# Chemistry 30A Review Sheet

Tau Beta Pi – Boelter 6266

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1. General Chemistry Topics

1.1 Electronegativity

Electronegativity is a measure of how much an atom attracts electrons. Electronegativity increases left to right across a period, and bottom to top down a group.

1.2 VESPR and Hybrid Orbitals

<table>
<thead>
<tr>
<th>Number of Bonded Electron Pairs</th>
<th>Number of Lone Pairs</th>
<th>Bond Angle (degrees)</th>
<th>Electron Pair Molecular geometry</th>
<th>Shape of the molecule</th>
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<tr>
<td>2</td>
<td>0</td>
<td>180</td>
<td>Linear</td>
<td>Linear</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>120</td>
<td>Trigonal planar</td>
<td>Bent</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>109.5</td>
<td>Tetrahedral</td>
<td>Bent</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>120</td>
<td>Trigonal planar</td>
<td>Trigonal planar</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>109.5</td>
<td>Tetrahedral</td>
<td>Trigonal pyramidal</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>109.5</td>
<td>Tetrahedral</td>
<td>Tetrahedral</td>
</tr>
</tbody>
</table>

1.3 Resonance

Resonance structures must:
- a) Both have the same number of valence electrons and obey the laws of covalent bonding (no more than 8 valence electrons in the valence shell of a second period element)
- b) Position of nuclei must be the same and only may differ in distribution of valence electrons
- c) Have the same numbers of paired and unpaired electrons

What makes one resonance structure better than another?
- a) Complete valence shells
- b) Separation of unlike charges
- c) Maximum number of covalent bonds
- d) Negative charge positioned on the most electronegative atom and positive charge positioned on the most electropositive atom

2. Isomerism and Chirality

2.1 Terminology

*Constitutional Isomers* - isomers with different connectivity but different connectivity and same formula.
Constitutional isomers do not share the same physical properties
*Stereoisomers* - isomers with same connectivity but different orientation of the atoms in space
Enantiomers - stereoisomers that are non-superimposable mirror images. Enantiomers have the same physical properties except for the bending of polarized light. Enantiomers react differently with other chiral molecules but react in the same way with achiral molecules.

Diastereomers - stereoisomers that are not mirror images of each other. Diastereomers are different compounds with different chemical and physical properties.

Stereocenter - an atom in a molecule around which exchanging two groups creates a different stereoisomer. The maximum stereoisomers available for any chiral molecule is \(2^n\), where \(n\) is the number of chiral centers.

Chiral molecule - a molecule that is not superimposable on its mirror image.

Achiral molecule - a molecule that has at least one element of symmetry.

Mesocompound - an achiral molecule with an even number of chiral centers and a plane of symmetry.

Racemic mixture - an equimolar mixture of both enantiomers of a molecule. The mixture is not optically active because it contains equal amounts of each enantiomer.

2.2 Differentiating between diastereomers and enantiomers using the R.S. Convention

First, locate a chiral center, identify the substituents and assign them priority from 1 (highest) to four (lowest). Priority is determined by atomic number (highest atomic number is the highest priority). If the substituents are chains, assign priority based on the first point of divergence. Also note that atoms participating in double or triple bonds are considered to be bonded to an equivalent number of similar atoms by single bonds (example: a carbon double bonded to another carbon is considered to be bonded to two carbon atoms).

Second, orient the molecule so the group of lowest priority is pointing away. Do this by rotating the atom, or creating a fake molecule where the lowest priority group points towards the back. The configuration of the actual molecule is opposite the configuration of this fake molecule.

Third, read the groups in order from highest to lowest priority. If they read in the counterclockwise direction, the molecule is in the ‘S’ configuration; if they read in the clockwise direction, the molecule is in the ‘R’ configuration.

If the two molecules are mirror images of each other (all chiral centers flip from R to S or S to R) they are enantiomers. If some of the chiral centers change configuration and others do not, the molecules are diastereomers. If the molecule has a plane of symmetry and an even number of chiral centers, it is achiral.

3. Acids and Bases

3.1 Terminology

Bronstad-Lowrey Acid - proton donor

Bronstad-Lowrey base - proton acceptor

Conjugate base - species formed from an acid when it donates a proton to a base. A stronger base corresponds to a weaker, more stable conjugate acid.

Conjugate acid - species formed from a base when it accepts a proton from an acid. A stronger acid corresponds to a weaker, more stable conjugate base.
3.2 A.R.I.O Method of Evaluating Acid/Base Stability

‘A’ stands for ‘Atom’
Consider the electronegativity and size of the atom.
The greater the electronegativity of the atom that will bear the negative charge following proton donation, the more strongly the electrons are held. The anion is more stable, and the acid is stronger. Used to compare atoms across a period.
The larger the atom bearing the negative charge, the more stable the anion is (because larger atoms have larger electron clouds and are more polarizable) and the stronger the acid.

