

CHEM202 – Review of CHEM201

This review is intended to help you prepare for the topics that we will be covering in CHEM202.

Be sure to review the in chapter examples and exercises associated with the bullet points below.

Particular attention should be paid to bullet points in **bold**.

Terms in *italics* should be defined.

The term 'understand' means that the related concept should make sense to you such that if it comes up in context you will immediately understand its relevance.

The term 'know' means that the related concept should make sense to you and that you should have the related information memorized for immediate recall.

Chapter 1 – Structure

- Know bonds formed (below and p 2) and be able to count the a stable octet (except H):
 - carbon (C) = 4 bonds
 - neutral nitrogen (N) = 3 bonds + 1 lone pair
 - neutral oxygen (O) = 2 bonds + 2 lone pairs
 - halogens (F, Cl, Br, I) = 1 bond + 3 lone pairs
 - hydrogen (H) = 1 bond
- Know what is a *heteroatom* and a *functional group* (p 3).
- Know *aliphatic* vs. *aromatic* (p 10) and structures of benzene (PhH), toluene (PhMe), aniline (PhNH₂), phenol (PhOH), benzoic acid (PhCO₂H) and benzaldehyde (PhCHO) (p 11).
- Know how to use R and Ar group designations (p 14).
- Know types of *constitutional isomer*: *skeletal*, *positional* and *functional* (p 19).
- **Be able to obtain a structure from an IUPAC name** and understand the significance of the naming field designations (p 9):
 - 1st Field – *substituent*
 - 2nd Field – *compound root*
 - 3rd Field – *multiple-bond index*
 - 4th Field – *principal functional group*
- **Know all from Tables R1.1 – R1.3 below. Use flash cards if necessary.**

Chapter 2 – Bonding

- Know how to draw *Lewis structures* (p 35) and how to assign formal charges (p 38).
- Know general *electronegativity* trends (Fig 2.2, p 40) and how to assign *polarity* ($\delta+$ and $\delta-$) (p 41).
- Understand the distinction between *electronegativity* and *polarizability* (p 41).
- **Important: "In general, the bonds between carbon and any element in groups 15-17 (VA)-(VIIA) are considered to be polar, with the carbon atom bearing the $\delta+$ designation. For bonds between carbon and a metal atom, including those of the transition metals, the carbon atom is $\delta-$ " (p 41).**
- Know how to show delocalization of electrons using *resonance structures* (p 43).
- Know how *hydrogen bonding* works (p 67) and understand its contribution to boiling point (Table 2.7).
- Understand the distinction between *inter-* and *intramolecular* (p 67).

Chapter 3 – Conformations

- Understand the distinction between *isomer* and *conformer* (p 77).
- Know how to draw a *Newman projection* (p 78).
- Understand the distinction between *eclipsed* and *staggered* conformers and how these conformers are expressed via *dihedral angle* (p78).
- Understand the distinction between *torsional strain* (p 79 and 83) and *steric strain* (p 80).
- Understand the distinction between *syn*, *anti* and *gauche* conformers (p 80).
- Understand *angle* (Baeyer) *strain* (p 82).
- Know the shape of the cyclopentane ring (p 83).
- **Important: “The six-membered ring of cyclohexane is the only ring with fewer than 14 carbons that can adopt a conformation essentially free from strain” (p 84). Cyclohexane is special!**
- Understand the distinction between *chair* and *boat* conformers of cyclohexane (p 84).
- Understand the distinction between *axial* and *equatorial* substituents and how this relationship can be changed by a *ring-flip* (p 85).
- Understand *1,3-diaxial interactions* (p 88).
- Understand the *geometric isomer* (p 106) distinction between *cis* and *trans* isomers (p 92).
- Understand *conformationally biased* as it relates to *tert-butyl* substituted cyclohexane (p 97).

Chapter 4 – Stereochemistry

- Understand the distinction between *stereoisomer* and *constitutional isomer* laid out in Fig. 4.1 (p 106).
- Understand the distinction between *cis* and *trans* isomers of alkenes with 2 H atoms (p 106).
- Understand the distinction between *E* and *Z* isomers of alkenes with less than 2 H atoms (p 107).
- Understand the *Cahn-Ingold-Prelog convention* for prioritization of stereochemical substituents (NOT the same as IUPAC prioritization in table R1.2 or 1.1) (p 107).
- **Know the definition of *enantiomer*** and understand the distinction between *chiral* and *achiral* (p 111).
- Understand the definitions in Table 4.1 (p 113).
- Understand the relationship between *chiral* and *optically active* (p 114).
- **Know how to assign (*R*) and (*S*) configuration to a stereocenter (p 116).**
- **Know the definition of *diastereomer* and understand Figure 4.6 (p 123).**
- Understand *meso compounds* (p 125).

