $OH^-$  ions, respectively, in solution. Although Arrhenius's ideas were widely accepted, his definition of acids and bases had two major limitations:

1. First, because acids and bases were defined in terms of ions obtained from water, the Arrhenius concept applied only to substances in aqueous solution.
2. Second, and more important, the Arrhenius definition predicted that *only* substances that dissolve in water to produce  $H^+$  and  $OH^-$  ions should exhibit the properties of acids and bases, respectively. For example, according to the Arrhenius definition, the reaction of ammonia (a base) with gaseous HCl (an acid) to give ammonium chloride is not an acid–base reaction because it does not involve  $H^+$  and  $OH^-$ :



### The Brønsted–Lowry Definition of Acids and Bases

Because of the limitations of the Arrhenius definition, a more general definition of acids and bases was needed. One was proposed independently in 1923 by the Danish chemist J. N. Brønsted (1879–1947) and the British chemist T. M. Lowry (1874–1936), who defined acid–base reactions in terms of the transfer of a proton ( $H^+$  ion) from one substance to another.

According to Brønsted and Lowry, an acid (A substance with at least one hydrogen atom that can dissociate to form an anion and an  $H^+$  ion (a proton) in aqueous solution, thereby forming an acidic solution) is any substance that can donate a proton, and



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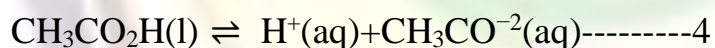
a base (a substance that produces one or more hydroxide ions ( $\text{OH}^-$  and a cation when dissolved in aqueous solution, thereby forming a basic solution) is any substance that can accept a proton. The Brønsted–Lowry definition of an acid is essentially the same as the Arrhenius definition, except that it is not restricted to aqueous solutions. The Brønsted–Lowry definition of a base, however, is far more general because the hydroxide ion is just one of many substances that can accept a proton.

Ammonia, for example, reacts with a proton to form  $\text{NH}_4^+$ , so in Equation (3),  $\text{NH}_3$  is a Brønsted–Lowry base and  $\text{HCl}$  is a Brønsted–Lowry acid.

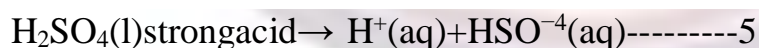
### Strengths of Acids and Bases

we can state that **strong acids** react essentially completely with water to give  $\text{H}^+$  and the corresponding anion. Similarly, **strong bases** dissociate essentially completely in water to give  $\text{OH}^-$  and the corresponding cation. Strong acids and strong bases are both strong electrolytes. In contrast, only a fraction of the molecules of weak acids and weak bases react with water to produce ions, so weak acids and weak bases are also weak electrolytes. Typically less than 5% of a weak electrolyte dissociates into ions in solution, whereas more than 95% is present in undissociated form.

In practice, only a few strong acids are commonly encountered:  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{H}_2\text{SO}_4$  ( $\text{H}_3\text{PO}_4$  is only moderately strong). The most common strong bases are ionic compounds that contain the hydroxide ion as the anion; three examples are  $\text{NaOH}$ ,  $\text{KOH}$ , and  $\text{Ca}(\text{OH})_2$ . Common weak acids include  $\text{HCN}$ ,  $\text{H}_2\text{S}$ ,  $\text{HF}$ , oxoacids such as  $\text{HNO}_2$  and  $\text{HClO}$ , and carboxylic acids such as acetic acid. The ionization reaction of acetic acid is as follows:



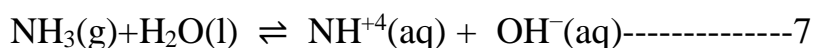
Although acetic acid is *very* soluble in water, almost all of the acetic acid in solution exists in the form of neutral molecules (less than 1% dissociates). Sulfuric acid is unusual in that it is a strong acid when it donates its first proton (Equation 5) but a weak acid when it donates its second proton (Equation 6) as indicated by the single and double arrows, respectively:



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Consequently, an aqueous solution of sulfuric acid contains  $\text{H}^+(\text{aq})$  ions and a mixture of  $\text{HSO}_4^-(\text{aq})$  and  $\text{SO}_4^{2-}(\text{aq})$  ions, but no  $\text{H}_2\text{SO}_4$  molecules. All other polyprotic acids, such as  $\text{H}_3\text{PO}_4$ , are weak acids.

