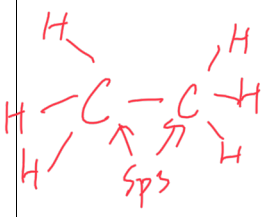
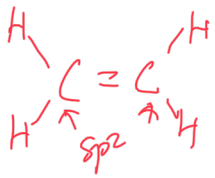
Chapter 3: Alkanes and Cycloalkanes

3.1 Hydrocarbons and Drawing Organic Molecules

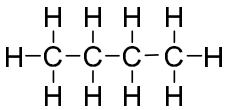
Hydrocarbons are non-polar compounds that contain only carbon and hydrogen atoms. Hydrocarbons can be divided into the following classes of saturated and unsaturated compounds:

	Alkanes	**Alkenes**	**Alkynes**	**Arenes** (aromatic compounds)
Types of C,C bonds	only	one (or more)	one (or more)	one (or more)
Structure				
Saturated/ Unsaturated				
Formula	C_nH_{2n+2}	(for one C=C bond) C_nH_{2n}	(for one C≡C bond) C_nH_{2n-2}	(one aromatic ring) C_nH_n

3.2 Alkanes and Constitutional Isomers

***Alkanes** are saturated hydrocarbons (aliphatic hydrocarbons)* which consist of only carbon and hydrogen atoms connected by single bonds
Alkanes can either be *unbranched (n-alkanes) or branched.*

- 4 bonds to each carbon atom
- All angles are 109.5°
- General formula C_nH_{2n+2}



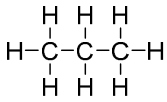
a) Condensed Structures

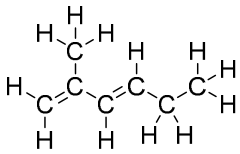
- Simplified versions of expanded structures
- Saves time but still unnecessarily complicated
- Often used by chemical companies in catalogs

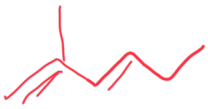
b) Drawing Line-Angle (Skeletal) Stuctures

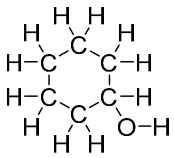
1. Each line represents a bond.
2. Each kink in the line represents a carbon atom unless another functional group is shown explicitly.
3. H atoms bound to C are only shown if needed to give a three-dimensional perspective to the molecule (see below), otherwise they are inferred by assuming that each carbon atom has a full octet.
4. If a carbon atom symbol is written explicitly, then all its substituents including hydrogen must be shown.
5. H is always shown if bonded to an atom different from carbon.

Draw the line-angle structure of the following molecules:









c) Constitutional Isomerism

Isomers are compounds that have the same molecular formula but different structures.

Constitutional Isomers: compounds that have the same molecular formula but differ in the connectivity of the atoms. They usually have different physical and chemical properties.

Branched and unbranched alkanes of the same molecular formula are constitutional isomers.
Example **C_5H_{12}:**

3.3 Nomenclature of Alkanes and Cycloalkanes (The IUPAC System)

a) Unbranched Hydrocarbons

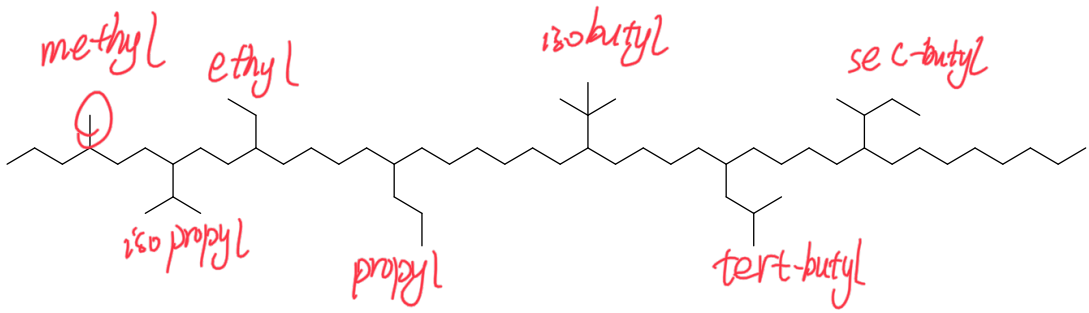
Name	Number of Carbon Atoms	Structure	Name	Number of Carbon Atoms	Structure
Methane	1	CH_4	Undecane	11	$CH_3(CH_2)_9CH_3$
Ethane	2	CH_3CH_3	Dodecane	12	$CH_3(CH_2)_{10}CH_3$
Propane	3	$CH_3CH_2CH_3$	Tridecane	13	$CH_3(CH_2)_{11}CH_3$
Butane	4	$CH_3(CH_2)_2CH_3$	Tetradecane	14	$CH_3(CH_2)_{12}CH_3$
Pentane	5	$CH_3(CH_2)_3CH_3$	Pentadecane	15	$CH_3(CH_2)_{13}CH_3$
Hexane	6	$CH_3(CH_2)_4CH_3$	Hexadecane	16	$CH_3(CH_2)_{14}CH_3$
Heptane	7	$CH_3(CH_2)_5CH_3$	Heptadecane	17	$CH_3(CH_2)_{15}CH_3$
Octane	8	$CH_3(CH_2)_6CH_3$	Octadecane	18	$CH_3(CH_2)_{16}CH_3$
Nonane	9	$CH_3(CH_2)_7CH_3$	Nonadecane	19	$CH_3(CH_2)_{17}CH_3$
Decane	10	$CH_3(CH_2)_8CH_3$	Eicosane	20	$CH_3(CH_2)_{18}CH_3$

