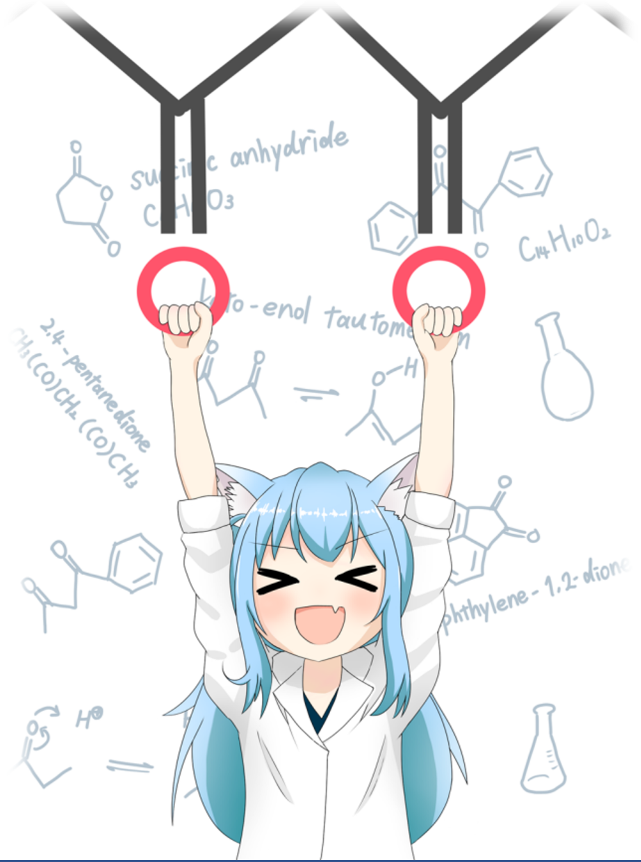
Organic Chemistry



A.U.Cor | Dept. of Chem.

Lecture 1

Introduction & Chem Principle Review

А.И.Соч

2020.10.22

Contents

- 绪论
  - 课程大纲
  - 评分标准
  - 作业形式
  - 有机化学简介
- 基础化学复习
  - 物质结构与性质
  - 化学热力学、动力学
  - 酸碱理论

Syllabus

Week	课程内容
1	绪论，基础化学复习
2	有机物的分类、表示及命名法
3	立体化学
4	立体化学，【实验】旋光度及其测定
5	共振式初步
6	卤代烃，饱和碳原子上的亲核取代反应
7	饱和碳原子上的亲核取代反应；β-消除反应
8	β-消除反应
9	烯烃，炔烃，加成反应
10	烯烃，炔烃，加成反应
11	醇，酚，醚
12	醇，酚，醚
13	期末检验

- 评分标准

3 ： 4 ： 3

出勤 平时表现 考试

Evaluation Standard

- 出勤(30%)
  - 只要来了就有
  - 病假/理由充分的事假不扣分
  - eg. 发烧了、去医院看病、签证、疫情隔离...
  - 别太让人伤心aaa...

- 平时表现(40%)
  - 作业的**上交情况**(20%)+课前小测(15%)+实验报告(5%)
  - 作业交了就有分哦！无论对错的
  - 但是也别瞎写啊…
  - 不会的可以随时来问我
  - 二层，科学组，进门正对的工位