The most common weak base is ammonia, which reacts with water to form small amounts of hydroxide ion:



Most of the ammonia (>99%) is present in the form of  $\text{NH}_3(\text{g})$ . Amines, which are organic analogues of ammonia, are also weak bases, as are ionic compounds that contain anions derived from weak acids (such as  $\text{S}^{2-}$ ).

### . Conjugate Base

The conjugate base of an acid is formed by removing one, and only one, proton from the acid.

After the acid loses a proton, it becomes a base because the species it becomes can gain the proton back. The loss of a single proton converts an acid into its **conjugate base**. It is important to realize that *an acid and its conjugate base differ by one, and only one proton*. All Brønsted reactions involve the transfer of a single proton. Thus, the acid is always converted to its conjugate base in a Brønsted reaction. The charge on the conjugate base is always lower than that on the acid by one because the acid loses  $\text{H}^+$ .

### . Conjugate Acid

The conjugate acid of a base is formed by adding one proton to the base.

After the base gains a proton, it becomes an acid because the species it becomes can donate the proton back. The gain of a single proton converts a base into its **conjugate acid**. All Brønsted reactions involve the transfer of a single proton. Thus, the base is always converted into its conjugate acid in a Brønsted reaction. The charge on the conjugate acid is always greater than that on the base by one because the base gains  $\text{H}^+$ . A base and an acid that

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differ by one, and only one proton, are said to be a *conjugate acid-base pair*.

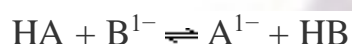
### . Comparing Conjugate Acid-Base Strengths

The weaker an acid is, the stronger is its conjugate base.

The strength of an acid is related to the ease with which it donates its proton to become its conjugate base, and the strength of a base is related to its ability to accept a proton to become its conjugate acid.

If  $A^{1-}$  is a strong base, then it must bind a proton strongly when it forms HA, and if its proton is bound strongly, then HA must be a weak acid. We conclude that the strength of a base varies inversely with the strength of its conjugate acid, i.e., strong acids have weak conjugate bases and *vice versa*.

Consider the following acid-base reaction.



If HA is the stronger of the two acids, then  $A^{1-}$  must be the weaker of the two bases due to the inverse relationship between conjugate acid-base strengths. This means that **the stronger acid is always on the same side of the chemical equation as the stronger base**. Similarly, the weaker acid and base are also on the same side of the equation.

Consequently, there are only three possible combinations in Brønsted acid-base reactions:

- 1-stronger acid + stronger base  $\rightarrow$  weaker base + weaker acid
- 2-reacting and produces acids of comparable strengths and reacting and produced bases of comparable strengths
- 3-weaker acid + weaker base  $\rightarrow$  stronger base + stronger acid

## LEWIS ACIDS AND BASES

A *Lewis acid* is a substance that has an empty orbital that it can use to share a lone pair to form a bond.

A *Lewis base* is a substance that has a lone pair that it can share in a covalent bond.

A *Lewis acid-base reaction* is the conversion of the lone pair on the base and the empty orbital of the acid into a covalent bond between the acid and the base.

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The product of a Lewis acid-base reaction is a covalent bond between the acid and the base. Both bonding electrons come from the base, so it is a coordinate covalent bond. A curved arrow from the lone pair to the atom with the empty orbital is used to show that the lone pair will become the bonding pair between the two atoms.

### **Lewis Bases**

A Lewis base must contain at least one lone pair of electrons.

All anions are Lewis bases, but not all Lewis bases are anions.

The lone pair is frequently, but not always, located on oxygen or nitrogen atoms.

The strength of a base is increased by electron density.

The strength of the base depends upon the electron density in the region of the lone pair, the greater the electron density the stronger the base. Consequently, the strength of a base depends upon the groups around the lone pair. For example, consider the relative base strengths of the following, which are basic due to the lone pairs on the oxygen atom.



$\text{CH}_3\text{O}^{1-}$  is the strongest base because the  $\text{CH}_3$  group pushes electron density onto the oxygen atom.  $\text{ClO}^{1-}$  is the weakest because the electronegative chlorine atom removes electron density from the oxygen.

### **Lewis Acids**

Lewis acids are often more difficult to identify. The following should help.

A Lewis acid must be able to accommodate an additional electron region (the new bond), so, if it obeys the octet rule, a Lewis acidic atom must have less than four regions.

Attack by a lone pair is facilitated by positive charge, so Lewis acidity is strengthened by positive charge.

