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Module I (9L)

Dilute solutions- Colligative properties

1.1 Dilute solutions

A dilute solution is one in which the amount of the solute is very small in comparison to the amount of the solvent.The dilute solutions show more or less ideal behavior as the heat and volume changes, accompanying the mixing of solute and solvent, are negligible for all practical purposes. Dilute solutions obey Raoult's law.

The properties of dilute solutions which depend only on number particles of solute present in the solution and not on their identity are called *colligative properties* (denoting depending upon collection).

Colligative properties are the properties of only dilute solution which are supposed to behave as ideal solutions. The various colligative properties are:

- Depression of freezing point
- Lowering of vapour pressure
- Osmotic pressure
- Elevation of boiling point

Mole fraction

Suppose in a solution n_1 gm-moles of component A and n_2 gm-moles of component B are present, then the total amount is (n_1+n_2) gm-moles. The mole fraction of the component A= $n_1/(n_1+n_2)= X_1$; mole fraction of the component B= $n_2/(n_1+n_2)= X_2$; so that $X_1+ X_2=1$.

Lowering of Vapour Pressure by Non Volatile Solute

It has been known for a long time that when a non-volatile solute is dissolved in a liquid, the vapour pressure of the solution becomes lower than the vapour pressure of the pure solvent. In 1886, the French chemist, Francois Raoult, after a series of experiments on a number of solvents including water, benzene and ether, succeeded in establishing a relationship between the lowering of vapour pressure of a solution and the mole fraction of the non-volatile solute.

Let us consider a solution obtained by dissolving n moles of a non-volatile solute in N moles of a volatile solvent. Then mole fraction of the solvent, $X_1 = n_1/(n_1+ n_2)$ and mole fraction of the solute, $X_2 = n_2/(n_1 + n_2)$. Since the solute is non-volatile, it would have negligible vapour pressure. The vapour pressure of the solution is, therefore merely the vapour pressure of the solvent. According to Raoult's law, the vapour pressure of a solvent (P_1) in an ideal solution is given by the expression;

$P_1 = X_1 P_1^0$ ....(1)

where P_1^0 is the vapour pressure of the pure solvent. Since $X_1 + X_2 = 1$, Eq. 1 may be written as:

$$P_1=(1-X_2)P_1^0 \qquad \ldots(2)$$

$$\text{or} \quad P_1/P_1^0=1-X_2$$

$$\text{or} \quad \frac{P_1^0-P_1}{P_1^0}=X_2 \qquad \ldots(3)$$

The expression on the left hand side of Equation (3) is usually called the relative lowering of vapour pressure. Equation (3) may thus be stated as: “The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute present in the solution.” This is one of the statements of the *Raoult's law.*

Since mole fraction of the solute, X_2 is given by $n_2/(n_1+n_2)$, Equation (3) may be expressed as:

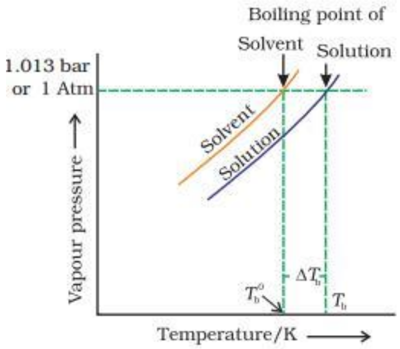
$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n_2}{(n_1+n_2)} \qquad \dots (4)$$

Limitations of Raoult’s Law

- Raoult’s law is applicable only to very dilute solutions.
- It is applicable to solutions containing non-volatile solute only.
- It is not applicable to solutes which dissociate or associate in a particular solution.

Boiling Point Elevation by a Non-Volatile Solute

The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to 760 mm (i.e. 1 atmospheric pressure). Since the addition of a non-volatile solute lowers the vapour pressure of the solvent, the vapour pressure of a solution is always lower than that of the pure solvent, and hence it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure. Thus the solution boils at a higher temperature than the pure solvent. If T_b^0 is the boiling point of the solvent and T_b is the boiling point of the solution, the difference in boiling points (δT_b) is called the **elevation of boiling point**.



Thus, $T_b - T_b^0 = \delta T_b$.

δT_b a molality where δT_b = elevation of boiling

point n= no. of moles of non-volatile solute

N= Total no. of moles in the solution

This implies that the boiling point elevation in a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is quite independent of the nature of the solute. Hence, **boiling point elevation is a colligative property**

$\delta T_b = K_b \times m$

k_b: molal elevation constant or Ebullioscopic constant

m: molality of the solution

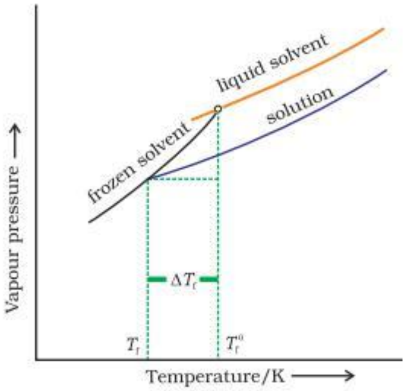
Molal boiling point elevation constant or ebullioscopic constant of the solvent is defined as the elevation in boiling point which may theoretically be produced by dissolving one mole of any solute in 1000 g of the solvent. or

$$\Delta T_b = \frac{1000 \times K_b \times w}{m_1 \times W},$$

Where, m_1 = molecular weight of solute and w and W are weights of solute and solvent.

Depression of Freezing Point by a Non-Volatile Solute

Freezing point is the temperature at which solid and liquid states of a substance have the same vapour pressure. It is observed that the freezing point of the solution (T_f) containing non volatile solute is always less than the freezing point of the pure solvent (T_f^0). Thus, $T_f^0 - T_f = \delta T_f$



It can be seen that

$\delta T_f \, \alpha$ molality

that, is freezing point depression of a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is independent of the nature of solute

or $\delta T_f = K_f m$

k_f : molal freezing point depression constant of the solvent or cryoscopic constant

m : molality of the solution

Molal freezing point depression constant of the solvent or cryoscopic constant, is defined as the depression in freezing point which may theoretically be produced by dissolving 1 mole of any solute in 1000g of the solvent.

$$\Delta T_f = \frac{1000 \times K_f \times w}{m_1 \times W}$$

Where, m_1 = molecular weight of solute and w and W are weights of solute and solvent.

Osmosis and Osmotic Pressure

The phenomenon of the passage of pure solvent from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane is called **osmosis**.

The driving force of osmosis is what is known as **osmotic pressure**. It is the difference in the pressure between the solution and the solvent system or it is the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane. Once osmosis is complete the pressure exerted by the solution and the solvent on the semi-permeable membrane is same. Van't Hoff equation for dilute solutions is (parallel to ideal gas equation).

$\pi V = nRT$

where π = Osmotic pressure

V= volume of solution

n= no. of moles of solute that is

dissolved R = Gas constant

T= Absolute temperature

1.2 Ionic Equilibria

Introduction

If some ordinary table salt is added into a glass of water, it "disappear". We refer to this as dissolution, and we explain it as a process in which the sodium and chlorine units break away from the crystal surface, get surrounded by H_2O molecules, and become hydrated *ions*.

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

But if you keep adding salt, there will come a point at which it no longer seems to dissolve. If this condition persists, we say that the salt has reached its solubility limit, and the solution is saturated in NaCl. The situation is now described by

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-$$

(aq) in which the solid and its ions are in equilibrium.

Solubility Product

Some salts and similar compounds (such as some metal hydroxides) dissociate completely when they dissolve, but the extent to which they dissolve is so limited that the resulting solutions exhibit only very weak conductivities. In these salts, which otherwise act as strong electrolytes, we can treat the dissolution-dissociation process as a true equilibrium. Although this seems almost trivial now, this discovery, made in 1900 by Walther Nernst who applied the Law of Mass Action to the dissociation scheme of Arrhenius, is considered one of the major steps in the development of our understanding of ionic solutions.

Using silver chromate as an example, we express its dissolution in water as

$Ag_2CrO_4(s) \rightarrow 2Ag^+(aq) + CrO_4^{2-}(aq)$ (4a)

When this process reaches equilibrium (*which requires that some solid be present*), we can write (leaving out the "*(aq)*s" for simplicity)

$Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+ + CrO_4{}_{2-}$ (4b)

The equilibrium constant is formally

$K = [Ag^+]^2\,[CrO_4^{2-}] / [Ag_2CrO_4(s)]$ (5a)

But because solid substances do not normally appear in equilibrium expressions, the equilibrium constant for this process is

$[Ag^+]^2\,[CrO_4^{2-}] = K_S = 2.76E{-}12$ (5b)

Because equilibrium constants of this kind are written as products, the resulting K's are commonly known as ***solubility products***, denoted by K_S or sometimes K_{sp}.

Ion product vs. solubility product

An expression such as $[Ag^+]^2\,[CrO_4^{2-}]$ in known generally as an ***ion product*** — this one being the ion product for silver chromate. An ion product can in principle have *any* positive value, depending on the concentrations of the ions involved. Only in the special case when its value is identical with K_S does it become the solubility product. A solution in which this is the case is said to be ***saturated***. Thus when $[Ag^+]^2\,[CrO_4^{2-}] = 2.76E{-}12$ at the temperature and pressure at which this value K_S of applies, we say that the "solution is saturated in silver chromate".

A solution must be saturated to be in equilibrium with the solid. This is a necessary condition for solubility equilibrium, but it is not by itself sufficient. True chemical equilibrium can only occur when all components are simultaneously present.

Solubility and Solubility product

For example, let us denote the solubility of Ag_2CrO_4 as S mol L^{-1}. Then for a saturated solution, we have

$$[Ag^+] = 2S\ [CrO_4^{2-}] = S.$$

Substituting this into Eq 5b above,

$$(2S)^2\ (S) = 4S^3 = 2.76E–12$$

$$S = \left(\frac{K_s}{4}\right)^{1/3} = (6.9\times10^{-13})^{1/3} = (.69\times10^{-12})^{1/3} = \sqrt[3]{.69}\times10^{-4} = .88\times10^{-4} \qquad (6)$$

Thus, the solubility is 8.8×10^{-5} M.