- 考试(30%)
  - 有期末检验，视大家完成情况动态调整给分模式
  - 只要好好学，考试肯定不会难！
  - 考前有复习的，记得来听

- **作业范围**

workbook习题，教材习题，各种题库+

- **作业要求**

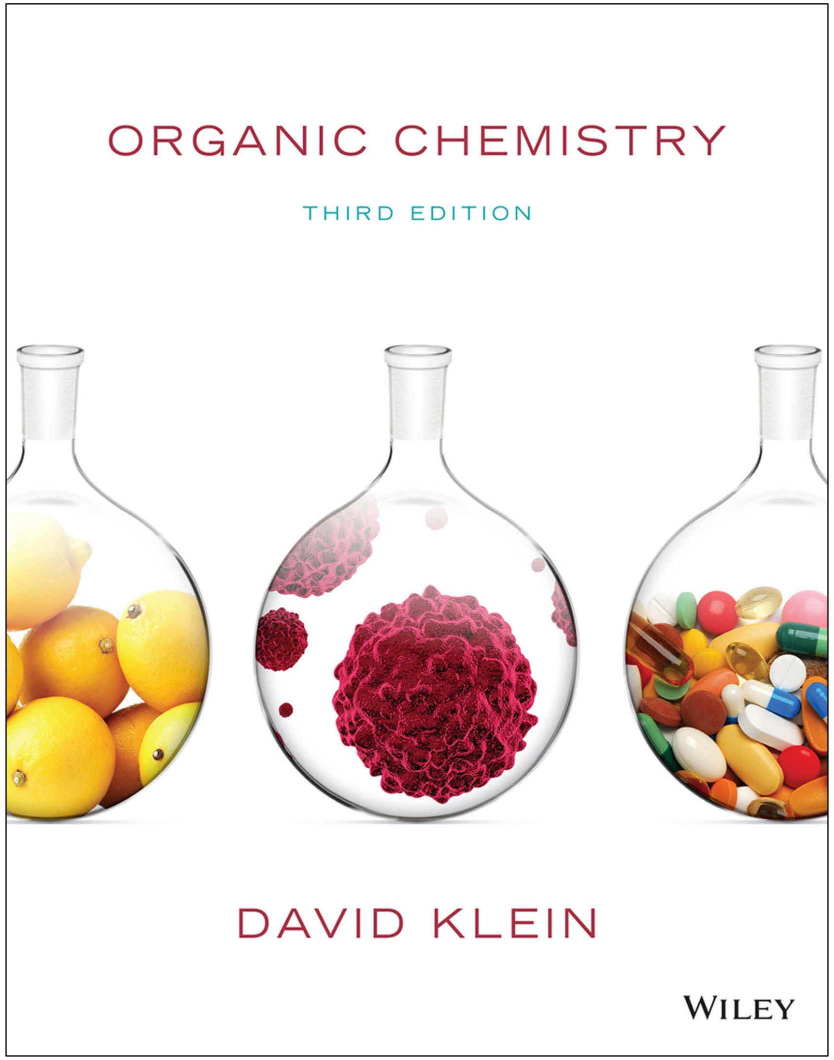
上课后统一布置，要求手写/电子版手写，独立完成，下次课前提交

【typical deadline: **Mon. 17:00 & Thur. 17:00**】

提前交会早点r给你反馈哦

作业是给自己写的！不！要！查！答！案！

Textbook



ORGANIC CHEMISTRY

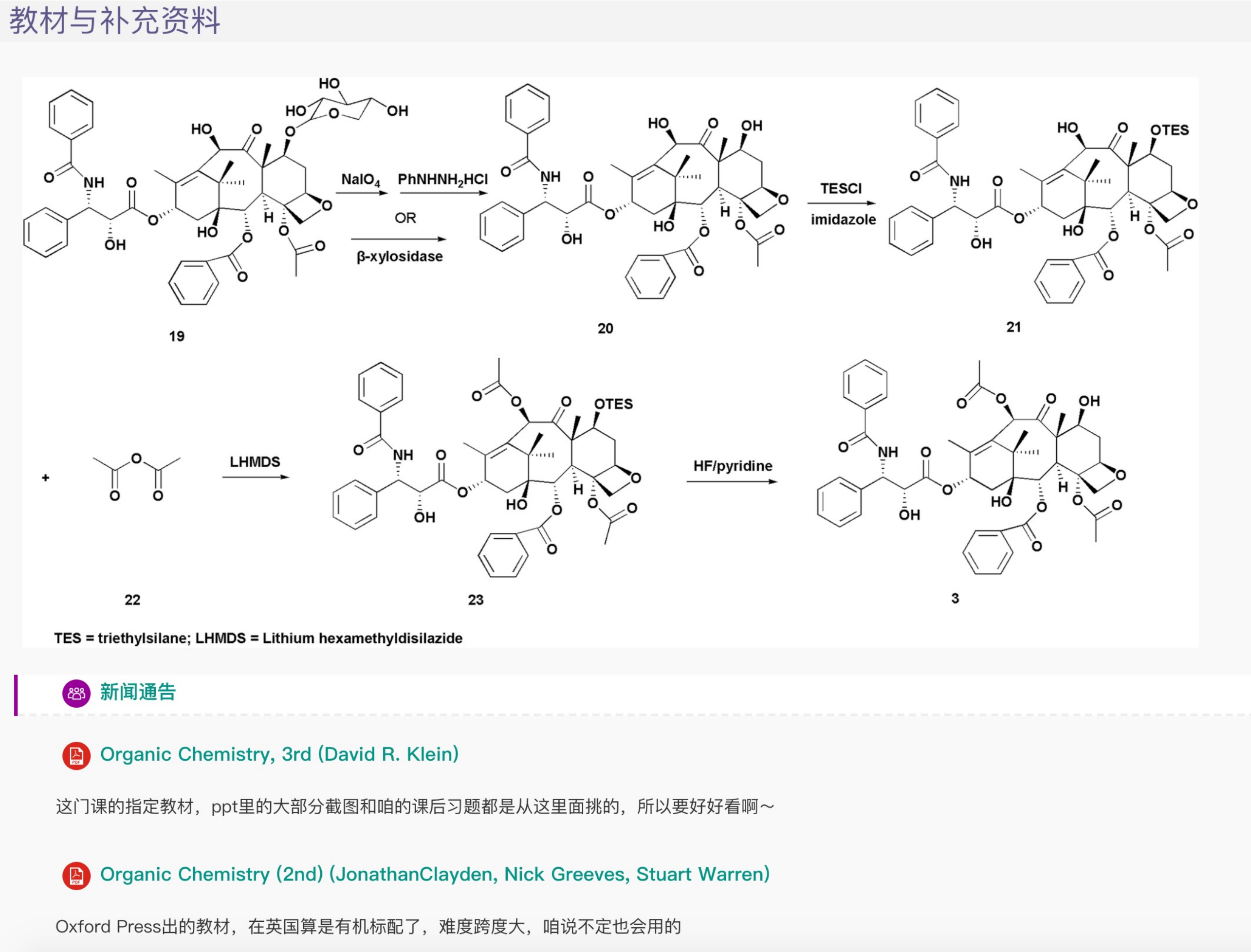
THIRD EDITION

DAVID KLEIN

WILEY

Organic Chemistry 3rd, David R. Klein

Resources



教材与补充资料

TES = triethylsilane; LHMDS = Lithium hexamethyldisilazide

新闻通告

Organic Chemistry, 3rd (David R. Klein)