All cations are Lewis acids, but not all Lewis acids are cations.

$\text{AlCl}_3$  is electron deficient because aluminum has only six valence electrons. Molecules with electron deficient atoms are strong Lewis acids.  $\text{SO}_3$  and  $\text{CO}_2$  are not electron deficient, but the central atom in each has less than four electron regions (three around S and two around C), so they are Lewis acids. Their acidity is strengthened by positive formal charge. Cations such as



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$\text{Ag}^{1+}$  and  $\text{H}^{1+}$  that have fairly low-energy empty orbitals are also good Lewis acids.

### **. Lewis Acidity and Basicity and Orbital Energy**

The bond between two atoms is covalent only when the interacting orbitals have similar energies because large energy separations favor ionic bonds. Thus, the formation of a coordinate covalent bond in a Lewis acid-base reaction is facilitated when the energy of the empty orbital of the Lewis acid is close to that of the lone pair of the Lewis base. The energies of lone pairs are typically lower than those of empty orbitals, so the strongest interactions occur when the energy of the lone pair is high for a lone pair and the energy of the empty orbital is low for an empty orbital. For example, consider the cases of  $\text{Na}^{1+}$  and  $\text{Ag}^{1+}$  as shown in the figure. The energy of the empty orbital of  $\text{Ag}^{1+}$  is much lower than that of  $\text{Na}^{1+}$ ; i.e., the energy of the empty orbital of  $\text{Ag}^{1+}$  is low for an empty orbital. Thus, the empty orbital on  $\text{Ag}^{1+}$  is sufficiently close to that of the lone pair on the  $\text{Br}^{1-}$  ion that the  $\text{Ag-Br}$  bond is covalent. However, the energy of the empty orbital on  $\text{Na}^{1+}$  is so high that the  $\text{Na-Br}$  bond is ionic. Thus,  $\text{Ag}^{1+}$  is a sufficiently strong Lewis acid to react with  $\text{Br}^{1-}$  ion, but the acidity of  $\text{Na}^{1+}$  is so weak that it does not. Indeed,  $\text{Na}^{1+}$  is such a weak Lewis acid (its orbitals are so high in energy) that it does not function as an acid in aqueous solutions. In general,  $\text{H}^{1+}$  and cations of metals with high effective nuclear charge (metals such as  $\text{Ag}$  and  $\text{Pb}$  that lie low and to the right of the periodic table) have empty orbitals that are relatively low in energy, so they are Lewis acidic, but the cations of metals on the left side of the periodic table are such weak Lewis acids that their acidity can be ignored in most cases. We conclude the following.

**Strong Lewis acids have low-energy empty orbitals, and strong Lewis bases have high-energy lone pairs.**

***The Hard/Soft Acid/Base (HSAB) Principle.***

HSAB is an extremely useful qualitative theory that enables predictions of what adducts will form in a complex mixture of potential Lewis acids and bases. Although there have been numerous attempts to make the theory quantitative by assigning numbers representing "hardness" and "softness" to acids and bases, these have not been particularly successful. Even if only qualitative, the theory is so useful that it is essential to know something about it.

Fundamentals. The basic premise of Hard/Soft Acid/Base Theory is very simple: Hard acids prefer hard bases; soft acids prefer soft bases.

**INTRODUCTION**

The HSAB concept is an acronym for 'hard and soft acids and bases'. Also known as the Pearson acid base concept, HSAB is widely used in chemistry for explaining stability of compounds, reaction mechanisms and pathways. It assigns the terms 'hard' or 'soft', and 'acid' or 'base' to chemical species. 'Hard' applies to species which are small, have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases), and are weakly polarizable. 'Soft' applies to species which are big, have low charge states and are strongly polarizable. HSAB theory is also useful in predicting the products of metathesis reactions. The gist of this theory is that soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases, all other factors being equal. The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid.

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Hard acids and hard bases tend to have:

- small atomic/ionic radius
- high oxidation state
- low polarizability
- high electronegativity
- energy low-lying HOMO (bases) or energy high-lying LUMO (acids).

Examples of hard acids are:  $H^+$ , alkali ions,  $Ti^{4+}$ ,  $Cr^{3+}$ ,  $Cr^{6+}$ ,  $BF_3$ .

Examples of hard bases are:  $OH^-$ ,  $F^-$ ,  $Cl^-$ ,  $NH_3$ ,  $CH_3COO^-$ ,  $CO_3^{2-}$ .