The common ion effect

It has long been known that the solubility of a sparingly soluble ionic substance is markedly decreased in a solution of another ionic compound when the two substances have an ion in common. This is just what would be expected on the basis of the Le-Châtelier principle; whenever the process

$$CaF_2(s) \rightleftharpoons Ca^{2+} + 2\ F^- \qquad (7)$$

is in equilibrium, addition of more fluoride ion (in the form of highly soluble NaF) will shift the composition to the left, reducing the concentration of Ca^{2+}, and thus effectively reducing the solubility of the solid.

We can express this quantitatively by noting that the solubility product expression

$$[Ca^{2+}][F^-]^2 = 1.7 \times 10^{-10} \qquad (8)$$

must always hold, even if some of the ionic species involved come from sources other than $CaF_2(s)$. For example, if some quantity x of fluoride ion is added to a solution initially in equilibrium with solid CaF_2, we have

$$[Ca^{2+}] = S, \qquad [F^-] = 2S + x$$

so that

$$K_S = [Ca^{2+}][\ F^-]^2 = S \times (2S + x)^2 \qquad (9a)$$

Dissociation of weak Acid and Base

When an uncharged weak acid is added to water, a homogeneous equilibrium forms in which aqueous acid molecules, HA(aq), react with liquid water to form aqueous hydronium ions and aqueous anions, A^-(aq). The latter are produced when the acid molecules lose H^+ ions to water.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

In writing an equilibrium constant expression for this homogeneous equilibrium, we leave out the concentration of the liquid water. The equilibrium constant for this expression is called the acid dissociation constant, K_a.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

= acid dissociation constant

When the equilibrium in question occurs in solution, the chemical formulas enclosed in brackets in the equilibrium constant expression represent the molarities of the substances (moles of solute per liter of solution).

Remember that H^+ can be used to represent H_3O^+, thus simplifying our depiction of the reaction between a weak acid and water and its acid dissociation constant expression:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

= acid dissociation constant

For example, acetic acid is a weak acid, because when it is added to water, it reacts with the water in a reversible fashion to form hydronium and acetate ions.

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

or $CH_3COOH\ (aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$$

$$= 1.8 \times 10^{-5}$$

The base dissociation constant, K_b, is a measure of basicity—the base's general strength. It is related to the acid dissociation constant, K_a, by the simple relationship $pK_a + pK_b = 14$, where pK_b and pK_a are the negative logarithms of K_b and K_a, respectively. The base dissociation constant can be expressed as follows:

$$K_b=[BH+][OH-]/[B]$$

where B is the base, BH+ is its conjugate acid, and OH− is hydroxide ions.

K_b is related to K_a for the conjugate acid. Recall that in water, the concentration of the hydroxide ion, $[OH^-]$, is related to the concentration of the hydrogen ion by the autoionization constant of water:

$$K_W=[H+][OH-]$$

Rearranging, we have:

$$[OH-]=K_w[H+]$$

Substituting this expression for $[OH^-]$ into the expression for K_b

yields: $K_b=K_W[HB+]/[B][H+]=K_W/K_a$

Therefore, for any base/conjugate acid pair, the following relationship always holds true:

$$K_W=K_aK_b$$

Taking the negative log of both sides yields the following useful

equation: $pK_a+pK_b=14$

Buffer solution

A buffer solution is one which resists changes in pH when small quantities of an acid or an alkali are added to it.

Acidic buffer solutions

An acidic buffer solution is simply one which has a pH less than 7. Acidic buffer solutions are commonly made from a weak acid and one of its salts - often a sodium salt. A common example would be a mixture of ethanoic acid and sodium ethanoate in solution. In this case, if the solution contained equal molar concentrations of both the acid and the salt, it would have a pH of 4.76. It wouldn't matter what the concentrations were, as long as they were the same.

Alkaline buffer solutions

An alkaline buffer solution has a pH greater than 7. Alkaline buffer solutions are commonly made from a weak base and one of its salts.

A frequently used example is a mixture of ammonia solution and ammonium chloride solution. If these were mixed in equal molar proportions, the solution would have a pH of 9.25. Again, it doesn't matter what concentrations you choose as long as they are the same.

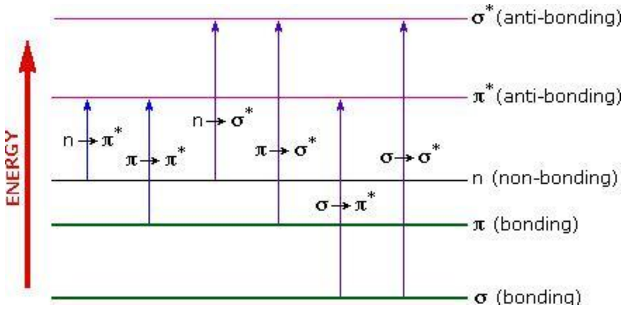
Module II (8L)

Instrumental methods for spectral analysis

2.1 UV-Visible Absorption Spectra

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole. Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**, and the resulting species is called an **excited state**.



When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colorless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). **Molar absorptivity** (ε) is defined as:

$$\boldsymbol{\varepsilon = A / c\, l}$$

where, A= absorbance, c = sample concentration in moles/litre& l = length of light path through the sample in cm.

If the isoprene spectrum on the right was obtained from a dilute hexane solution (c =4*10^{-5} moles per litre) in a 1 cm sample cuvette, a simple calculation using the above formula indicates a molar absorptivity of 20,000 at the maximum absorption wavelength. Indeed the entire vertical absorbance scale may be changed to a molar absorptivity scale once this information about the sample is in hand.

Chromophore	**Example**	**Excitation**	**λ_{max}, nm**	**ε**	**Solvent**
C=C	Ethene	π —> π*	171	15,000	hexane
C≡C	1-Hexyne	π —> π*	180	10,000	hexane
		n —> π*	290	15	hexane
C=O	Ethanal	π —> π*	180	10,000	hexane
		n —> π*	275	17	ethanol
N=O	Nitromethane	π —> π*	200	5,000	ethanol
C-X; X=Br	Methyl bromide	n —> ζ*	205	200	hexane
X=I	Methyl Iodide	n —> ζ*	255	360	hexane

From the chart above it should be clear that the only molecular moieties likely to absorb light in the 200 to 800 nm region are pi-electron functions and hetero atoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred to as **chromophores**. A list of some simple chromophores and their light absorption characteristics is provided on the left above. The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies.

The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for wavelengths below 200 nm makes the detection of isolated chromophores problematic. Fortunately, conjugation generally moves the absorption maxima to longer wavelengths, as in the case of isoprene, so conjugation becomes the major structural feature identified by this technique. Molar absorptivities may be very large for strongly absorbing chromophores (>10,000) and very small if absorption is weak (10 to 100). The magnitude ofε reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.

Terminology for Absorption Shifts

Nature of Shift	Descriptive Term
To Longer Wavelength	Bathochromic
To Shorter Wavelength	Hypsochromic
To Greater Absorbance	Hyperchromic
To Lower Absorbance	Hypochromic

Applications

UV/Vis spectroscopy is routinely used in analytical chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied.

- Solutions of transition metal ions can be colored (i.e., absorb visible light) because electrons within the metal atoms can be excited from one electronic state to another. The colour of metal ion solutions is strongly affected by the presence of other species, such as certain anions or ligands. For instance, the colour of a dilute solution of copper sulfate is a very light blue; adding ammonia intensifies the colour and changes the wavelength of maximum absorption (λ_{max}).

- Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water-soluble compounds, or ethanol for organic-soluble compounds. (Organic solvents may have significant UV absorption; not all solvents are suitable for use in UV spectroscopy. Ethanol absorbs very weakly at most wavelengths.) Solvent polarity and pH can affect the absorption spectrum of an organic compound. Tyrosine, for example, increases in absorption maxima and molar extinction coefficient when pH increases from 6 to 13 or when solvent polarity decreases.
- While charge transfer complexes also give rise to colours, the colours are often too intense to be used for quantitative measurement.

2.2 Infrared Spectroscopy

Infrared Spectroscopy is the analysis of infrared light interacting with a molecule. This can be analyzed in three ways by measuring absorption, emission and reflection. The main use of this technique is in organic and inorganic chemistry. It is used by chemists to determine functional groups in molecules. IR Spectroscopy measures the vibrations of atoms, and based on this it is possible to determine the functional groups. Generally, stronger bonds and light atoms will vibrate at a high stretching frequency (wavenumber).

Theory

Infrared (IR) spectroscopy is one of the most common and widely used spectroscopic techniques employed mainly by inorganic and organic chemists due to its usefulness in determining structures of compounds and identifying them. Chemical compounds have different chemical properties due to the presence of different functional groups.

Absorbing groups in the infrared region absorb within a certain wavelength region. The absorption peaks within this region are usually sharper when compared with absorption peaks from the ultraviolet and visible regions. In this way, IR spectroscopy can be very sensitive to determination of functional groups within a sample since different functional group absorbs different particular frequency of IR radiation. Also, each molecule has a characteristic spectrum often referred to as the fingerprint. A molecule can be identified by comparing its absorption peak to a data bank of spectra. IR spectroscopy is very useful in the identification and structure analysis of a variety of substances, including both organic and inorganic compounds. It can also be used for both qualitative and quantitative analysis of complex mixtures of similar compounds.

Polyatomic Molecular Vibration

The bond of a molecule experiences various types of vibrations and rotations. This causes the atom not to be stationary and to fluctuate continuously. Vibrational motions are defined by stretching and bending modes. These movements are easily defined for diatomic or triatomic molecules. This is not the case for large molecules due to several vibrational motions and interactions that will be experienced. When there is a continuous change in the interatomic distance along the axis of the bond between two atoms, this process is known as a stretching vibration. A change in the angle occurring between two bonds is known as a bending vibration. Four bending vibrations exist namely, wagging, twisting, rocking and scissoring.