这门课的指定教材，ppt里的大部分截图和咱的课后习题都是从这里面挑的，所以要好好看啊～

Organic Chemistry (2nd) (JonathanClayden, Nick Greeves, Stuart Warren)

Oxford Press出的教材，在英国算是有机标配了，难度跨度大，咱说不定也会用的

————————分割线————————

这套书老有名了！

前身是北大刑其毅教授编的《基础有机化学》第三版

当时叫做刑大本

现在这版是裴【成】坚【环】带头编的第四版

（已经改叫裴巨本了

内容很丰富 作为中文教材和参考书是绝对够用的

（毕竟 这个还是考研化学的指定教材嘛

《基础有机化学》第四版 上册

《基础有机化学》第四版 下册

基础有机化学第四版习题解析

————————分割线————————

演习で学ぶ 有机反应机构，福山 透

这个是我们未来可能会用到的习题集（福山透的反应机理还是很有名的啊

A Collection of Detailed Mechanismsand Synthetic Applications, Fifth Edition

经典的有机人名反应参考书，以后讲合成和反应的时候会用到:)

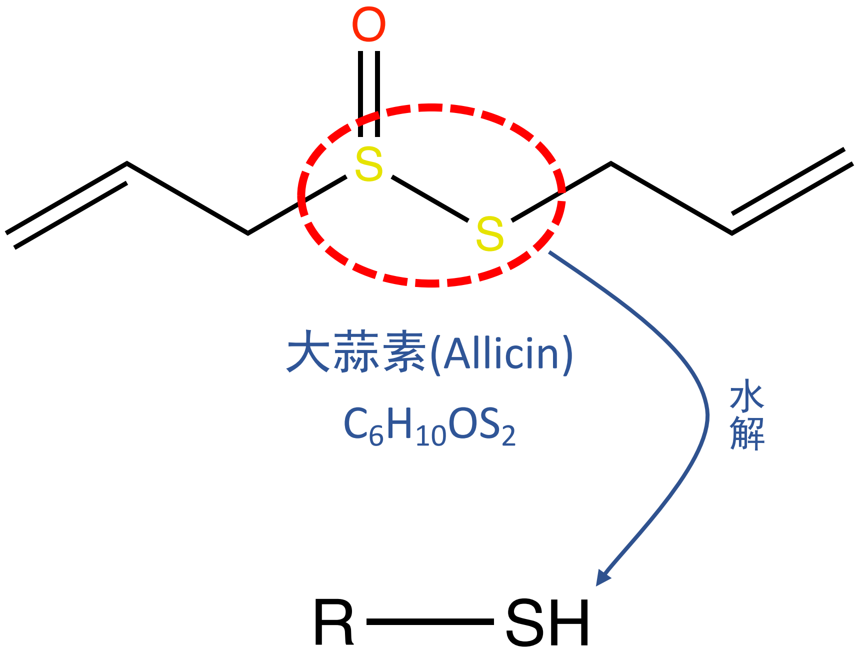
The Art of Writing Reasonable Organic Reaction Mechanisms

工具书，教你画反应机理的，可以看看，说不定对你后期画箭头有帮助呢(doge

https://m.shsbnu.net/course/view.php?id=477

Introduction to Organic Chemistry

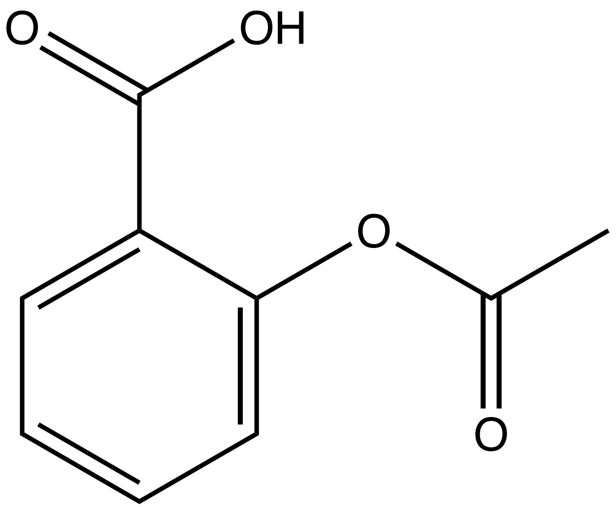
History, Development, Future



大蒜素(Allicin)