The affinity of hard acids and hard bases for each other is mainly ionic in nature.

Soft acids and soft bases tend to have:

- large atomic/ionic radius
- low or zero oxidation state
- high polarizability
- low electronegativity
- energy high-lying HOMO (bases) and energy-low lying LUMO (acids).

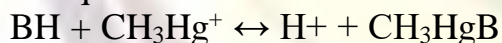
Examples of soft acids are:  $CH_3Hg^+$ ,  $Pt^{4+}$ ,  $Pd^{2+}$ ,  $Ag^+$ ,  $Au^+$ ,  $Hg^{2+}$ ,  $Hg_2^{2+}$ ,  $Cd^{2+}$ ,  $BH_3$ .

Examples of soft bases are:  $H^-$ ,  $R_3P$ ,  $SCN^-$ ,  $I^-$ .

The affinity of soft acids and bases for each other is mainly covalent in nature.

Borderline cases are also identified: borderline acids are trimethylborane, sulfur dioxide and ferrous  $Fe^{2+}$ , cobalt  $Co^{2+}$  and lead  $Pb^{2+}$  cations.

Borderline bases are: aniline, pyridine, nitrogen  $N_2$  and the azide, bromine, nitrate and sulfate anions. The acids and bases, in general, interact and the most stable interactions are hard-hard (ionogenic character) and soft-soft (covalent character). An attempt to quantify the 'softness' of a base consists in determining the equilibrium constant for the following equilibrium:



Where  $CH_3Hg^+$  (methylmercury ion) is a very soft acid and  $H^+$  (proton) is a hard acid, which compete for B (the base to be classified).

Some examples illustrating the effectiveness of the theory:

- Bulk metals are soft acids and are poisoned by soft bases such as phosphines and sulfides.

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□ Hard solvents such as hydrogen fluoride, water and the protic solvents tend to solvate strong solute bases such as the fluoride anion and the oxygen anions. On the other hand dipolar aprotic solvents such as dimethyl sulfoxide and acetone are soft solvents with a preference for solvating large anions and soft bases.

□ In coordination chemistry soft-soft and hard-hard interactions exist between ligands and metal centers.

### Combining Pearson's and Klopman's Ideas

□ Hard Lewis acids:

- Atomic centres of small ionic radius
- High positive charge
- Species do not contain electron pairs in their valence shells
- Low electron affinity
- Likely to be strongly solvated
- High energy LUMO

□ Soft Lewis acids:

- Large radius
- Low or partial ( $\delta^+$ ) positive charge
- Electron pairs in their valence shells
- Easy to polarise and oxidize
- Low energy LUMOs, but large magnitude LUMO coefficients

□ Hard Lewis bases:

- Small, highly solvated, electronegative atomic centres: 3.0-4.0
- Species are weakly polarisable
- Difficult to oxidise
- High energy HOMO

□ Soft Lewis bases:

- Large atoms of intermediate electronegativity: 2.5-3.0
- Easy to polarise and oxidize
- Low energy HOMOs but large magnitude HOMO coefficients.

□ Borderline species have intermediate properties.

□ • There is a qualifier in Klopman's paper saying that it is not necessary for species to possess all properties.

### The Hard Soft [Lewis] Acid Base Principle

Ralph Pearson introduced the Hard Soft [Lewis] Acid Base (HSAB) principle in the early nineteen sixties, and in doing so attempted to unify inorganic and organic reaction chemistry. The impact of the new idea was immediate, however over time the HSAB principle has rather fallen by the wayside while other



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approaches developed at the same time, such as frontier molecular orbital (FMO) theory and molecular mechanics, have flourished.

The Irving-Williams stability series (1953) pointed out that for a given ligand the stability of dipositive metal ion complexes increases:

It was also known that certain ligands formed their most stable complexes with metal ions like  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$  and  $\text{Co}^{3+}$  while others formed stable complexes with  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$  and  $\text{Pt}^{2+}$ .