b) Branched and Substituted Hydrocarbons

Alkyl Groups (as substituents – a group of atoms that are substituted in place of one hydrogen on the parent carbon chain)
R is used as a general symbol to represent any alkyl group.

Alkane	Alkyl group	Abbreviation	Bond-line
Methane	methyl	Me	~ CH_3
Ethane	ethyl	Et	~ CH_2CH_3
Propane	propyl	Pr (or *n*-Pr)	
	isopropyl	*i*-Pr	
Butane	butyl.	Bu (or *n*-Bu)	
	Secbutyl	*sec*-Bu	
	tert-butyl	*tert*-Bu	
	isobutyl	*i*-Bu	

Identify the alkyl substituents:



c) Primary, Secondary, Tertiary and Quaternary Carbons

Carbons are classified as 1°, 2°, 3°, or 4° based on what is attached:

Primary (1°) carbon	Secondary (2°) carbon	Tertiary (3°) carbon	Quaternary (4°) carbon
R-CH3	R-C(R)(H)-H	R-C(R)(H)-R	R-C(R)(R)-R
bonded to 1 other carbon	bonded to 2 other carbons	bonded to 3 other carbons	bonded to 4 other carbons

R is used as a general symbol to represent any alkyl group.

General 1° alcohol

Specific 1° alcohols

R-CH2OH

d) Guidelines for naming branched-chain alkanes (IUPAC system)

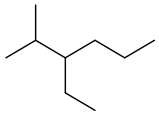
1. Find the parent chain
   - longest continuous carbon chain
   - if two chains of equal length are present, use the one with more substituents

2. Number the atoms in the main chain beginning at the end nearest to the first branch point
   - If substituents are equal distant from each end, begin numbering to give 3rd branch the lowest number
   - If no 3rd branch is present, go by alphabetical order

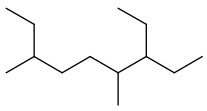
3. Identify and number the substituents

4. Write the name as a single word
   - (-) between a letter and a number
   - (,) between numbers
   - place substituents in alphabetical order
   - use **di-, tri-, tetra-** prefixes to indicate multiple substituents of the same name
   - don't include **di-, tri-, tetra-, *sec-, or tert-*** when alphabetizing
   - do include ***iso-*** when alphabetizing
   - **halogens** are treated the same as alkyl substituents (use fluoro-, chloro-, bromo-, iodo-)

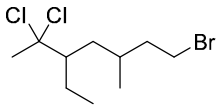
Name the following branched hydrocarbons:



3-ethyl-2-methylhexane



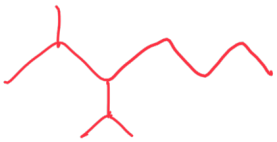
3-ethyl-4,7-dimethylnonane



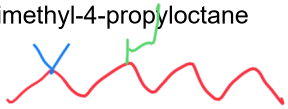
1 bromo-6,6-dichloro-5-ethyl-3-methyl heptane

Draw the following structures:

3-isopropyl-2-methylhexane



2,2-dimethyl-4-propyloctane



4-ethyl-3,4-dimethyloctane

Cycloalkanes

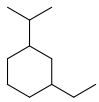
General formula: C_nH_{2n}

Nomenclature of substituted cycloalkanes:

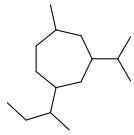
1. Count the number of carbons in the ring and add ***cyclo-*** to the corresponding alkane to make the parent name
2. With substituents, name the substituents and then number from the one with alphabetical priority around the ring to give the second substituent the lowest number

Write the IUPAC names for the following structures:

1,1, dimethyl cyclopentane



1 iso propyl, 3 ethyl cyclo hexane

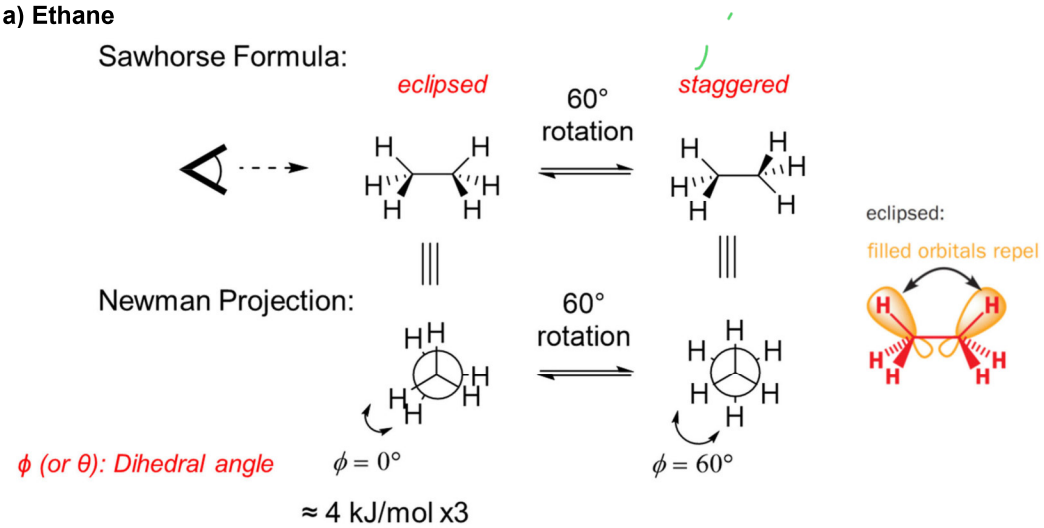


1 sec-butyl, 3 iso propyl, 5 methyl cycloheptane

<u>3.4 Conformational Analysis of *Acyclic Compounds - sp^3-sp^3*</u> *Conformations* – different arrangements of atoms that result from rotation

Conformers (Conformational Isomers) – Isomers that differ from each other by rotation about a single bond

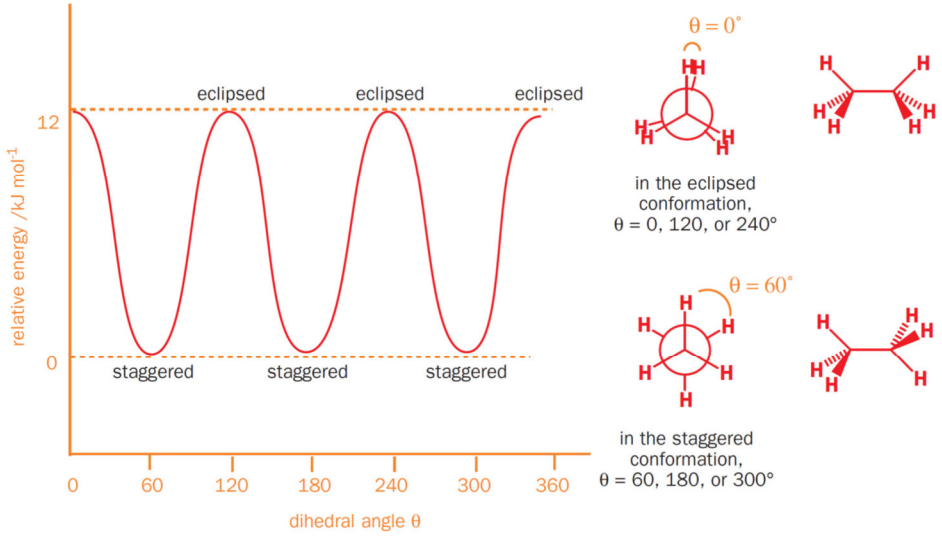
a) Ethane



Barrier to rotation in ethane is 12 kJ/mol - *Torsional energy*

Ethane (continued)