Chapter 5 – Reactions and Mechanisms

- Understand the 7 reaction types: *proton-transfer*, *substitution*, *addition / elimination*, *oxidation / reduction* and *rearrangement*.
- **Understand how organic reactivity is largely based on matching polarities ($\delta+$ and $\delta-$) (p 142).**
- **Understand the Bronsted-Lowry definition of *acid* and *base* (eq. 5.1) and know the definition of pK_a (p 143).**
- **Know the approximate pK_a values in Table 5.1 for compounds with $pK_a = 25$ or less.**
- **Know the distinction between *electrophile* and *nucleophile* (p 155).**
- Understand the relationship between *transition state* and reactants / products (p 159).
- Understand *LeChatelier's Principle* (p 162).

Chapter 6 – Substitution Reactions of Alkyl Halides

- **Understand the factors that govern *leaving group* quality (p178).**
- **Understand the factors that govern nucleophile quality (p 179).**
- **Know what distinguishes an S_N1 from and S_N2 reaction (p 182).**
- Understand the factors that govern the order of *carbocation* stability (p 189), S_N1 reaction rate (p 191) and S_N2 reaction rate (p 197).
- Understand the distinction between *retention of configuration*, *inversion of configuration* and *racemization* (p 196).
- Understand what is meant by a *concerted* mechanism (p 196).
- **Know the significance of putting a structure in brackets in a mechanism (p 197).**

Chapter 7 – Substitution Reactions of Alcohols and Related Compounds

- Understand the factors that govern relative leaving group abilities of sulfonates relative to halides (p 214).
- Understand why S_N2 substitution of an alcohol as a sulfonate gives inversion of configuration while conversion of the alcohol to a halide (using PBr₃ or SOCl₂) prior to substitution gives overall retention of configuration (pp 214-218).
- Understand why a nucleophile adds to the less-hindered position of an epoxide under basic conditions but adds to the more substituted position under acidic conditions (p 224).

Chapter 8 – Elimination Reactions

- **Know what distinguishes an E1 (p 240) from an E2 reaction (p 246).**
- Understand the regioselectivity of the E1 (p 241) and E2 reaction (p 247).
- Understand the distinction between *thermodynamic* and *kinetic control* (p 242).
- Understand the factors that contribute to the relative stability of alkenes (p 244).

Chapter 9 – Addition Reactions of Alkenes and Alkynes

- Understand the regioselective distinction between Markovnikov alkene hydration (p 269) and anti-Markovnikov alkene hydroboration-oxidative hydrolysis (p 289).
- Understand how hydration or hydrohalogenation of a double bond is the opposite of dehydration or dehydrohalogenation (p 270).
- **Understand why the example halohydrin reaction (p 272) and hydroboration reaction (p 287) is regioselective, stereospecific and NOT enantioselective.**
- Understand the formation of an alkylborane via a four-centered transition state (p 286).

Chapter 10 – Addition Reactions of Conjugated Dienes

- Understand the distinction between isolated, *conjugated* and cumulated double bonds (p 304).
- Understand the distinction between 1,2- and 1,4-addition to conjugated dienes (p 313).

Chapter 11 – Oxidation and Reduction Reactions

- Know how the number of heteroatoms attached to a carbon or nitrogen and the presence of double or triple bonds affects the *oxidation level* of that carbon or nitrogen (p 332).
- Understand why epoxides obtained by direct epoxidation have the same stereochemistry as those obtained from a halohydrin (p345).
- Understand how alcohol oxidations similar to the E2 reaction (p 346-349).
- Understand that an *ylide* is a carbanion center bonded directly to a positively charged heteroatom (p 347).

Chapter 12 – Free Radical Reactions

- Understand how radicals are formed by homolysis (p 364).
- Understand the three parts of a radical chain reaction: *initiation*, *propagation* and *termination* (p 364).
- Understand the distinction between *hydrogenation* (p 334) and *hydrogenolysis* (p 374).