Region of IR

The IR region of the electromagnetic spectrum ranges in wavelength from 2 -15 µm. Conventionally the IR region is subdivided into three regions, near IR, mid IR and far IR. Most of the IR used originates from the mid IR region.

IR deals with the interaction between a molecule and radiation from the electromagnetic region ranging (4000- 40 cm^{-1}). The cm^{-1} is the wave number scale and it can also be defined as 1/wavelength in cm. A linear wavenumber is often used due to its direct relationship with both frequency and energy. The frequency of the absorbed radiation causes the molecular vibrational frequency for the absorption process.

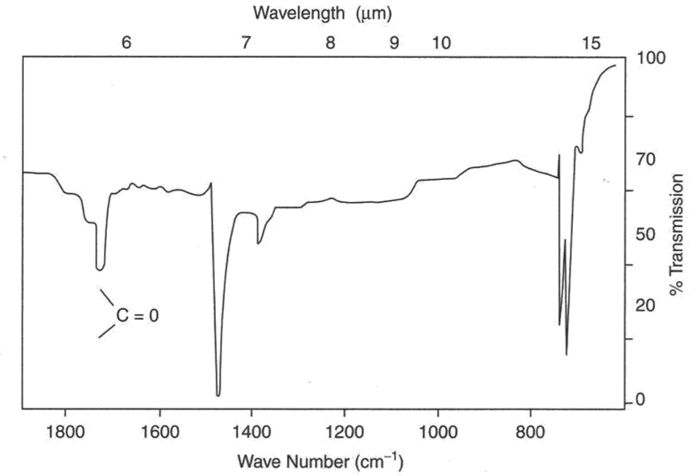
Near Infra-Red Spectroscopy: Absorption bands in the near infrared (NIR) region (750 - 2500 nm) are weak because they arise from vibrational overtones and combination bands. Combination bands occur when two molecular vibrations are excited simultaneously. The intensity of overtone bands reduces by one order of overtone for each successive overtone. When a molecule is excited from the ground vibrational state to a higher vibrational state and the vibrational quantum number v is greater than or equal to 2 then an overtone absorption results. The first overtone results from $v = 0$ to $v = 2$. The second overtone occurs when $v = 0$ transitions to $v = 3$. Transitions arising from the near IR absorption are weak, hence they are referred to as forbidden transitions but these transitions are relevant when non-destructive measurements are required such as a solid sample. Near IR spectra though have low absorption they have a high signal to noise ratio owing to intense radiation sources and NIR is able to penetrate undiluted samples and use longer path lengths; it becomes very useful for rapid measurement of more representative samples.

Far Infra-Red Spectroscopy: The far IR region is particularly useful for inorganic studies due to stretching and bending vibrations of bonds between the metal atoms and ligands. The frequencies, which these vibrations are observed, are usually lower than 650 cm^{-1}. Pure rotational absorption of gases is observed in the far IR region when there is a permanent dipole moment present. Examples include H_2O, O_3, HCl.

IR Analysis

IR spectroscopy is a great method for identification of compounds, especially for identification of functional groups. Therefore, we can use group frequencies for structural analysis. Group frequencies are vibrations that are associated with certain functional groups. It is possible to identify a functional group of a molecule by comparing its vibrational frequency on an IR spectrum to an IR stored data bank.

Here, we take the IR spectrum of Formaldehyde for an example. Formaldehyde has a C=O functional group and C-H bond. The value obtained from the following graph can be compared to those in reference data banks stored for Formaldehyde. A molecule with a C=O stretch has an IR band which is usually found near 1700 cm^{-1} and around 1400 cm^{-1} for CH_2 bend. It's important to note that this value is dependent on other functional groups present on the molecule. The higher 1700 cm^{-1} indicates a large dipole moment change. It is easier to bend a molecule than stretch it, hence stretching vibrations have higher frequencies and require higher energies than bending modes. The finger print region is a region from 1400-650 cm^{-1}. Each molecule has its own characteristic print and is often cumbersome to attach any values to this region.



IR Spectrum of Formaldehyde

Applications

- Infrared spectroscopy is a simple and reliable technique widely used in both organic and inorganic chemistry, in research and industry. It is used in quality control, dynamic measurement, and monitoring applications such as the long-term unattended measurement of CO_2 concentrations in greenhouses and growth chambers by infrared gas analysers.
- It is also used in forensic analysis in both criminal and civil cases, for example in identifying polymer degradation.
- IR-spectroscopy has been successfully used in analysis and identification of pigments in paintings and other art objects.
- Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics, for example, infrared spectroscopy can be applied to semiconductors like silicon.

2.3 NMR Spectroscopy

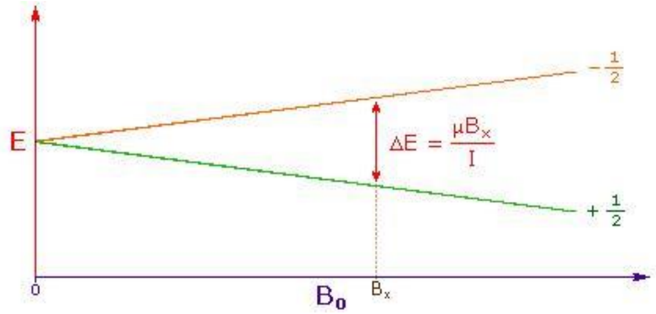
Over the past fifty years nuclear magnetic resonance spectroscopy, commonly referred to as nmr, has become the preeminent technique for determining the structure of organic compounds. Of all the spectroscopic methods, it is the only one for which a complete analysis and interpretation of the entire spectrum is normally expected. Although larger amounts of sample are needed than for mass spectroscopy, NMR is non-destructive, and with modern instruments good data may be obtained from samples weighing less than a milligram. To be successful in using NMR as an analytical tool, it is necessary to understand the physical principles on which the methods are based.

The nuclei of many elemental isotopes have a characteristic spin (**I**). Some nuclei have integral spins (e.g. I = 1, 2, 3 ....), some have fractional spins (e.g. I = 1/2, 3/2, 5/2 ....), and a few have no spin, I = 0 (e.g. ^{12}C, ^{16}O, ^{32}S). Isotopes of particular interest and use to organic chemists are ^{1}H, ^{13}C, ^{19}F and ^{31}P, all of which have I = 1/2. Since the analysis of this spin state is fairly straightforward, our discussion of NMR will be limited to these and other I = 1/2 nuclei.

The following features lead to the NMR phenomenon:

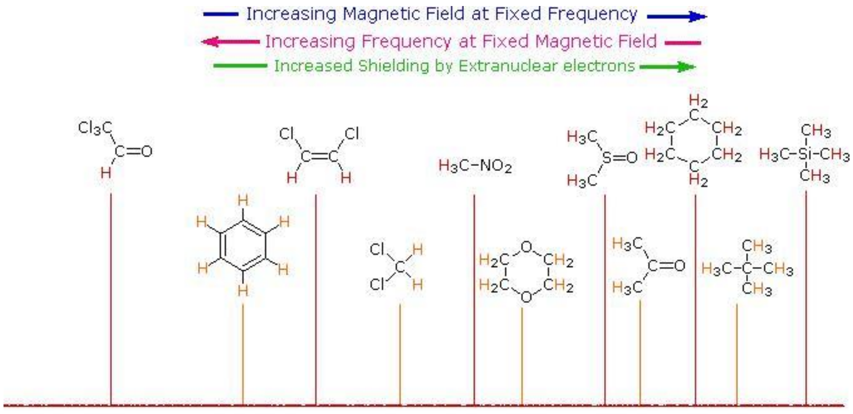
1. A spinning charge generates a magnetic field, as shown by the animation on the right. The resulting spin-magnet has a magnetic moment (**μ**) proportional to the spin.

2. In the presence of an external magnetic field (B_0), two spin states exist, +1/2 and -1/2. The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field. Note that the arrow representing the external field points north.
3. The difference in energy between the two spin states is dependent on the external magnetic field strength, and is always very small. The following diagram illustrates that the two spin states have the same energy when the external field is zero, but diverge as the field increases. At a field equal to B_X a formula for the energy difference is given (remember I = 1/2 and μ is the magnetic moment of the nucleus in the field).



Chemical Shift

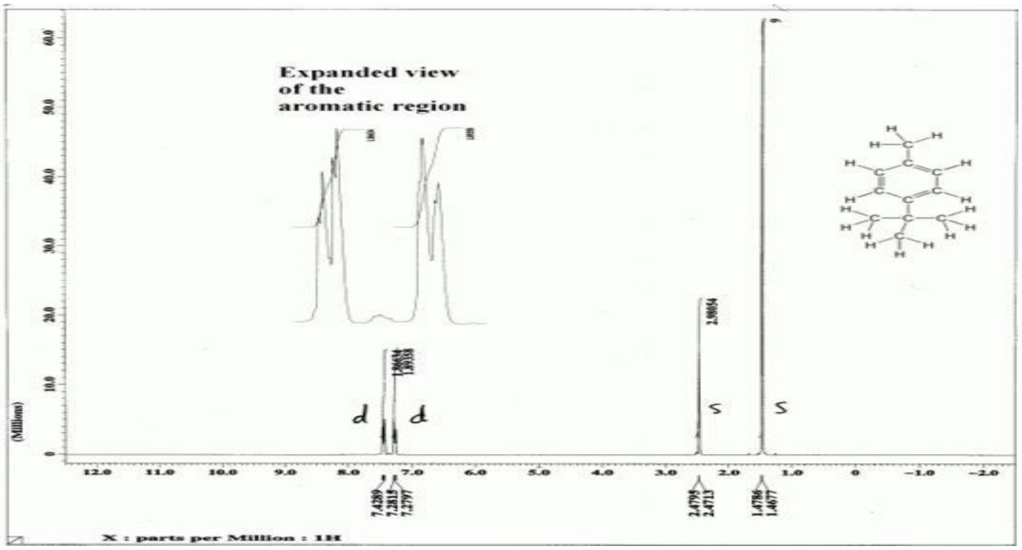
Unlike Infra-Red and UV-Visible spectroscopy, where absorption peaks are uniquely located by a frequency or wavelength, the location of different NMR resonance signals is dependent on both the external magnetic field strength and the rf frequency. Since no two magnets will have exactly the same field, resonance frequencies will vary accordingly and an alternative method for characterizing and specifying the location of NMR signals is needed. This problem is illustrated by the eleven different compounds shown in the following diagram. Although the eleven resonance signals are distinct and well separated, an unambiguous numerical locator cannot be directly assigned to each.