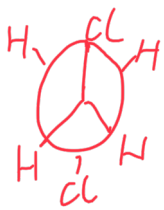
- Barrier to rotation in ethane is 12 kJ/mol - *Torsional energy*
- *Torsional strain* - Repulsion between neighboring bonds (electron clouds) in the eclipsed conformation
- Different conformations arise from rotation about a single (sp^3-sp^3) bond



C–CH2Cl
H2Cl

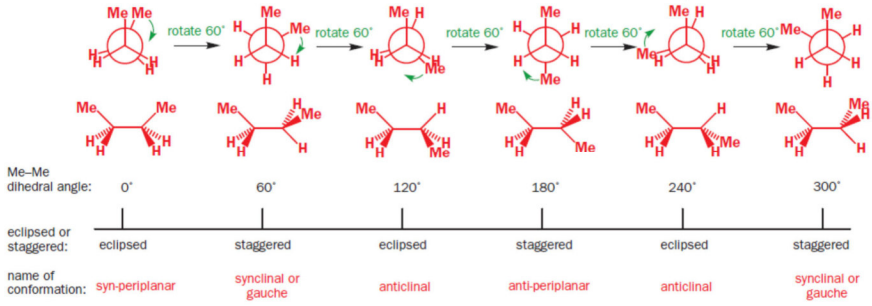
b) 1,2-Dichloroethane (as example)

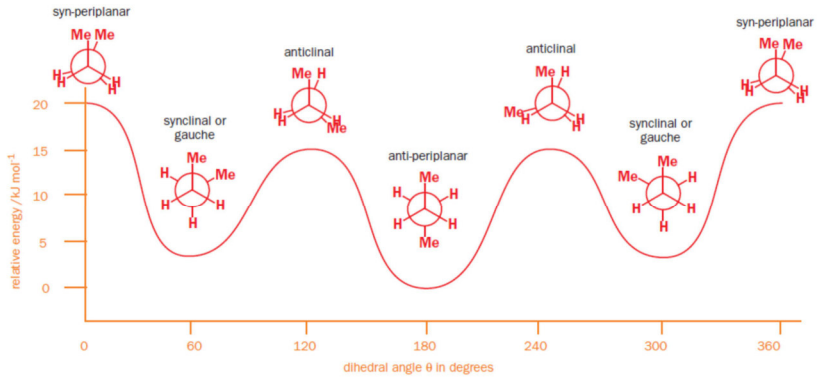
Draw the Newman projections for 1,2-dichloroethane both in its staggered and eclipsed conformation.



Which is the lower energy conformation?

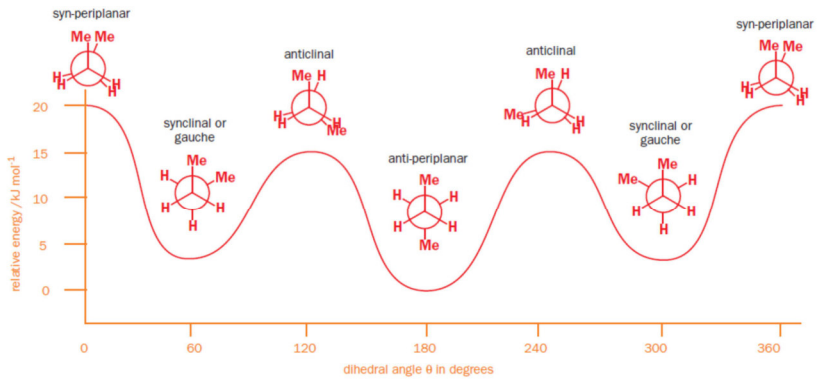
c) Butane





Conformations ≠ Conformers

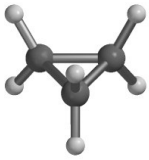
Butane exists in an infinite number of *conformations* (of which only the "extremes" are shown in the energy diagram) but only has three *conformers* (= potential energy minima).