Chapter 13 – Proton and Carbon NMR Spectroscopy

- Know how to determine if atoms are *magnetically equivalent* (p 399).
- Understand *chemical shift* (p 401), *integration* (p 406) and *spin coupling* (p 408) as they apply to NMR spectroscopy.
- We will revisit NMR data interpretation, also call structural elucidation, during the first week of class.

Table R1.1 (similar to Table 1.3, p 10). Memorize this table. Use the mnemonic if it helps.

Structure	Mnemonic	Name (R = H)	Substituent (1 st Field)	Compound Root (2 nd Field)
RCH ₃	ma	methane	methyl-	-meth-
RCH ₂ CH ₃	eats	ethane	ethyl-	-eth-
R(CH ₂) ₂ CH ₃	pot	propane	<i>n</i> -propyl-	-prop-
RCH(CH ₃) ₂	-	-	<i>iso</i> -propyl-	-
R(CH ₂) ₃ CH ₃	brownies	butane	<i>n</i> -butyl-	-but-
RC(CH ₃) ₃	-	-	<i>tert</i> -butyl-	-
R(CH ₂) ₄ CH ₃	pa	pentane	<i>n</i> -pentyl-	-pent-
R(CH ₂) ₅ CH ₃	has	hexane	<i>n</i> -hexyl-	-hex-
R(CH ₂) ₆ CH ₃	hash	heptane	<i>n</i> -heptyl-	-hept-
R(CH ₂) ₇ CH ₃	or	octane	<i>n</i> -octyl-	-oct-
R(CH ₂) ₈ CH ₃	no	nonane	<i>n</i> -nonyl-	-non-
R(CH ₂) ₉ CH ₃	dope	decane	<i>n</i> -decyl-	-dec-

Table R1.2 (similar to Table 1.1, p 4). Ordered vertically by IUPAC naming priority. Columns 'Structure', 'Condensed' and 'Name' should be memorized. In other words, you should know the name if given the structure or condensed form and vice versa.

Structure	Condensed	Name	Substituent (1 st Field)	Principal FG (4 th Field)
	RCO ₂ H or RCOOH	carboxylic acid	carboxy-	-oic acid (-carboxylic acid)
	RCO ₂ R' or RCOOR'	ester	-	-oate (-carboxylate) alkyl(R')alkan(R)oate
	RCOX (X = Cl, Br, I)	acid halide	-	-oyl halide
	RCONH ₂	amide	-	-amide (-carboxamide)
	RCN	nitrile	cyano-	-nitrile (-carbonitrile)
	RCHO	aldehyde	formyl-	-al (-carbaldehyde)
	RCOR'	ketone	acetyl- (R = Me)	-one
see Table 1.3	R-OH	alcohol	hydroxy-	-ol
see Table 1.3	R-SH	thiol	mercapto-	-thiol
see Table 1.3	R-NH ₂	amine	amino-	-amine
	-	alkene	vinyl- (ethenyl-)	-ene
	-	alkene	allyl- (2-propenyl-)	-ene
	-	alkyne	alkynyl-	-yne
	-	alkyne	propargyl-	-yne
	ROR'	ether	alkoxy- (by alkyl name)	ether
	-	benzene	phenyl- (aryl-)	benzene
	-	toluene (R = H)	benzyl-	benzene
see Table 1.3	R-X	halogen	fluoro- chloro- bromo- iodo-	N/A
see Table 1.3	R-NO ₂	nitro	nitro-	N/A

Table R1.3 (similar to structures on p 20). Memorize all. For example, you should be able to correctly draw the structure of a primary, secondary or tertiary amine.

	Primary (1°)	Secondary (2°)	Tertiary (3°)	Quaternary (4°)
alkane	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{H} \end{array}$ methyl	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$ methylene	$\begin{array}{c} \text{H} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$ methine	$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{R} \end{array}$
alcohol, (thiol, halide, nitro)	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{OH} \end{array}$	$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{OH} \end{array}$	$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{OH} \end{array}$	N/A
amines	$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{N} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{N} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{N} \\ \\ \text{R} \end{array}$	N/A
amides	$\begin{array}{c} \text{O} \\ \\ \text{C} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{C} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{R} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \\ \text{C} \\ \diagdown \quad \diagup \\ \text{N} \quad \text{R} \\ \\ \text{R} \end{array}$	N/A