In 1958 Ahrland et al. Classified metal cations as Type A and Type B, where:

Type A metal cations included:

- Alkali metal cations:  $\text{Li}^+$  to  $\text{Cs}^+$
- Alkaline earth metal cations:  $\text{Be}^{2+}$  to  $\text{Ba}^{2+}$
- Lighter transition metal cations in higher oxidation states:  $\text{Ti}^{4+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$

Type B metal cations include:

- Heavier transition metal cations in lower oxidation states:

$\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$

. Ligands were classified as Type A or Type B depending upon whether they formed more stable complexes with Type A or Type B metals

From this analysis, a principle can be derived: Type A metals prefer to bind to Type A ligands and Type B metals prefer to bind to Type B ligands. These empirical (experimentally derived) rules tell us that Type A metals are more likely to form oxides, carbonates, nitrides and fluorides, while Type B metals are more likely to form phosphides, sulfides and selenides. This type of analysis is of great economic importance because some metals are found in nature as sulfide ores:  $\text{PbS}$ ,  $\text{CdS}$ ,  $\text{NiS}$ , etc., while others are found as carbonates:  $\text{MgCO}_3$  and  $\text{CaCO}_3$  and others as oxides:  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ . This approach has been very successfully developed in recent years by Bruce Railsback with his excellent and highly recommended "Earth Scientist's Periodic Table", here. The Railsback analysis uses contours of behaviour superimposed upon the Mendeleev periodic table. (As Bruce told me in a personal communication: "Earth scientists love contours..."). See the paper: A Synthesis of Systematic Mineralogy by Bruce Railsback that develops this analysis. Pearson's Hard Soft [Lewis] Acid Base Principle In the nineteen sixties, Ralph Pearson developed the Type A and Type B logic by explaining the differential complexation behaviour of cations and ligands in

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terms of electron pair donating Lewis bases and electron pair accepting Lewis acids:

Lewis acid + Lewis base  $\rightarrow$  Lewis acid/base complex

Pearson classified Lewis acids and Lewis bases as hard, borderline or soft. According to Pearson's hard soft [Lewis] acid base (HSAB) principle: Hard [Lewis] acids prefer to bind to hard [Lewis] bases and Soft [Lewis] acids prefer to bind to soft [Lewis] bases. At first sight, HSAB analysis seems rather similar to the Type A and Type B system. However, Pearson classified a very wide range of atoms, ions, molecules and molecular ions as hard, borderline or soft Lewis acids or Lewis bases, moving the analysis from traditional metal/ligand inorganic chemistry into the realm of organic chemistry.

### **SYMMETRY**

Symmetry elements and symmetry operations

- What is symmetry? In simple language we can say that an object has symmetry, if it has some special characteristics, such as pleasing designs, while we look at it. As an example, when we see the telephone posts or electric lamp posts, we say that there is symmetry because they are arranged in a straight line at equal distance. Similarly, when we look at the gates of houses, they will appear symmetric because of their designs. Naturally, our eyes will compare the design on one half of the gate with that of the other half and if they find some characteristic feature such as mirror image or other, then we feel there is symmetry. A suspension bridge, a butterfly, the rose petal etc. are some examples to show the pleasing designs and hence, they are symmetric.

### **INTRODUCTION**

If we say something is 'symmetrical', we usually mean it has mirror symmetry, or 'left-right' symmetry, and would look the same if viewed in a mirror. Symmetry is also very important in chemistry. Some molecules are clearly 'more symmetrical' than others, but what consequences does this have, if any?

The aim of this course is to provide a systematic treatment of symmetry in chemical systems within the mathematical framework known as group theory (the reason for the name will become apparent later on). Once we have classified the symmetry

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of a molecule, group theory provides a powerful set of tools that provide us with considerable insight into many of its chemical and physical properties. Some applications of group theory that will be covered in this course include:

- i) Predicting whether a given molecule will be chiral, or polar.
- ii) Examining chemical bonding and visualising molecular orbitals.
- iii) Predicting whether a molecule may absorb light of a given polarisation, and which spectroscopic transitions may be excited if it does.
- iv) Investigating the vibrational motions of the molecule.

### **SYMMETRY OPERATIONS AND SYMMETRY ELEMENTS**

symmetry operation is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by  $180^\circ$  about an axis passing through the central O atom (between the two H atoms) it will look the same as before. It will also look the same if we reflect it through either of two mirror planes.

Each symmetry operation has a corresponding symmetry element, which is the axis, plane, line or point with respect to which the symmetry operation is carried out. The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a symmetry axis; in a reflection the points that remain unchanged make up a plane of symmetry.