3.5 Conformational Analysis of Cycloalkanes

a) Cyclopropane is symmetrical with 60° bond angles

- Deviation from 109.5° is caused by angle strain results in cyclopropane being more reactive

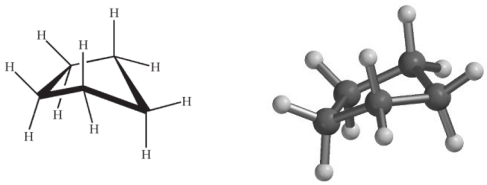


b) Cyclobutane & Cyclopentane are slightly puckered causing smaller angles and some angle strain

- Puckering relieves eclipsing of adjacent C-H bonds

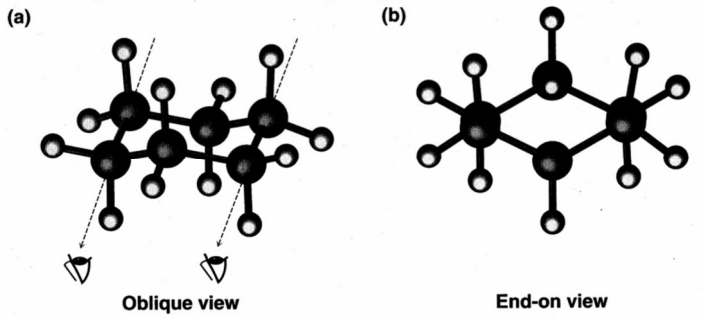
Cyclobutane:

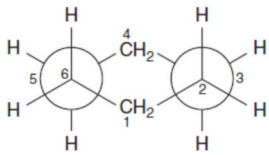
Cyclopentane:



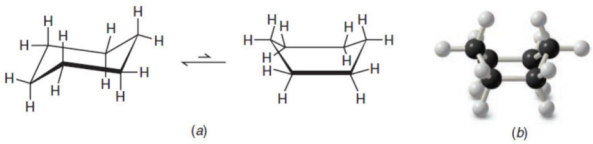
c) Cyclohexane has a **chair conformation** that is strain-free

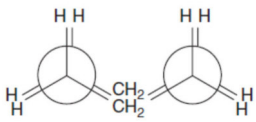
- Bond angles are approx. 109.5°
- All adjacent C-H bonds are staggered





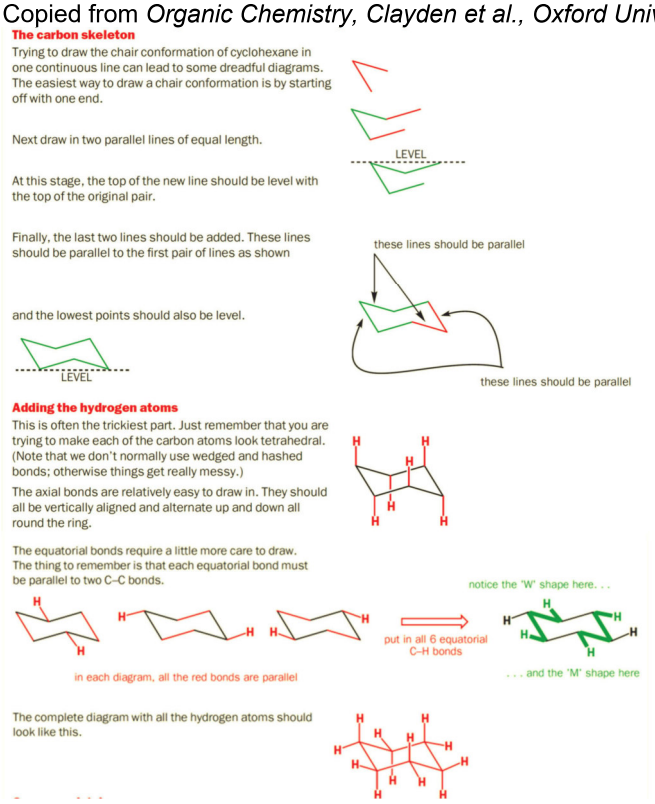
Cyclohexane can adopt the following conformations: Chair, Half-chair, Twist boat, and Boat.
The chair conformation is generally the most stable one.