^{1}H NMR Resonance Signals for some Different Compounds

One method of solving this problem is to report the location of an nmr signal in a spectrum relative to a reference signal from a standard compound added to the sample. Such a reference standard should be chemically unreactive and easily removed from the sample after the measurement. Also, it should give a single sharp NMR signal that does not interfere with the resonances normally observed for organic compounds. Tetramethylsilane, $(CH_3)_4Si$, usually referred to as TMS, meets all these characteristics, and has become the reference compound of choice for proton and carbon nmr. Since the separation (or dispersion) of NMR signals is magnetic field dependent, one additional step must be taken in order to provide an unambiguous location unit. To correct these frequency differences for their field dependence, we divide them by the spectrometer frequency (100 or 500 MHz in the example). The resulting number would be very small, since we are dividing Hz by MHz, so it is multiplied by a million, as shown by the formula in the blue shaded box. Note that

ν_{ref} is the resonant frequency of the reference signal and ν_{samp} is the frequency of the sample signal. This operation gives a locator number called the **Chemical Shift**, having units of parts-per-million (ppm), and designated by the symbol **δ**.



^{1}H NMR spectrum of *para*-(*tert*-butyl)toluene

A typical example shown in the above figure. The difference (in parts per million, ppm) from the zero point is referred to as the **chemical shift** (δ). A typical range for δ is around 12 ppm for ^{1}H. It is customary to have the zero point at the right hand end of the spectrum, with numbers increasing to the left ("downfield") as shown in the figure.

Applications

Today, NMR has become a sophisticated and powerful analytical technology that has found a variety of applications in many disciplines of scientific research, medicine, and various industries. Modern NMR spectroscopy has been emphasizing the application in bio-molecular systems and plays an important role in structural biology. Together with X-ray crystallography, NMR spectroscopy is one of the two leading technologies for the structure determination of bio-macromolecules at atomic resolution. In addition, NMR provides unique and important molecular motional and interaction profiles containing pivotal information on protein function. The information is also critical in drug development. Some of the applications of NMR spectroscopy are listed below:

- **Solution structure** The only method for atomic-resolution structure determination of biomacromolecules in aqueous solutions under near physiological conditions or membrane mimeric environments.
- **Molecular dynamics** The most powerful technique for quantifying motional properties of biomacromolecules.
- **Protein folding** The most powerful tool for determining the residual structures of unfolded proteins and the structures of folding intermediates.

- **Ionization state** The most powerful tool for determining the chemical properties of functional groups in bio-macromolecules, such as the ionization states of ionizable groups at the active sites of enzymes.
- **Weak intermolecular interactions** Allowing weak functional interactions between macrobiomolecules (e.g., those with dissociation constants in the micromolar to millimolar range) to be studied, which is not possible with other technologies.
- **Protein hydration** A power tool for the detection of interior water and its interaction with bio-macromolecules.
- **Hydrogen bonding** A unique technique for the DIRECT detection of hydrogen bonding interactions.

Module III (7L)

Coordination Chemistry

3.1 Introduction

Coordination chemistry emerged from the work of Alfred Werner, a Swiss chemist who examined different compounds composed of cobalt(III) chloride and ammonia. Upon the addition of hydrochloric acid, Werner observed that ammonia could not be completely removed. He then proposed that the ammonia must be bound more tightly to the central cobalt ion. However, when aqueous silver nitrate was added, one of the products formed was solid silver chloride. The amount of silver chloride formed was related to the number of ammonia molecules bound to the cobalt(III) chloride. For example, when silver nitrate was added to $CoCl_3 \cdot 6NH_3$, all three chlorides were converted to silver chloride. However, when silver nitrate was added to $CoCl_3 \cdot 5NH_3$, only 2 of the 3 chlorides formed silver chloride. When $CoCl_3 \cdot 4NH_3$ was treated with silver nitrate, one of the three chlorides precipitated as silver chloride.

The resulting observations suggested the formation of **complex** or **coordination compounds**. In the **inner coordination sphere**, which is also referred to in some places as the **first sphere**, ligands are directly bound to the central metal. In the **outer coordination sphere**, sometimes referred to as the **second sphere**, other ions are attached to the complex ion. Werner was awarded the Nobel Prize in 1913 for his coordination theory.

Properties of Coordination Complexes

Some methods of verifying the presence of complex ions include studying its chemical behavior. This can be achieved by observing the compounds' color, solubility, absorption spectrum, magnetic properties, etc. The properties of complex compounds are separate from the properties of the individual atoms. By forming coordination compounds, the properties of both the metal and the ligand are altered.Metal-ligand bonds are typically thought of Lewis acid-base interactions. The metal atom acts as an electron pair acceptor (Lewis acid), while the ligands act as electron pair donors (Lewis base). The nature of the bond between metal and ligand is stronger than intermolecular forces because they form directional bonds between the metal ion and the ligand, but are weaker than covalent bonds and ionic bonds.

Common Ligands

Monodentate ligands donate one pair of electrons to the central metal atoms. An example of these ligands are the haldide ions (F^-, Cl^-, Br^-, I^-). Polydentate ligands, also called chelates or chelating agents, donate more than one pair of electrons to the metal atom forming a stronger bond and a more stable complex. A common chelating agent is ethylenediamine (en), which, as the name suggests, contains two ammines or $:NH_2$ sites which can bind to two sites on the central metal. An example of a tridentate ligand is bis-diethylenetriammine. An example of such a coordination complex is bis-diethylenetriaminecobalt(III).

Nomenclature of Coordination Compounds

The coordination compounds are named in the following way.

A. To name a coordination compound, no matter whether the complex ion is the cation or the anion, always name the cation before the anion. (This is just like naming an ionic compound.)

B. In naming the complex ion:

1. Name the ligands first, in alphabetical order, then the metal atom or ion. Note: The metal atom or ion is written before the ligands in the chemical formula.

2. The names of some common ligands are listed in Table 1.

Table 1: Names of Some Common Ligands

Anionic Ligands	**Names**		**Neutral Ligands**	**Names**
Br^-	bromo		NH_3	ammine
F^-	fluoro		H_2O	aqua
O^{2-}	oxo		NO	Nitrosyl
OH^-	Hydroxo		CO	Carbonyl
CN^-	cyano		O_2	dioxygen
$C_2O_4^{2-}$	oxalato		N_2	dinitrogen
CO_3^{2-}	carbonato		C_5H_5N	pyridine
CH_3COO^-	acetato		$H_2NCH_2CH_2NH_2$	ethylenediamine

For anionic ligands end in "-o"; for anions that end in "-ide"(e.g. chloride), "-ate" (e.g. sulfate, nitrate), and "-ite" (e.g. nirite), change the endings as follows: -ide → -o; -ate → -ato; -ite → -ito

For neutral ligands, the common name of the molecule is used e.g. $H_2NCH_2CH_2NH_2$ (ethylenediamine). **Important exceptions**: water is called 'aqua', ammonia is called 'ammine', carbon monoxide is called 'carbonyl', and the N_2 and O_2 are called 'dinitrogen' and 'dioxygen'.

3. Greek prefixes are used to designate the number of each type of ligand in the complex ion, e.g. di-, tri- and tetra-. If the ligand already contains a Greek prefix (e.g. ethylene**di**amine) or if it is polydentate ligands (ie. can attach at more than one binding site) the prefixes bis-, tris-, tetrakis-, pentakis-, are used instead.

4. After naming the ligands, name the central metal. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is call cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix –ate. For example, Co in a complex anion is called cobaltate and Pt is called platinate. For some metals, the Latin names are used in the complex anions e.g. Fe is called ferrate (not ironate).

5. Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses.

C. To name a neutral complex molecule, follow the rules of naming a complex cation. **Remember:** Name the (possibly complex) cation **BEFORE** the (possibly complex) anion. For historic reasons, some coordination compounds are called by their common names. For example, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are named ferricyanide and ferrocyanide respectively, and $Fe(CO)_5$ is called iron carbonyl.

Examples:

1. $[Cr(NH_3)_3(H_2O)_3]Cl_3$

triamminetriaquachromium(III) chloride

2. $[Pt(NH_3)_5Cl]Br_3$

pentaamminechloroplatinum(IV) bromide

3. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$
tris(ethylenediamine)cobalt(III) sulfate
4. $Na_2[NiCl_4]$
sodiumtetrachloronickelate(II)

5. $(NH_4)_2[Ni(C_2O_4)_2(H_2O)_2]$
ammoniumdiaquabis(oxalato)nickelate(II)

6. $[Ag(NH_3)_2][Ag(CN)_2]$
diamminesilver(I) dicyanoargentate(I)

The Valence-Bond Approach to Bonding in Coordination Complexes

The idea that atoms form covalent bonds by sharing pairs of electrons was first proposed by G. N. Lewis in 1902. It was not until 1927, however, that Walter Heitler and Fritz London showed how the sharing of pairs of electrons holds a covalent molecule together. The Heitler-London model of covalent bonds was the basis of the valence-bond theory. The last major step in the evolution of this theory was the suggestion by Linus Pauling that atomic orbitals mix to form hybrid orbitals, such as the sp, sp^2, sp^3, dsp^3, and d^2sp^3 orbitals.