$C_6H_{10}OS_2$

臭味的元凶——硫醇



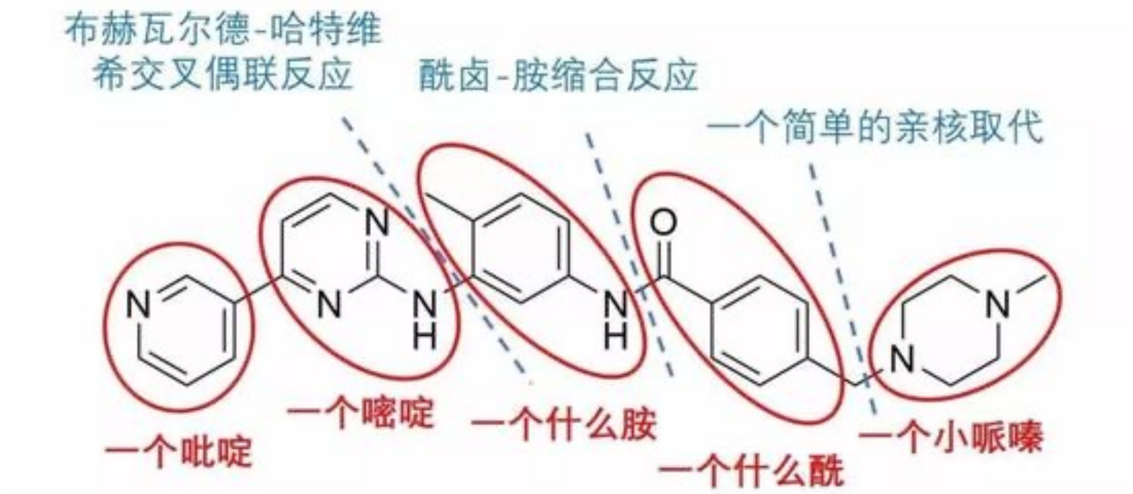
乙酰水杨酸

$C_9H_8O_4$

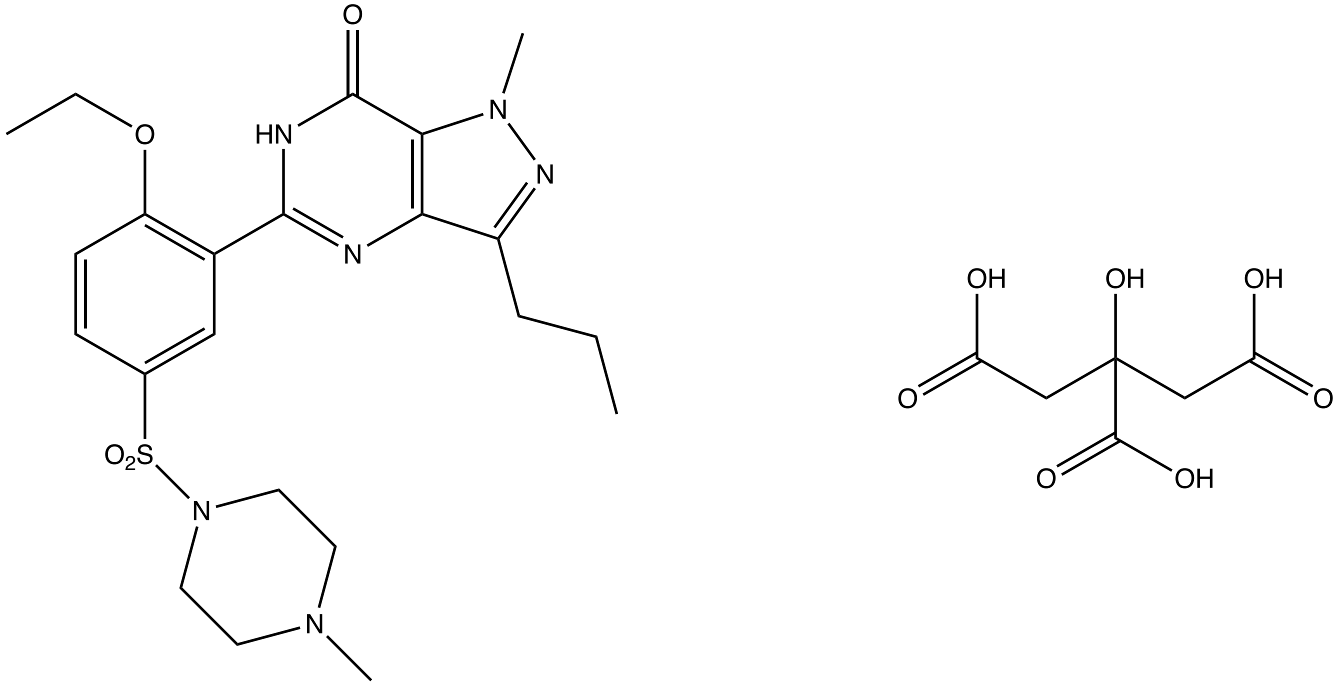
阿司匹林

Organic Chemistry and Life

Buchwald-Hartwig
Cross Coupling Reaction



（甲磺酸）伊马替尼
Imatinib (Mesylate)



枸橼酸西地那非

$C_{28}H_{38}N_6O_{11}S$

- 19世纪初，瑞典化学家J. Berzelius将从动植物体内得到的物质称为有机化合物(organic compound)，意为“有生机之物”。
- 当时的人们认为有机物只能从生命体中被制造出来，因此，“有机”(organic)一词是作为“无机”(inorganic)的对立而被创造出来的。