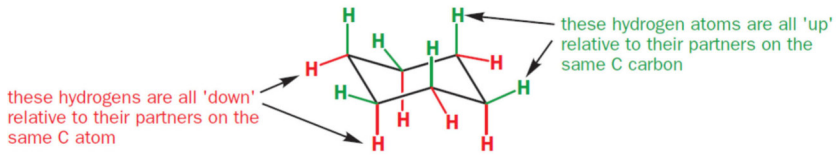


3.6. How to Draw Cyclohexane Chairs Correctly

Copied from *Organic Chemistry, Clayden et al., Oxford University Press.*

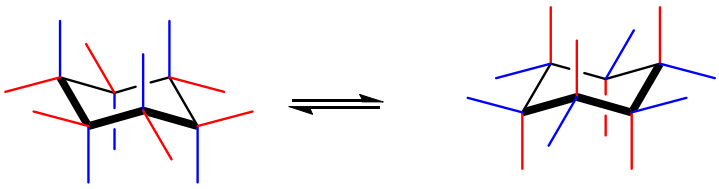


3.7 Conformational Changes During the Inversion of Cyclohexane



"Ring flip"

Axial and equatorial hydrogen atoms interchange during a "ring-flip":



In unsubstituted cyclohexane, the interconversion of one chair to the other occurs at room temperature, thus preventing isolation of the conformers.

3.8 Monosubstituted Cyclohexanes

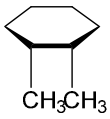
Cyclohexanol

1,3-diaxial interactions

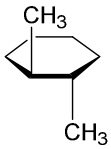
3.9 *Cis-Trans* Isomers in Cycloalkanes

cis-1,2-Dichlorocyclopropane *trans*-1,2-Dichlorocyclopropane

Stereoisomers - same connections, but differ in spatial orientation
Cis-trans isomers are separate, unique compounds that do not interconvert by rotation around C-C bonds

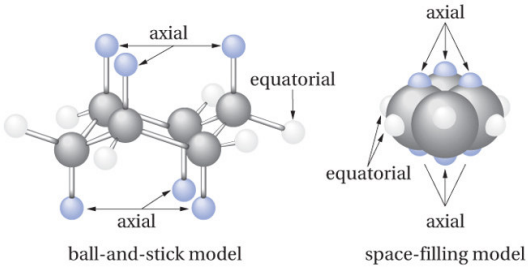


cis (same side)



trans (across)

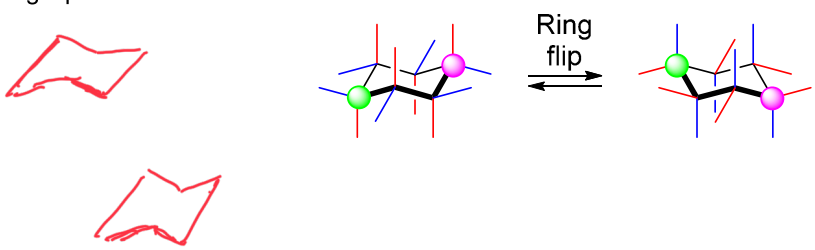
3.10 Conformational Mobility in Substituted Cyclohexanes



Notice that the 3 axial hydrogens on the same face almost touch

- If H is replaced by larger substituents, axial crowding becomes worse
- Steric strain caused by large groups experiencing 1,3-diaxial interactions decreases stability
- Steric strain can be reduced by a ring-flip which moves large groups out of an axial position into an equatorial position

Ring flip:



cis-1-*tert*-butyl-4-fluorocyclohexane

trans-1-*tert*-butyl-4-fluorocyclohexane

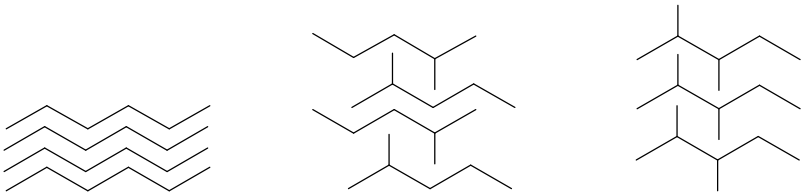
Cis and *trans* isomers are different compounds and therefore have different physical properties.

cis-1,4-cyclohexanediol (m.p. 113-114 ºC)

trans-1,4-cyclohexanediol (m.p. 143-144 ºC)

3.11 Properties of Alkanes

- 1–4 Carbons in the molecule = gas
- >4 Carbons in the molecule = liquid (density ~0.7-0.8 g/mL)
- Boiling point, melting point, and density increase as molecular weight increases
- Alkanes have lower b.p. than other compounds of similar MW due to weak van der Waals attractions
- Alkanes with more branching will have lower b.p. due to decreased van der Waals interactions



Known as paraffins for their “slight affinity” for other substances

- Will react with oxygen (combustion) and the halogens (radical)
- Do not normally react with acids, bases, or oxidizing or reducing agents