‘R’ stands for ‘Resonance’
Resonance delocalizes negative charge in the base, making the base more stable and its conjugate acid more acetic.

‘I’ stands for ‘Inductive Effect’
The inductive effect is the polarization of electron density around one covalent bond by the electronegativity of a neighboring covalent bond. Electron donating groups (like methyl groups) induce a partial negative charge on whatever atom they are bound to. Electron withdrawing groups (all electronegative atoms) induce partial positive charges on whatever atoms they are bound to. These partial charges can stabilize or destabilize anions The inductive effect is weak, and falls off rapidly with increasing distance.

‘O’ stands for ‘Orbital Hybridization’
For anions differing only in the hybridization of the charged atom, the greater the percent ‘s’ character in the hybridization (i.e. the more bonds) the more stable the anion (see diagram below). Therefore, triple bonds are more stable than double bonds and single bonds.

![Diagram of hybridization]

4. Alkane Nomenclature

First, name the parent chain (in cycloalkanes, this is the number of carbons in the ring).
Start with the prefix. The prefix indicates the length of the longest carbon chain in the atom, or the parent chain (see table below).

<table>
<thead>
<tr>
<th>Number of atoms in parent chain</th>
<th>Prefix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Meth</td>
</tr>
<tr>
<td>2</td>
<td>Eth</td>
</tr>
<tr>
<td>3</td>
<td>Prop</td>
</tr>
<tr>
<td>4</td>
<td>But</td>
</tr>
</tbody>
</table>
Next, the infix indicates the type of bond. In this case, since the molecule is an alkane, it only has single bonds, and the infix is -an-.

Finally, the suffix is used to denote what type of compound the alkane is (see table below).

<table>
<thead>
<tr>
<th>Type</th>
<th>Suffix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>-e</td>
</tr>
<tr>
<td>Alkane</td>
<td>-ane</td>
</tr>
<tr>
<td>Alcohol</td>
<td>-ol</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>-al</td>
</tr>
<tr>
<td>Amine</td>
<td>-amine</td>
</tr>
<tr>
<td>Ketone</td>
<td>-one</td>
</tr>
<tr>
<td>Carboxylic Acid</td>
<td>-oic acid</td>
</tr>
</tbody>
</table>

Next, number the parent chain, giving the first substituent the lowest number possible. This will allow you to locate the position of all substituents along the parent chain. For cycloalkanes, start numbering from the substituent that comes first alphabetically.

Locate and identify all substituents. Place the names of the substituents, along with its numerical positions on the parent chains, before the name of the parent chain alphabetically. Separate the substituents with hyphens.

Below is a list of common substituent groups, and their names.
5. Alkane Conformations and Strain

5.1 Conformations

*Staggered conformation* - conformation a that has the atoms or groups on one carbon as far apart as possible from the atoms or groups in an adjacent carbon. There are two types:

a) *Anti conformation* - staggered conformation where groups lie at a dihedral angle of 180 degrees.

![Anti conformation diagram](image)

b) *Gauche conformation* - staggered conformation about a carbon-carbon single bond in which groups lie at a dihedral angle of 30 degrees.

![Gauche conformation diagram](image)

*Eclipsed conformation* - conformation where atoms or groups on one carbon are as close as possible to the atoms or groups on an adjacent carbon. That is, groups lie at dihedral angles of 0 degrees.

![Eclipsed conformation diagram](image)

*Cyclohexane chair conformation* - This conformation is the most stable conformation of a cyclohexane ring, and is generally considered to have no strain. Around the cyclohexane ring, there are six axial and six equatorial substituents, as shown below. In general, it is better if larger groups are equatorial.

![Cyclohexane chair conformation diagram](image)

The chair has two equivalent conformations, which switch in a process called a “chair flip”. When a chair flips, substituents pointing up stay pointing up and vise versa. Axial substituents become equatorial and equatorial substituents become axial. All substituents are moved over one position. An example chair flip is shown below.
5.2 Types of Strain

*Torsional* - arises when non-bonded atoms separated by three bonds are forced to form a staggered conformation from an eclipsed conformation.

*Steric* - arises when atoms separated by four or more bonds are forced closer together than their atomic radii will allow.

*Ring strain* - arises when a bond angle is either compressed or expanded compared to its optimal value.

6. Alkenes

6.1 Physical Properties and Conformations

Alkenes are nonpolar compounds that are insoluble in water, but soluble in other alkenes and non-polar solvents. Alkenes only experience London Dispersion intermolecular attractive forces. Alkenes can be classified as cis (matching substituents are on the same side of the molecule) and trans (matching substituents are on opposite sides of the molecule), E (groups of higher priority are on opposite sides of the double bond), and Z (groups of higher priority are on the same side of the double bond).