Jöns Jakob Berzelius
(1779-1848)

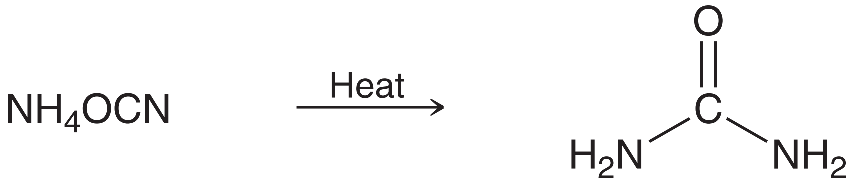
- 现代化学命名体系的建立者
- 硅(Si)、硒(Se)、钍(Th)、铈(Ce)元素的发现者
- 提出催化等概念
- “有机化学之父”

History

- Wohler与尿素
- 1824年，德国化学家Wohler从氰经水解制得草酸；1828年他无意中用加热的方法又使氰酸铵转化为尿素。氰和氰酸铵都是无机化合物，而草酸和尿素都是有机化合物。 Wohler的实验结果给予“生命力”学说第一次冲击。

Friedrich Wohler

(1800-1882)

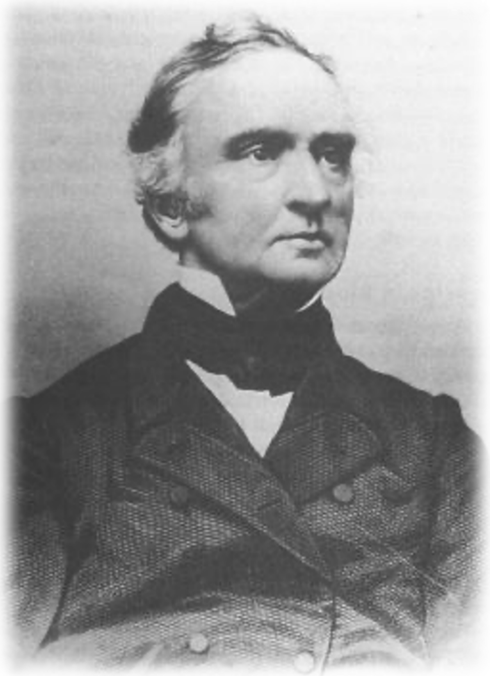


Ammonium cyanate
(Inorganic)

Urea
(Organic)

- 早期有机化学的分析法
- 化学反应的质量守恒
- 化学方程式的发明
- 有机物的燃烧产物：CO_2、H_2O
- 通过还原法（eg. CuO）定量测定有机物所含元素比例，进而推测分子式

Antoine-Laurent de Lavoisier
(1743-1794)



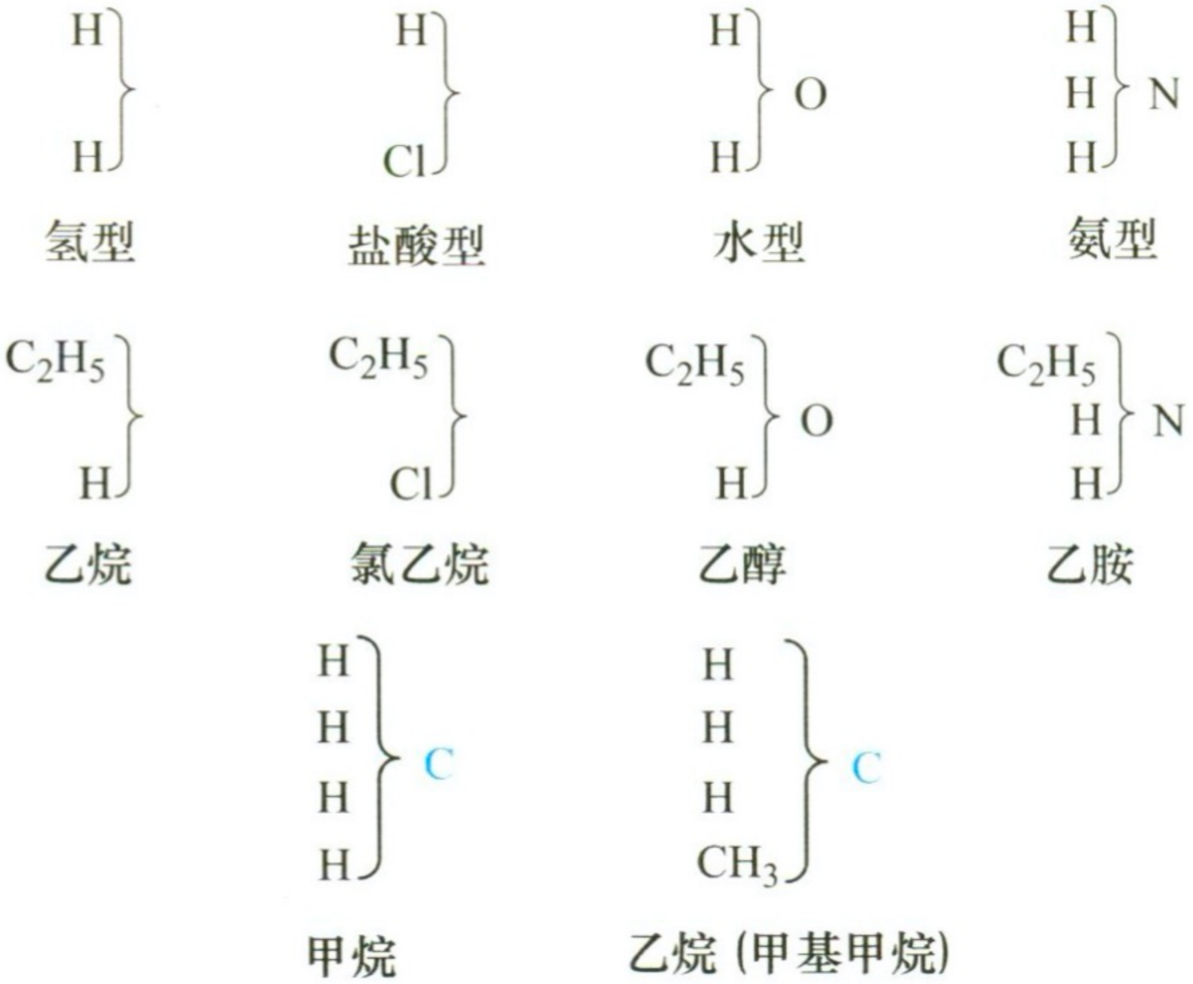
Justus von Liebig
(1803-1873)