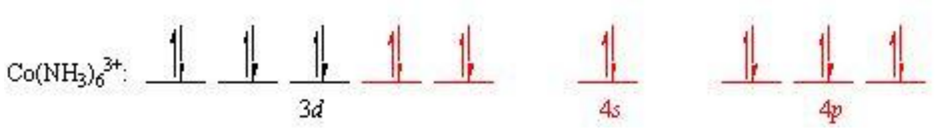
It is easy to apply the valence-bond theory to some coordination complexes, such as the $[Co(NH_3)_6]^{3+}$ ion. We start with the electron configuration of the transition- metal ion. Co^{3+}: [Ar] $3d^6$

We then look at the valence-shell orbitals and note that the $4s$ and $4p$ orbitals are empty.

Co^{3+}: [Ar] $3d^6$ $4s^0$ $4p^0$

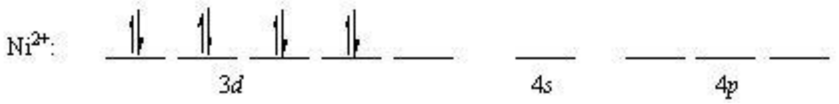
Concentrating the $3d$ electrons in the d_{xy}, d_{xz}, and d_{yz} orbitals in this subshell gives the following electron configuration.

The $3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p_x$, $4p_y$ and $4p_z$ orbitals are then mixed to form a set of empty d^2sp^3 orbitals that point toward the corners of an octahedron. Each of these orbitals can accept a pair of nonbonding electrons from a neutral NH_3 molecule to form a complex in which the cobalt atom has a filled shell of valence electrons.

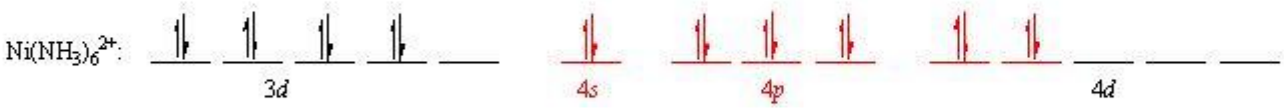


At first glance, complexes such as the $[Ni(NH_3)_6]^{2+}$ ion seem hard to explain with the valence-bond theory. We start, as always, by writing the configuration of the transition-metal ion. Ni^{2+}: [Ar] $3d^8$

This configuration creates a problem, because there are eight electrons in the $3d$ orbitals. Even if we invest the energy necessary to pair the $3d$ electrons, we can't find two empty $3d$ orbitals to use to form a set of d^2sp^3 hybrids.



There is a way around this problem. The five $4d$ orbitals on nickel are empty, so we can form a set of empty sp^3d^2 hybrid orbitals by mixing the $4d_{x^2-y^2}$, $4d_{z^2}$, $4s$, $4p_x$, $4p_y$ and $4p_z$ orbitals. These hybrid orbitals then accept pairs of nonbonding electrons from six ammonia molecules to form a complex ion.



The valence-bond theory therefore formally distinguishes between "inner-shell" complexes, which use 3*d*, 4*s* and 4*p* orbitals to form a set of d^2sp^3 hybrids, and "outer-shell" complexes, which use 4*s*, 4*p* and 4*d* orbitals to form sp^3d^2 hybrid orbitals.

Crystal Field Theory

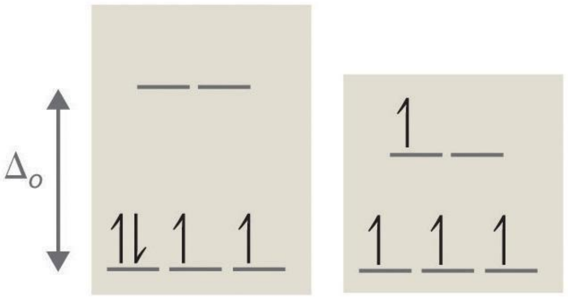
At almost exactly the same time that chemists were developing the valence-bond model for coordination complexes, physicists such as Hans Bethe, John Van Vleck, and Leslie Orgel were developing an alternative known as crystal field theory. This theory tried to describe the effect of the electrical field of neighboring ions on the energies of the valence orbitals of an ion in a crystal.

Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color. In Crystal Field theory, it is assumed that the ions are simple point charges (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful.

When examining a single transition metal ion, the five *d*-orbitals have the same energy. When ligands approach the metal ion, some experience more opposition from the *d*-orbital electrons than others based on the geometric structure of the molecule. Since ligands approach from different directions, not all *d*-orbitals interact directly. These interactions, however, create a splitting due to the electrostatic environment.For example, consider a molecule with octahedral geometry. Ligands approach the metal ion along the x, y, and z axes. Therefore, the electrons in the d_z^2 and $d_x^2{-}_y^2$ orbitals (which lie along these axes) experience greater repulsion. It requires more energy to have an electron in these orbitals than it would to put an electron in one of the other orbitals. This causes a splitting in the energy levels of the *d*-orbitals. This is known as Crystal Field Splitting. For octahedral complexes, crystal field splitting is denoted by $_o$ (or $_{oct}$). The energies of the d_z^2 and $d_x^2{-}_y^2$ orbitals increase due to greater interactions with the ligands. The d_{xy}, d_{xz} and d_{yz} orbitals decrease with respect to this normal energy level and become more stable.

Electrons in Orbitals

According to the Aufbau principle, electrons are filled from lower to higher energy orbitals. For the octahedral case above, this corresponds to the d_{xy}, d_{xz}, and d_{yz} orbitals. Following Hund's rule, electrons are filled in order to have the highest number of unpaired electrons. For example, if one had a d^3 complex, there would be three unpaired electrons. If one were to add an electron, however, it has the ability to fill a higher energy orbital (d_{z^2} or $d_{x^2-y^2}$) or pair with an electron residing in the d_{xy}, d_{xz}, or d_{yz} orbitals. This pairing of the electrons requires energy (spin pairing energy). If the pairing energy is less than the crystal field splitting energy, Δ_0, then the next electron will go into the d_{xy}, d_{xz}, or d_{yz} orbitals due to stability. This situation allows for the least amount of unpaired electrons, and is known as low spin. If the pairing energy is greater than Δ_0, then the next electron will go into the d_{z^2} or $d_{x^2-y^2}$ orbitals as an unpaired electron. This situation allows for the most number of unpaired electrons, and is known as high spin. Ligands that cause a transition metal to have a small crystal field splitting, which leads to high spin, are called *weak* *field ligands*. Ligands that produce a large crystal field splitting, which leads to low spin, are called*strong field ligands*.



Low Spin, Strong Field (Δ_o>P) **High Spin, Weak Field (Δ_o<P)**

Splitting for a d^4 complex under a strong field (left) and a weak field (right). The strong field is a low spin complex, while the weak field is a high spin complex.

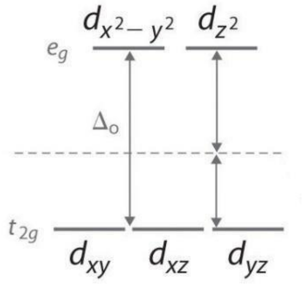
Description of *d*-Orbitals

To understand CFT, one must understand the description of the lobes:

- d_{xy}: lobes lie in-between the x and the y axes.
- d_{xz}: lobes lie in-between the x and the z axes.
- d_{yz}: lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

Octahedral Complexes

In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels. The bottom three energy levels are named d_{xy}, d_{xz}, and d_{yz} (collectively referred to as t_{2g}). The two upper energy levels are named $d_{x^2-y^2}$, and d_{z^2} (collectively referred to as e_g).



Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field shown in Figure 3

The reason they split is because of the electrostatic interactions between the electrons of the ligand and the lobes of the d-orbital. In an octahedral, the electrons are attracted to the axes. Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of e_g are higher ($0.6\Delta_o$) while t_{2g} is lower ($0.4\Delta_o$). The distance that the electrons have to move from t_{2g} from e_g and it dictates the energy that the complex will absorb from white light, which will determine the color. Whether the complex is paramagnetic or diamagnetic will be determined by the spin state. If there are unpaired electrons, the complex is paramagnetic; if all electrons are paired, the complex is diamagnetic.

Tetrahedral Complexes

In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three consist of the d_{xy}, d_{xz}, and d_{yz} orbitals. The bottom two consist of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not. The difference in the splitting energy is tetrahedral splitting constant (Δ_t), which less than (Δ_o) for the same ligands:

$$_t=0.44\Delta_o$$

Consequentially, $_t$ is typically smaller than the spin pairing energy, so tetrahedral complexes are usually high spin.

Isomerism in Coordination Compounds

Two or more different compounds having the same formula are called isomers. Two principal types of isomerism are known among coordination compounds. Each of which can be further subdivided.

1. Stereoisomerism
   a) Geometrical isomerism
   b) Optical isomerism
2. Structural isomerism
   a) Coordinationisomerism
   b) Ionisationisomerism
   c) Hydrateisomerism
   d) Linkage isomerism

1. Stereoisomers

Stereoisomers have the same atoms, same sets of bonds, but differ in the relative orientation of these bonds.

Geometric isomers are possible for both square planar and octahedral complexes, but not tetrahedral.

Optical isomers are possible for both tetrahedral and octahedral complexes, but not square planar.

The earliest examples of stereoisomerism involve complexes of Co(III). In 1889, Jorgensen observed purple and green salts of $[CoCl_2(en)_2]^+$, which Werner later correctly identified as the *cis*- and *trans*- geometric isomers.

2. Structural Isomers

There are several types of this isomerism frequently encountered in coordination chemistry and the following represents some of them.

a) Coordination isomerism: where compounds containing complex anionic and cationic parts can be thought of as occurring by interchange of some ligands from the cationic part to the anionic part.

One isomer $[Co(NH_3)_6][Cr(C_2O_4)_3]$

another isomer $[Co(C_2O_4)_3]$ $[Cr(NH_3)_6]$

b) Ionisation isomers: where the isomers can be thought of as occurring because of the formation of different ions in solution.