6.2 Nomenclature

First, number the longest chain of carbon atoms that contains the double bond in the direction that gives the double bond the lowest number. Next, locate the double bond by the number of its first carbon. Number the carbons, locate and name substituents, locate the double bond and name the main carbon using the following structure:

(E or Z)-(substituent position)-(substituent name)-(substituent position)-(substituent name)-...-(location of double bond)-(name based on number of carbons in parent chain)

6.3 Reactions

*Electrophilic addition of H-X*: Addition of H and a halogen across the double bond. The addition follows Markovnikov’s rule, that is, the hydrogen adds to the carbon of the double bond that has the greater number of hydrogens attached to it already; the halogen adds to the other side of the double bond.
Addition of water (acid, water); addition of H and OH across the double bond. The H is added to the less substituted side of the double bond, and the OH is attached to the more substituted side of the double bond. The reaction is acid catalyzed.

Addition of Cl or Br: (Cl or Br₂ and CH₂Cl₂): Anti-addition of two bromine or two chlorine atoms across the double bond.

Addition of HOCl and HOBr: Anti-addition of OH and Br or Cl across the double bond in an analogous mechanism to the one for Cl or Br₂ addition. The OH is added to the more substituted side of the double bond, and the Cl or Br is added to the less substituted side of the double bond.

Oxymercuration/Reduction (1. Hg(OAc)₂, H₂O; 2. NaBH₄): Anti-addition of OH and H across the double bond. The OH group is added to the more substituted side of the double bond and the H is added to the less substituted side.

Hydroboration/Oxidation (1. BH₃, 2. H₂O₂, H₂O): Syn-addition of H and OH across the double bond. The addition does not follow Markovnikov’s rule; the hydrogen is added to the more substituted side of the double bond and the OH is added to the less substituted side.

Oxidation with OsO₄ (OsO₄, NaHSO₄, H₂O): Syn-addition of two OH groups across the double bond.
Oxidation with \( O_3 \) (O₃, Me₂S): The double bond is cleaved into two carboxylic acids.

Hydrogenation/Reduction (H₂Pd or H₂Pt or H₂Ni): The double bond is reduced to a single bond via syn addition of two hydrogens across the double bond.

7. Alkynes

7.1 Physical and Chemical Properties

Like alkenes, the only intermolecular forces acting on alkynes are London Dispersion forces. Alkynes are more acidic than alkanes and alkenes (the pH of a terminal alkyne is approximately 2.5). Terminal alkynes can be deprotonated by NaNH₂, NaH or LDA.

7.2 Nomenclature

Use the infix –yn- to show the presence of a carbon-carbon triple bond. The format of the name is as follows:

(position of substituent)-(substituent)-...-(position of triple bond)-(longest carbon chain)

7.3 Reactions

Addition of \( Br_2 \): Bromine is added across the triple bond to form an alkene with Bromine on either side of the double bond. If \( Br_2 \) is present in excess, the reaction will repeat to form an alkane bonded to four bromine atoms.
Addition of HBr: Hydrogen and bromine are added across the triple bond to form an alkene connected to one hydrogen and one bromine. The reaction follows Markovnikov’s rule, and the hydrogen will add to the less substituted side of the triple bond. If HBr is present in excess, the reaction will repeat to form an alkane bonded to two Bromine molecules.

Hydroboration:

a) Internal alkyne (BH₃, H₂O₂, NaOH): Addition of H and OH across the triple bond.

b) Terminal alkyne [(sia)BH, H₂O₂, NaOH]: Addition of H and OH across the triple bond. The addition does not follow Markovnikov’s rule; the hydrogen is added to the more substituted side of the triple bond.

Hydroboration-Proteolysis [internal alkyne, BH₃/THF, (CH₃COO)₃]: The internal alkyne is reduced to an internal alkene via addition of H₂ across the double bond.
Dissolving Metal Reduction [internal alkyne, Na⁺, NH₃ (l)]: Reduction of the internal alkyne to an trans-alkene.

Hydration (H₂O, H₂SO₄, HgSO₄): Terminal alkynes are transformed into ketones.