- 到19世纪后期，越来越多的有机物被合成出来，这一局面已然打破了“有生机之物”这一初始的含义——即使是有机物，也能在体外被合成出来。不过，由于历史习惯的原因，人们仍旧保留了“有机物”这一说法。

Organic is not “Organic! ”

- 价键理论的提出
  - “价键”之概念
  - 碳是四价的
  - 碳的四面体结构
  - 旋光异构现象与立体化学

代表人物：
Friedrich August Kekulé
(1829-1896)



$\left.\begin{matrix}H\\H\end{matrix}\right\}$

氢型

$\left.\begin{matrix}H\\Cl\end{matrix}\right\}$

盐酸型

$\left.\begin{matrix}H\\H\end{matrix}\right\}O$

水型

$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$

氨型

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}$

乙烷

$\left.\begin{matrix}C_2H_5\\Cl\end{matrix}\right\}$

氯乙烷

$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$

乙醇

$\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N$

乙胺

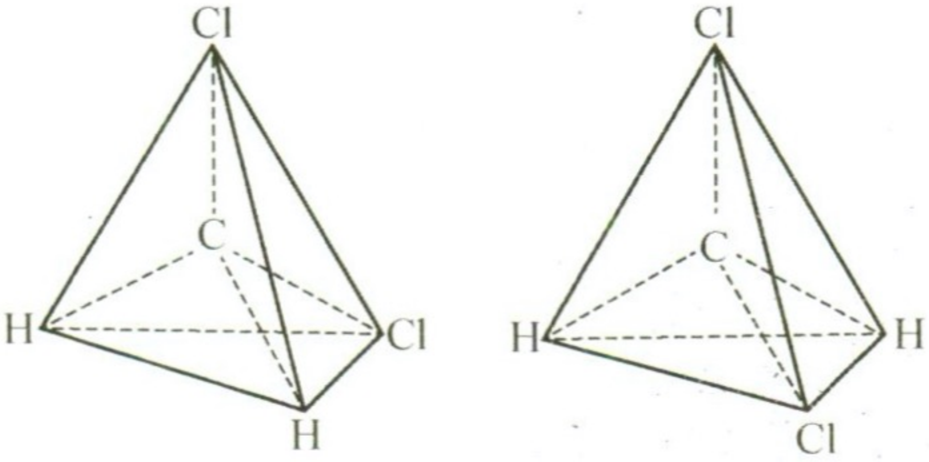
$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C$

甲烷

$\left.\begin{matrix}H\\H\\H\\CH_3\end{matrix}\right\}C$

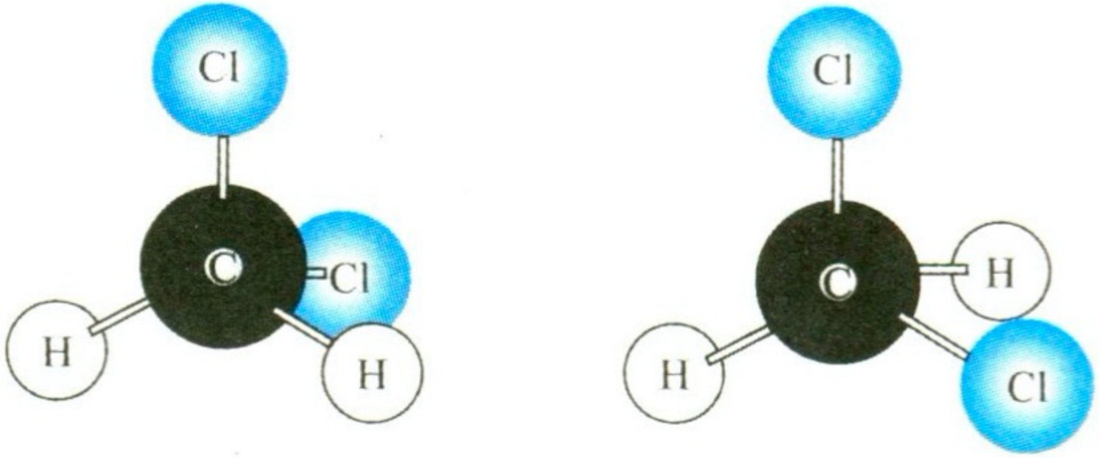
乙烷 (甲基甲烷)