One isomer $[PtBr(NH_3)_3]NO_2$ -; it gives NO_2- anions in solution

another isomer $[Pt(NO_2)(NH_3)_3]Br$ -; it gives Br- anions in solution

c) Hydrate isomerism: the best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, or 6 coordinated water molecules.
$[CrCl_2(H_2O)_4]Cl.2H_2O$: bright-green
$[CrCl(H_2O)_5]Cl_2.H_2O$: grey-green
$[Cr(H_2O)_6]Cl_3$: violet
d) Linkage isomerism occurs with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands SCN- / NCS- and NO_2^- / ONO^-.

3.2 Colloid Chemistry

The term *colloidal* refers to a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1µm, or that in system discontinuities are found at distances of that order. It is not necessary for all three dimensions to be in the colloidal range: fibers in which only two dimensions are in this range and thin films, in which one dimension is in this range, may also be classified as colloidal. Nor is it necessary for the units of a *colloidal system* to be discrete: continuous network structures, the basic units of which are of colloidal dimensions also fall in this class (e.g. porous solids, gels and foams).

Classification of colloid

Lyophilic sols: These tem lyophilic means liquid-loving (i.e. solvent loving). Certain substances have an affinity for certain liquids and readily form colloidal dispersions with them. The substances which when mixed with a suitable liquid (dispersion medium) readily form colloidal solutions are called **lyophilic colloids** or **intrinsic colloids** and the sols thus formed are called lyophilic sols. Arabic gum, gelatin, albumin, starch etc. are some common examples of lyophilic colloids. Gum sol, starch sol, sols of proteins in water, sols of polymers in organic solvents etc. is some examples of lyophilic sols.

Lyophobic sols: The term lyophilic means liquid-hating (i.e. solvent-hating). The substances which do not pass much affinity for the dispersion medium and do not readily pass into the sol state when mixed with the medium are called hydrophobic colloids or extrinsic colloids. Their sols are prepared by using special techniques and they are referred to as hydrophobic sols. Sols of metals e.g. gold sol, platinum sol etc. and the sols of insoluble substances such as metal sulphides and oxides are some examples of lyophilic sols.

Colloid preparation

The preparation of colloidal sol usually involves three operations.

i) To obtain the substance directly or indirectly in the desired state of fine division in the dispersion medium. There are two general ways, **a)** Condensation Method **b)** Disintegration or dispersion method.

ii) To add protective or stabilizing agent to maintain the stability of the system.

iii) Purifications of sols: The final stage in sol preparation is its purification. Not all sols need purification process. Even those systems where purification is imperative it is carried out only to a certain limit as complete purification induces instability of the sols. The property common to all sols is the inability of the disperse phase to percolate through semi permeable membrane such as parchment paper, cellophanes etc. where as the dispersion medium, free ions, and molecules in solution can easily get through, this is taken as advantage in the purification of a sol. The commonly employed techniques are dialysis and electro-dialysis.

Dialysis

Dialysis works on the principles of the diffusion of solutes and ultrafiltration of fluid across a semi-permeable membrane. Diffusion is a property of substances in water; substances in water tend to move from an area of high concentration to an area of low concentration. Sol flows by one side of a semi-permeable membrane, and a dialysate, or special dialysis fluid, flows by the opposite side. A semipermeable membrane is a thin layer of material that contains holes of various sizes, or pores. Smaller solutes and fluid pass through the membrane, but the membrane blocks the passage of larger substances (for example, red blood cells, large proteins). This replicates the filtering process that takes place in the kidneys, when the blood enters the kidneys and the larger substances are separated from the smaller ones in the glomerulus.

Properties of colloid

The lyophobic sols are characterized by two unique properties.

i) Optical properties: The lyophobic sols are often coloured and the colour of the sol depends upon the size of the particles in suspension an some times on the shape also. The most important property of the lyophobic sol is thye scattering of light by the suspended particles commonly known as Tyndall effect. When the visible light passes through the colloid sol the rays are scattered.

ii) Electricals properties: the electrical properties of lyophobic sols are studied from their behavior towards **a) Electrolyte added**: the presence of small traces of suitable ions is necessary to impart stability to the sol if the system be divested of all the ions the colloid particles will grow bigger and ultimately thrown out as ppt. while small amount of specific foreign ions are essential, the addition of comparatively larger amount of a neutral electrolyte becomes destructive to the stability of the sol. The experimental observation on the coagulation of the various sols with different electrolytes led to two general conclusions known as Schultz-Hardy rule.

b) Effect of applied electric field: if two electrodes are inserted in a lyophobic sol the disperse phase migrate slowly either to the cathode or to the anode. The migration of the colloidal dispersed particle in the electric field is called electrophoresis or cataphoresis.

Association of colloid and emulsion

Association colloids are micro heterogeneous systems in which the particles of the colloidal dispersed phase (micelles) are formed by the agglomeration of molecules or ions of the substance dissolved in the dispersion medium. The micelles, or associates, are in thermodynamic equilibrium with the surrounding solution; therefore, a change in the external conditions, the composition of the dissolving medium, or the concentration of the dissolved (dispersed) substance causes redistribution of the substance between the micelles and the solution. Strong dilution or a rise in temperature may cause complete decomposition of all the micelles into their constituent molecules (ions), in which case the system becomes homogeneous or single phase. Restoration of the previous conditions returns the system to its original micro heterogeneous state. Thus, the characteristic feature of association colloidal systems is the reversibility of the true solution ⇄ sol transformation. Association colloidal systems include solutions of micelle-forming surface-active substances, such as soap and synthetic detergents, and also certain organic dyes, tanning agents (tannins), and alkaloids. e.g. milk (oil in water emulsion)

Module IV (8L)

Structure and reactivity of Organic molecule

Electronegativity

Electronegativity (E) is defined as the power of an atom in a molecule to attract the electron pair towards itself. The ionic character is developed in a covalent bond due to electronegativity difference between the connected atoms of a bond. Carbon-halogen bond has the ionic character because halogens are more electronegative than carbon.

Factors on which E depends (i) Size of the atom, (ii) Atomic no., (iii) Electron affinity, (iv) Oxidation state, (v) Hybridization

Electron affinity

Electron affinity (EA) is defined as the amount of energy (eV) evolved when a charged species or a neutral molecule gains one electron in the gaseous state. A coordinate bond will be formed more rapidly if EA of the acceptor atom is high. F, Cl, Br, I has high electron affinity.

Inductive effect

The inductive effect in chemistry is an experimentally observable effect of the transmission of charge through a chain of atoms in a molecule by electrostatic induction. The net polar effect exerted by a substituent is a combination of this inductive effect and the mesomeric effect.

The electron cloud in a σ-bond between two unlike atoms is not uniform and is slightly displaced towards the more electronegative of the two atoms. This causes a permanent state of bond polarization, where the more electronegative atom has a slight negative charge (δ-) and the other atom has a slight positive charge(δ+).

If the electronegative atom is then joined to a chain of atoms, usually carbon, the positive charge is relayed to the other atoms in the chain. This is the electron-withdrawing inductive effect, also known as the -I effect.

Some groups, such as the alkyl group are less electron-withdrawing than hydrogen and are therefore considered as electron-releasing. This is electron releasing character is indicated by the +I effect.

As the induced change in polarity is less than the original polarity, the inductive effect rapidly dies out, and is significant only over a short distance. The inductive effect is permanent but feeble, as it involves the shift of strongly held σ-bond electrons, and other stronger factors may overshadow this effect.

The inductive effect may be caused by some molecules also. Relative inductive effects have been experimentally measured with reference to hydrogen..

Inductive Effect can also be used to determine whether a molecule is stable or instable depending on the charge present on the atom under consideration and the type of groups bonded to it. For example, if an atom has a positive charge and is attached to a -I group its charge becomes 'amplified' and the molecule becomes more unstable than if I-effect was not taken into consideration. Similarily, if an atom has a negative charge and is attached to a +I group its charge becomes 'amplified' and the molecule becomes more unstable than if I-effect was not taken into consideration. But, contrary to the above two cases, if an atom has a negative charge and is attached to a -I group its charge becomes 'de-amplified' and the molecule becomes more stable than if I-effect was not taken into consideration. Similarily, if an atom has a positive charge and is attached to a +I group its charge becomes 'de-amplified' and the molecule becomes more stable than if I-effect was not taken into consideration. The explanation for the above is given by the fact that more charge on an atom decreases stability and less charge on an atom increases stability.

Resonance

Resonance in chemistry is a key component of valence bond theory used to graphically represent and mathematically model certain types of molecular structures when no single, conventional Lewis structure can satisfactorily represent the observed structure or explain its properties. Resonance instead considers such molecules to be an intermediate or an average (called a resonance hybrid) between several Lewis structures that differ only in the placement of the valence electrons.

Hyperconjugation

Hyperconjugation in organic chemistry is the stabilizing interaction that results from the interaction of the electrons in a sigma bond (usually C–H or C–C) with an adjacent empty (or partially filled) non-bonding p-orbital or antibonding π orbital or filled π orbital to give an extended molecular orbital that increases the stability of the system. Only electrons in bonds that are β to the positively charged carbon can stabilize a carbocation by hyperconjugation.

Electromeric Effect

Electromeric effect refers to a temporary polarization between atoms in a multiple bond in the presence of an attacking reagent. The effect is temporary and it will revert when the reagent is removed.The electron transfer facilitates the bonding of the attacking group to the atom. If the transfer is towards the attacking group, it is indicated as +E and if it is away from the attacking group, it is termed as -E.

For example, consider the carbonyl group, >C=O, present in aldehydes and ketones. When a negatively charged reagent approaches the molecule seeking positive site, it causes instantaneous shift of the bond electron pair of the C=O bond in carbonyl group to oxygen (which is more electronegative than carbon). The carbon then acquires positive charge. In the meanwhile oxygen takes complete control of the electron pair and becomes negatively charged. Therefore, in the presence of attacking reagent, one bond is lost and this negatively charged attacking reagent links to the carbon having positive charge.