The symmetry elements that a molecule may possess are:

1. E - the identity. The identity operation consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule has at least this element.
2.  $C_n$  - an n-fold axis of rotation. Rotation by  $360^\circ/n$  leaves the molecule unchanged. The  $H_2O$  molecule above has a  $C_2$  axis. Some molecules have more than one  $C_n$  axis, in which case the



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one with the highest value of  $n$  is called the principal axis . Note that by convention rotations are counterclockwise about the axis.

3.  $\sigma$  - a plane of symmetry. Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labelled  $\sigma_v$ , while one perpendicular to the axis is called a horizontal mirror plane and is labelled  $\sigma_h$ . A vertical mirror plane that bisects the angle between two  $C_2$  axes is called a dihedral mirror plane,  $\sigma_d$ .

4.  $i$  - a centre of symmetry. Inversion through the centre of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the centre of inversion and out to the same distance on the other side of the molecule.

5.  $S_n$  - an  $n$ -fold improper rotation axis (also called a rotary-reflection axis). The rotary reflection operation consists of rotating through an angle  $360^\circ/n$  about the axis, followed by reflecting in a plane perpendicular to the axis. Note that  $S_1$  is the same as reflection and  $S_2$  is the same as inversion. The molecule shown above has two  $S_2$  axes.

The identity  $E$  and rotations  $C_n$  are symmetry operations that could actually be carried out on a molecule. For this reason they are called proper symmetry operations . Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed improper symmetry operations .

A note on axis definitions: Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the  $z$  axis lies along the principal axis of the molecule, the  $x$  axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the  $y$  axis makes up a right handed axis system.

### ***SYMMETRY CLASSIFICATION OF MOLECULES – POINT GROUPS***

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called point groups (due to the fact that there is at least one point in space that remains



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unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labelling symmetry groups, called the Schoenflies and Hermann-Mauguin (or International ) systems. The symmetry of individual molecules is usually described using the Schoenflies notation,

Note: Some of the point groups share their names with symmetry operations, so be careful you don't mix up the two. It is usually clear from the context which one is being referred to.

The molecular point groups are listed below.

1.  $C_1$  – contains only the identity (a  $C_1$  rotation is a rotation by  $360^\circ$  and is the same as the identity operation E) e.g.  $CH_2Cl_2$ .
2.  $C_i$  - contains the identity E and a centre of inversion i.
3.  $C_s$  - contains the identity E and a plane of reflection  $\sigma$ .
4.  $C_n$  – contains the identity and an n-fold axis of rotation.
5.  $C_{nv}$  – contains the identity, an n-fold axis of rotation, and n vertical mirror planes  $\sigma_v$ .
6.  $C_{nh}$  - contains the identity, an n-fold axis of rotation, and a horizontal reflection plane  $\sigma_h$  (note that in  $C_{2h}$  this combination of symmetry elements automatically implies a centre of inversion).
7.  $D_n$  - contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.
8.  $D_{nh}$  - contains the same symmetry elements as  $D_n$  with the addition of a horizontal mirror plane.
9.  $D_{nd}$  - contains the same symmetry elements as  $D_n$  with the addition of n dihedral mirror planes.
10.  $S_n$  - contains the identity and one  $S_n$  axis.

Note that molecules only belong to  $S_n$  if they have not already been classified in terms of one of the preceding point groups (e.g.  $S_2$  is the same as  $C_i$ , and a molecule with this symmetry would already have been classified).

The following groups are the cubic groups, which contain more than one principal axis. They separate into the tetrahedral groups ( $T_d$ ,  $T_h$  and  $T$ ) and the octahedral groups ( $O$  and  $O_h$ ). The icosahedral group also exists but is not included below.

11.  $T_d$  – contains all the symmetry elements of a regular tetrahedron, including the identity, 4  $C_3$  axes, 3  $C_2$  axes, 6 dihedral mirror planes, and 3  $S_4$  axes e.g.  $CH_4$ .
12.  $T$  - as for  $T_d$  but no planes of reflection.
13.  $T_h$  – as for  $T$  but contains a centre of inversion.
14.  $O_h$  – the group of the regular octahedron e.g.  $SF_6$ .
15.  $O$  - as for  $O_h$  but with no planes of reflection.

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The final group is the full rotation group  $R_3$ , which consists of an infinite number of  $C_n$  axes with all possible values of  $n$  and describes the symmetry of a sphere. Atoms (but no molecules) belong to  $R_3$ , and the group has important applications in atomic quantum mechanics.