- 二氯甲烷(CH_2Cl_2)模型与立体化学



(i) (ii)

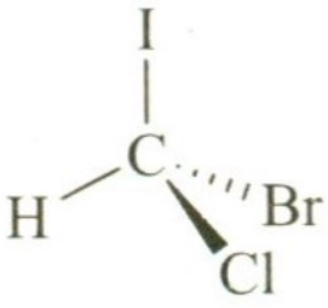
图 1-1 二氯甲烷的四面体模型



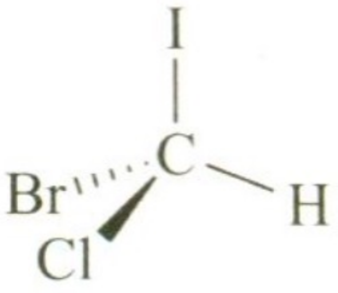
(i) (ii)

图 1-2 二氯甲烷的球棍模型

- 立体异构现象(stereo-isomerism)与立体异构体(stereoisomer)



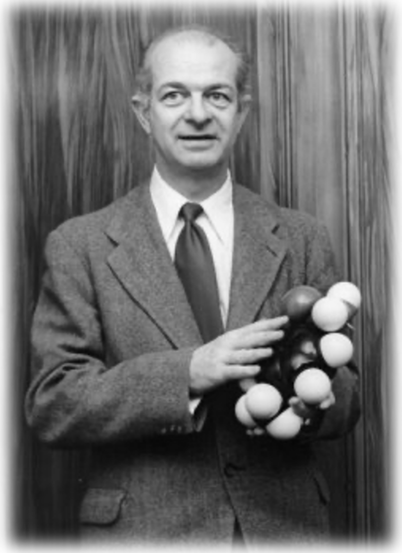
CHClBrI (R)



CHClBrI (S)

- **现代价键理论发展**
- Lewis电子式
- Heitler, London对价键理论的贡献——量子力学模型
- Mulliken与分子轨道理论(MO)

Lewis
(1875-1946)



Heitler
(1904-1981)

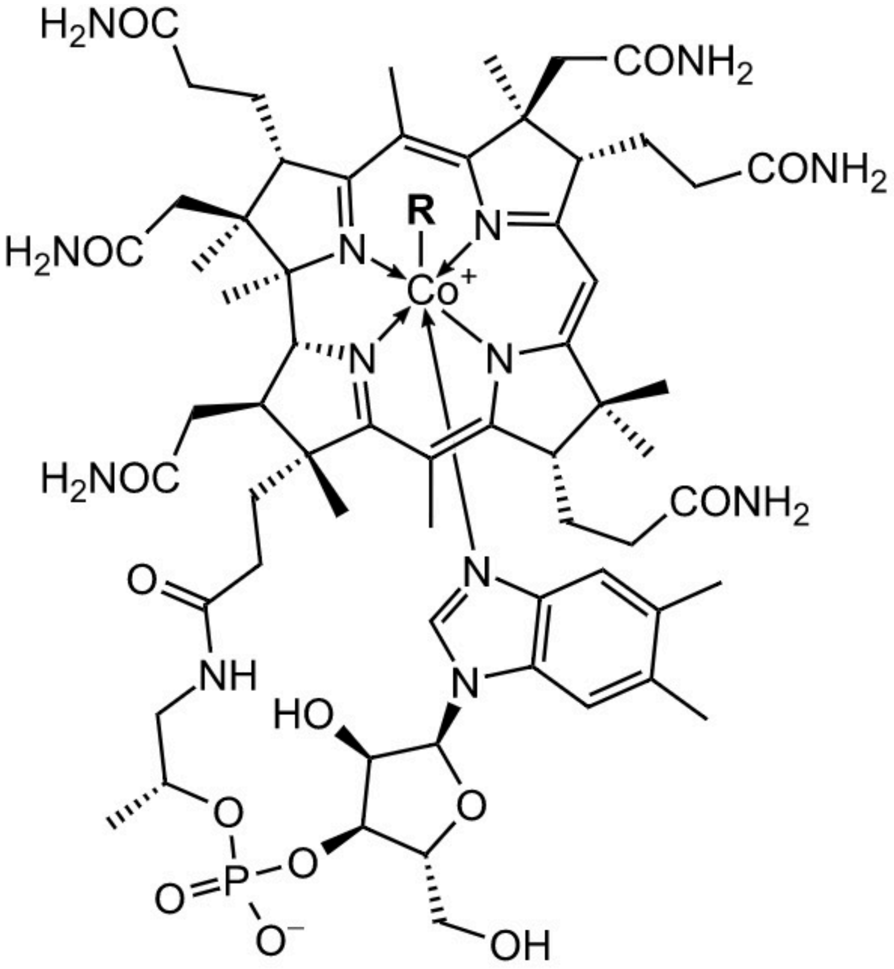
London
(1900-1954)