Nowadays electromeric effect is often considered along with inductive effect as an electron displacement.

Carbocation

In case when a positive charge is carried on the carbon atom Carbon is electron deficient species known as carbocation or carbonium ion. It is sp^2 hybridized having planner geometry with bond angle 120°. Carbocation is more stable in polar solvent. Stability order of the carbocation is 3°>2°>1°>methyl

Carbanion

Carbanion is negatively charged carbon species. It is sp^3 hybridized having having tetrahedral (T_d) geometry with bond angle 109°28". A carbanion is a nucleophile. The stability and reactivity of a carbanion is determined by several factors. These include

1. The inductive effect. Electronegative atoms adjacent to the charge will stabilize the charge;

2. Hybridization of the charge-bearing atom. The greater the s-character of the charge-bearing atom, the more stable the anion;

3. The extent of conjugation of the anion. Resonance effects can stabilize the anion. This is especially true when the anion is stabilized as a result of aromaticity.

Free radicals

In chemistry, radicals (often referred to as free radicals) are atoms, molecules, or ions with unpaired electrons on an open shell configuration. The unpaired electrons cause them to be highly chemically reactive. Free radicals are sp^2 hybridized with an unpaired electron. The reaction involving free radicals occurs in gas phase or in non polar solvent in the presence of sunlight or some radical producing substance like peroxide. Radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes, including human physiology. For example, superoxide and nitric oxide regulate many biological processes, such as controlling vascular tone.

Bond Fission, Reaction Mechanism

The homolytic cleavage of the breaking bond is drawn with a 'fish-hook' arrow to distinguish from the usual movement of two electrons depicted by a standard curly arrow. It should be noted that the second electron of the breaking bond also moves to pair up with the attacking radical electron; this is not explicitly indicated in this case.

In chemistry, free radicals take part in radical addition and radical substitution as reactive intermediates. Chain reactions involving free radicals can usually be divided into three distinct processes: initiation, propagation, and termination.

Initiation reactions are those that result in a net increase in the number of free radicals. They may involve the formation of free radicals from stable species as in Reaction 1 above or they may involve reactions of free radicals with stable species to form more free radicals.

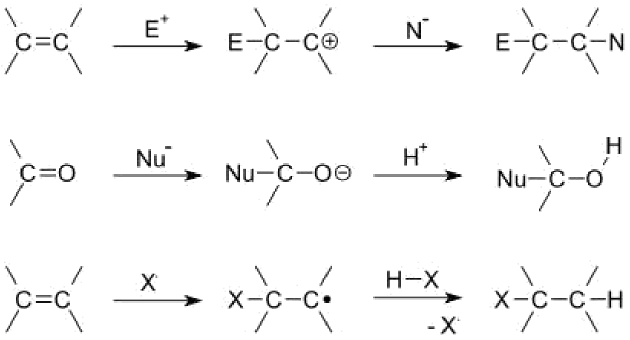
Propagation reactions are those reactions involving free radicals in which the total number of free radicals remains the same.

Termination reactions are those reactions resulting in a net decrease in the number of free radicals. Typically two free radicals combine to form a more stable species, for example:

$2Cl\bullet \rightarrow Cl_2$

Addition reaction

A type of chemical reaction in which two substances combine to form a third substance, with no other substance being produced. Addition reactions occur mainly in organic chemistry, particularly in situations where a simple molecule is added across a carbon-carbon double bond in an unsaturated compound. For example, the addition reaction between chlorine (Cl_2) and ethene ($CH_2=CH_2$) produces 1,2-dichloroethane ($ClCH_2(CH_2)Cl$).



Mechanism of Addition reaction

Some plastics (such as polystyrene) are made by addition polymerization, usually initiated by the action of a free radical.

Substitution Reaction

A chemical reaction in which one atom or group of atoms replaces (usually in the same structural position) another atom or group in a molecule or ion. Substitution reactions are of three types.

(i) Free radical substitution reaction

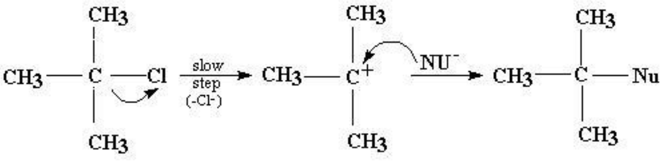
When an atom or group is substituted by a free radical, the reaction is called free radical substitution reaction. E_a of this reaction is very low. e.g. Chlorination of methane in presence of sunlight yields CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 respectively.

(ii) Electrophilic substitution reaction

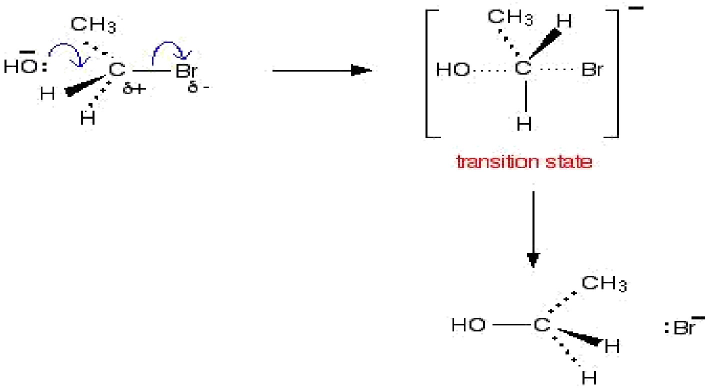
Electrophilic substitution reactions are typical reaction for aromatic species. The aromatic ring is electron rich at the above and below the plane. So attacked by the electrophile (E+) is highly facilitated. e.g. nitration, sulphonation reaction of benzene, Friedel Craft reaction of benzene.

(iii) Nucleophilic substitution reaction

The replacement of one nucleophile by another nucleophile is known as nucleophilic substitution reaction. These reactions are classified into two categories (a) Substitution Nucleophilic Unimolecular (S_N^1) and (b) Substitution Nucleophilic Bimolecular (S_N^2).

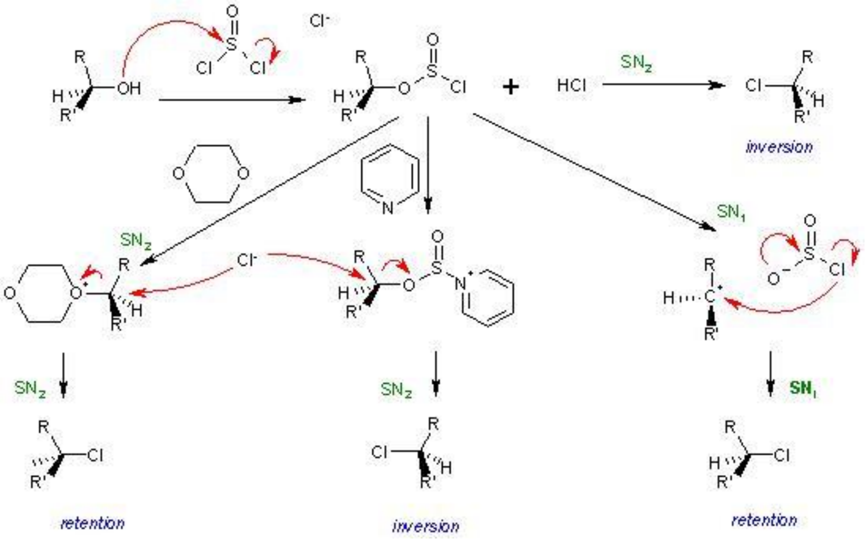


Mechanism of S_N^1 reaction



Mechanism of S_N^2 reaction

SNi or Substitution Nucleophilic internal stands for a specific but not often encountered nucleophilic aliphatic substitution reaction mechanism. A typical representative organic reaction displaying this mechanism is the chlorination of alcohols with thionyl chloride. Thionyl chloride first reacts with the alcohol to form an alkyl chloro sulfite, actually forming an intimate ion pair. The second step is the concerted loss of a sulfur dioxide molecule and its replacement by the chloride, which was attached to the sulphite group. The difference between SN1 and SNi is actually that the ion pair is not completely dissociated, and therefore no real carbocation is formed, which else would lead to a racemisation.



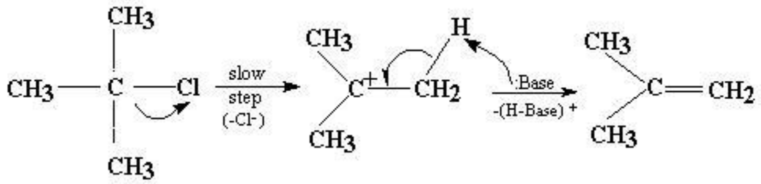
Mechanism of S_N^i reaction

Elimination Reaction

An elimination reaction is a type of organic reaction in which two substituents are removed from a molecule in either a one or two-step mechanism. Either the unsaturation of the molecule increases (as in most organic elimination reactions) or the valence of an atom in the molecule decreases by two, a process known as reductive elimination.

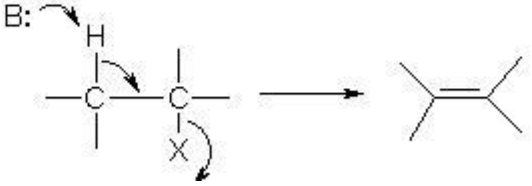
Elimination reactions are classified into two categories (a) 1,1- elimination or α-elimination and (b) 1,2- elimination or β- elimination.

An important class of elimination reactions is those involving alkyl halides or alkanes in general, with good leaving groups, reacting with a Lewis base to form an alkene in the reverse of an addition reaction. When the substrate is asymmetric, regioselectivity is determined by Zaitsev's rule. The one and two-step mechanisms are named and known as E2 reaction and E1 reaction, respectively.