Reduction of Alkynes:

a) H₂Pd reduces the alkyne to an alkane.

b) H₂Pd and Lindlar’s Catalyst reduce the alkyne to a cis alkene
8. Haloalkanes

8.1 Terminology

*Alkyl Halide* – compound containing a halogen covalently bonded to an sp\(^3\) hybridized carbon  
*Vinylic Halide* – compound containing a halogen bonded to an sp\(^2\) hybridized carbon  
*Radical* – chemical species that contains one or more unpaired electrons formed by hemolytic bond cleavage. Radical carbons are slightly electron deficient and stabilized by attached methyl group. Different radicals have different stabilities, as shown below:

<table>
<thead>
<tr>
<th>Name of Radical</th>
<th>Type of Radical</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂⁺</td>
<td>Allylic</td>
</tr>
<tr>
<td>Alkyl</td>
<td>Allylic</td>
</tr>
<tr>
<td>Benzylic</td>
<td>Allylic</td>
</tr>
<tr>
<td>Tert-Butyl</td>
<td>3°</td>
</tr>
<tr>
<td>Isopropyl</td>
<td>2°</td>
</tr>
<tr>
<td>Ethyl</td>
<td>1°</td>
</tr>
<tr>
<td>Methyl</td>
<td>Methyl</td>
</tr>
<tr>
<td>Vinyl</td>
<td>Vinylec</td>
</tr>
<tr>
<td>CH₃⁺</td>
<td>Methyl</td>
</tr>
</tbody>
</table>

8.2 Reactions

*Halogenation of Alkanes* (light and heat): Yields a mixture of halogenated alkanes. The regioselectivity is higher for bromine than chlorine, which is accounted for by the stability of the alkyl radicals. The addition of chlorine is an exothermic process, so the transition state resembles the reactants. As a result, in the transition state the carbon has very little radical character and radical stability has a small influence on regioselectivity. The addition of bromine is an endothermic process, so the transition state resembles the products. As a result, in the transition state the carbon has high radical character and radical stability has a large influence on regioselectivity.
**Allylic Halogenation** (heat, NBS): Results in the bonding of a halogen to an allylic carbon. An allylic carbon is a carbon adjacent to a carbon-carbon double bond. When adding bromine, NBS is used instead of Br₂ to prevent di-bromination from occurring.

**Radical Addition of HBr to Alkenes** (alkene, HBr, peroxide): Peroxides create radicals. The HBr adds across the double bond in a non-Markovnikov manner, with the bromine on the less substituted side of the double bond. Note that if no peroxides are present, the bromine will be added to the more substituted side of the double bond.
9. S\textsubscript{1}, S\textsubscript{2}, E1, E2

9.1 S\textsubscript{2} Nucleophilic Substitution

Mechanism: one step, both reactants are involved in the transition state of the rate determining step. The nucleophile attacks from the back.

Stereochemistry: for S\textsubscript{2} reactions at a chiral center the result is an inversion of the chiral center because the nucleophile attacks from the back and pushes all other substituents to the other side. Note: depending on the nucleophile you may or may not have an inversion of ‘R’ and ‘S’ at the chiral center.

9.2 S\textsubscript{1} Nucleophilic Substitution

Mechanism: two steps, the bond between the carbon and the leaving group is entirely broken before a new bond is formed with the nucleophile.

Stereochemistry: R and S enantiomers are both formed; the product is racemic.

9.3 E2 Elimination

Mechanism: breaking of the carbon-leaving group bond and the formation of the carbon-hydrogen bond occurs at the same time. Note that this type of elimination requires the presence of a strong base.

Regioselectivity: if a strong base is used the more substituted alkene will be the major product. If a strong, sterically hindered base is used, the major product will be the less substituted alkene because the base will deprotonate the most accessible hydrogen.

Stereochemistry: this type of elimination is most favorable when the hydrogen and leaving group are oriented antiperiplanar (or 180 degrees apart)
9.4 E1 Elimination

Mechanism: the bond between the carbon and the leaving group breaks before the base deprotonates the alkane, so a carbocation is formed.
Regioselectivity: the major product is the most stable alkene, because the base is able to choose which proton to deprotonate because the reaction occurs in two steps.
Stereochemistry: the alkene can be either cis or trans. Since the reaction occurs in two steps, the base will deprotonate whichever hydrogen allows for formation of the most stable isomer.

9.5 Which mechanism?

If you have a primary alkyl group:
   a) S₂ and E₁ are NOT POSSIBLE because primary carbocations are unstable and will not form
   b) Strong sterically hindered base -> E₂
   c) Strong unhindered base that is an ammide anion will result in E₂. If your base is a good nucleophile, (OH, acetylide, methoxide, RS, CN, I, N₃) you will have S₂. If your base is a moderate nucleophile you will have S₂

If you have a secondary alkyl group:
   a) Strong bases (sterically hindered or unhindered) will result in E₂
   b) Weak bases that are good/moderate nucleophiles will result in S₂
   c) Weak bases that are bad nucleophile and in a polar protic solvent will result in E₁ and S₁

If you have a tertiary alkyl group:
   a) S₂ is not possible because a tertiary carbocation is too sterically hindered
   b) Strong bases will result in E₂
   c) Polar Protic solvents will facilitate S₁ and E₁