Mechanism of E1 reaction

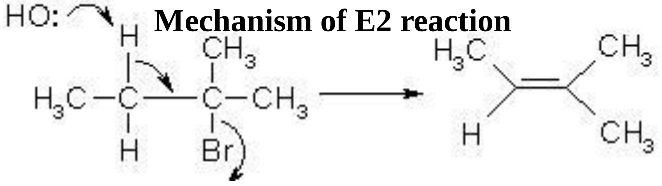
The general form of the **E2** mechanism is as follows:



B**:** = base
X = leaving group (usually halide or tosylate)

In the E2 mechanism, a base abstracts a proton neighboring the leaving group, forcing the electrons down to make a double bond, and, in so doing, forcing off the leaving group. When numerous things happen simultaneously in a mechanism, such as the E2 reaction, it is called a concerted step.
An example of the E2 reaction:

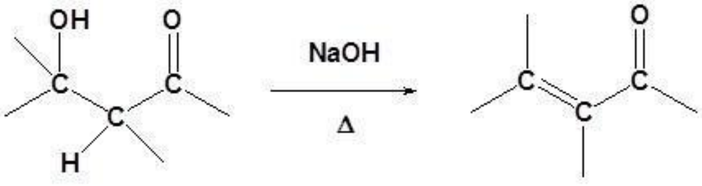
Mechanism of E2 reaction



Mechanism of E2 reaction

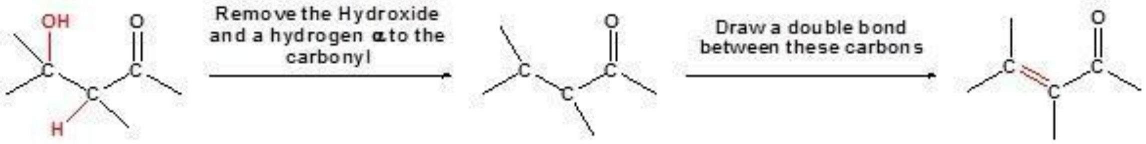
Although E1 reactions typically involves a carbocation intermediate, the E1cB reactoin utilizes a carbanion intermediate. This reaction is generally utilized when a poor leaving group, such an and alcohol, is involved. This poor leaving group makes the direct E1 or E2 reactions difficult. This reaction is used later in a reaction called an aldol condensation.

The product of this ββ-elimination reaction is an α,β-unsaturated aldehyde or ketone. Base-catalyzed elimination occurs with heating. The additional stability provided by the conjugated carbonyl system of the product makes some aldol reactions thermodynamically and mixtures of stereoisomers (E & Z) are obtained from some reactions.



General reaction for an E1cB condensation

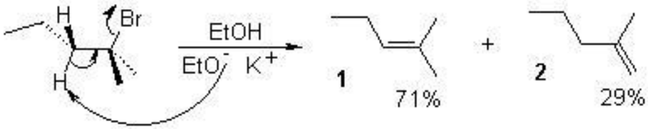
Going from reactants to products simply



***The E1cB* example**

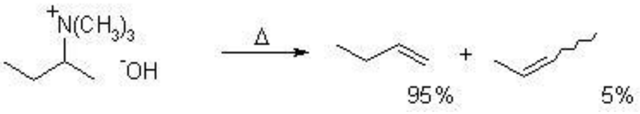
Saytzeff Rule

Saytzeff Rule implies that base-induced eliminations (E_2) will lead predominantly to the olefin in which the double bond is more highly substituted, i.e. that the product distribution will be controlled by thermodynamics.



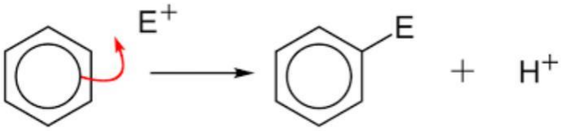
Hofmann Rule

Hofmann's Rule implies that steric effects have the greatest influence on the outcome of the Hofmann or similar eliminations. The loss of the β-hydrogen occurs preferably from the most unhindered (least substituted) position [$-CH_3$ > $-CH_2-R$ > $-CH(R_2)$]. The product alkene with fewer substitutents will predominate.

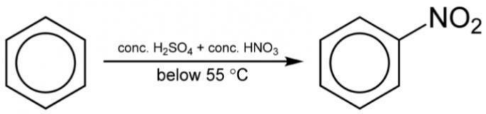


Electrophilic Substituion Reactions of Benzene

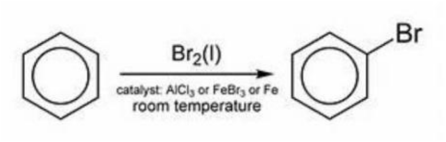
Resonance involved in the benzene ring makes the delocalized electron span effectively over the carbon atoms in the benzene ring. It partially stabilizes the arenium ion too. Partial stability of arenium ion makes benzene highly prone to electrophilic substitution reactions. An electrophilic substitution reaction of benzene is the one where an electrophile substitutes the hydrogen atom of benzene. As the aromaticity of benzene is not disturbed in the reaction, these reactions are highly spontaneous in nature. Basic examples of electrophilic substitution reaction of benzene are nitration, sulfonation, halogenation, Friedel Craft’s alkylation and acylation, etc.



Nitration of Benzene: Benzene reacts with nitric acid at 323-333k in presence of sulphuric acid to form nitrobenzene. This reaction is known as nitration of Benzene.

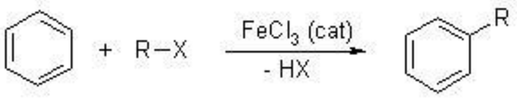


Halogenation of Benzene: Benzene reacts with halogens in presence of Lewis acid like $FeCl_3$, $FeBr_3$ to form aryl halides. This reation is termed as halogenation of benzene.



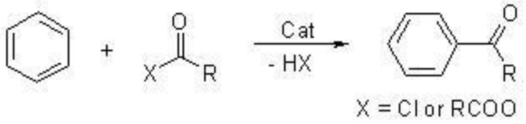
Friedel-Crafts Alkylation

This Lewis acid-catalyzed electrophilic aromatic substitution allows the synthesis of alkylated products via the reaction of arenes with alkyl halides or alkenes. Since alkyl substituents activate the arene substrate, polyalkylation may occur. A valuable, two-step alternative is Friedel-Crafts Acylation followed by a carbonyl reduction.



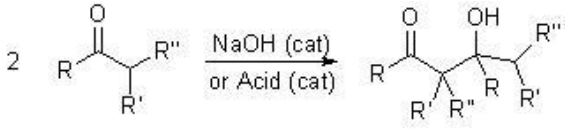
Friedel-Crafts Acylation

This electrophilic aromatic substitution allows the synthesis of monoacylated products from the reaction between arenes and acyl chlorides or anhydrides. The products are deactivated, and do not undergo a second substitution. Normally, a stoichiometric amount of the Lewis acid catalyst is required, because both the substrate and the product form complexes. The Friedel-Crafts Alkylation may give polyalkylated products, so the Friedel-Crafts Acylation is a valuable alternative.



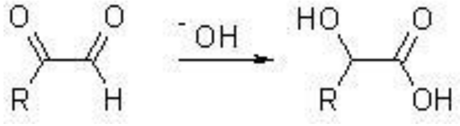
Chemistry and mechanism of some selective organic name reactions: Aldol condensation

'Aldol' is an abbreviation of **ald**ehyde and alcoh**ol**. When the enolate of an aldehyde or a ketone reacts at the α-carbon with the carbonyl of another molecule under basic or acidic conditions to obtain β-hydroxy aldehyde or ketone, this reaction is called Aldol Reaction.



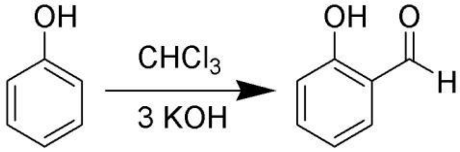
Cannizaro reaction

This redox disproportionation of non-enolizable aldehydes to carboxylic acids and alcohols is conducted in concentrated base. α-Keto aldehydes give the product of an intramolecular disproportionation in excellent yields.



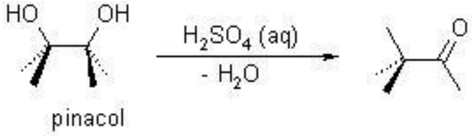
Reimer-Teiman reaction

The Reimer-Tiemann reaction is an organic reaction used to convert a phenol to o-hydroxy benzalde-hyde using chloroform, a base, and acid work-up.



Pinacol-pinacolone rearrangement

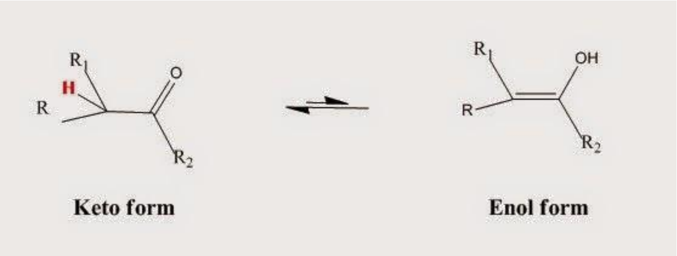
In the conversion that gave its name to this reaction, the acid-catalyzed elimination of water from pinacol gives *t*-butyl methyl ketone.



Keto-enol tautomerism

For most compounds in organic chemistry all the molecules have the same structure – even if this structure cannot satisfactory represented by a Lewis formula – but for many compounds there is a mixture of two or more structurally distinct compounds that are in rapid equilibrium. This phenomenon is called tautomerism.

Tautomerism is the phenomenon that occurs in any reaction that simply involves the intramolecular transfer of a proton. An equilibrium is established between the two tautomers (structurally distinct compounds) and there is a rapid shift back and forth between the distinct compounds.



Benzoin condensation

The Benzoin Condensation is a coupling reaction between two aldehydes that allows the preparation of α-hydroxyketones. The first methods were only suitable for the conversion of aromatic aldehydes.