Mulliken
(1896-1986)

- Robert Burns Woodward
- “现代有机合成之父”
- 1933-1936 MIT, Bachelor Degree
- 1937 Harvard University, PhD
- 以极其精巧的方法，合成了包括奎宁，胆固醇，可的松，士的宁，麦角酸，利血平，叶绿素，头孢菌素、秋水仙碱、维生素B_{12}等多种复杂有机化合物
- The Nobel Prize in Chemistry, 1965
- ***“Organic Synthesis... is an Art.”***

Robert Burns Woodward
(1917-1979)

- 部分合成法
- 合成部分再拼装

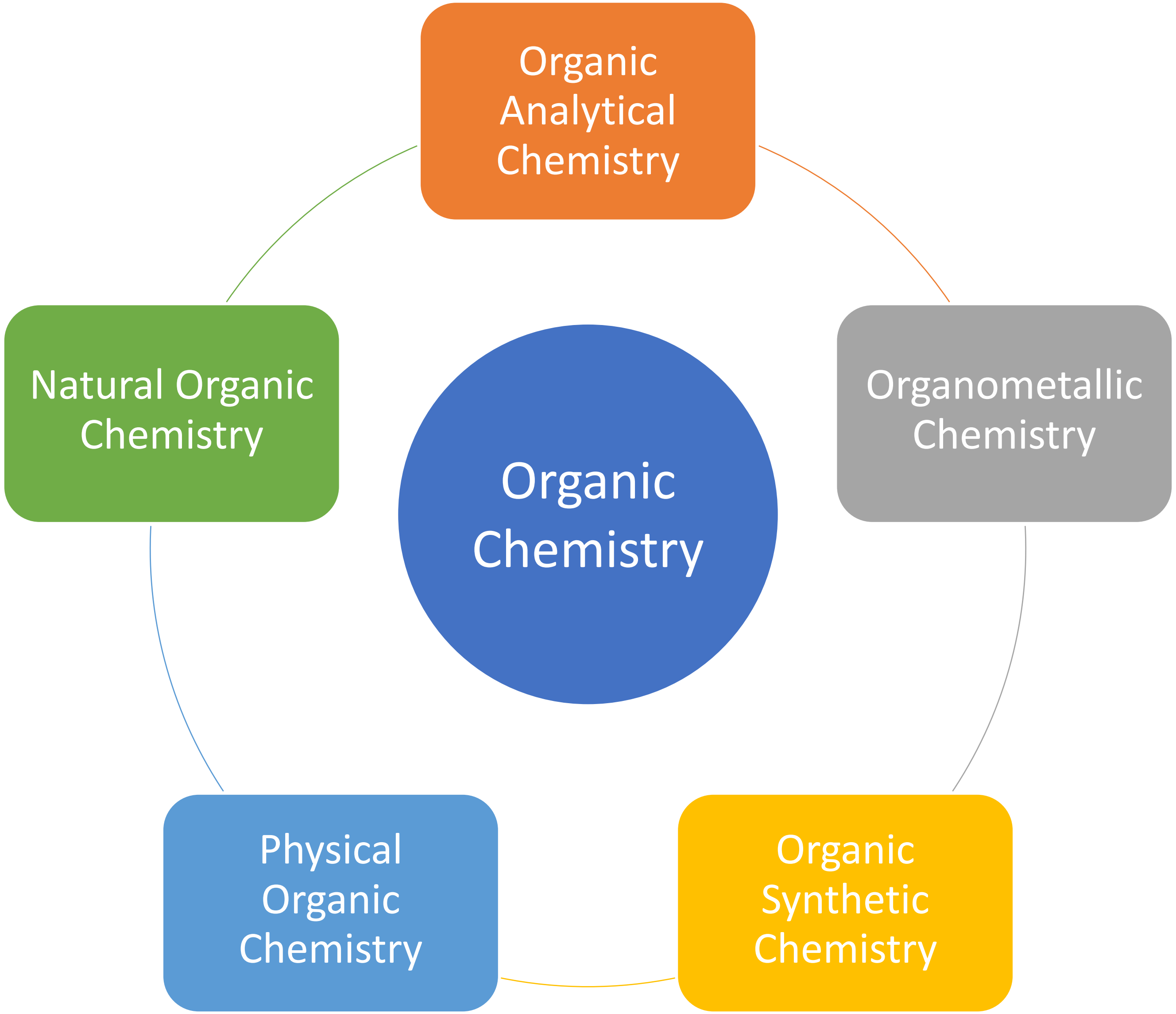


R = 5'-deoxyadenosyl, CH_3, OH, CN

维生素B_{12}

钴胺素

Today and... Future



Organic Chemistry

Organic Analytical Chemistry

Organometallic Chemistry

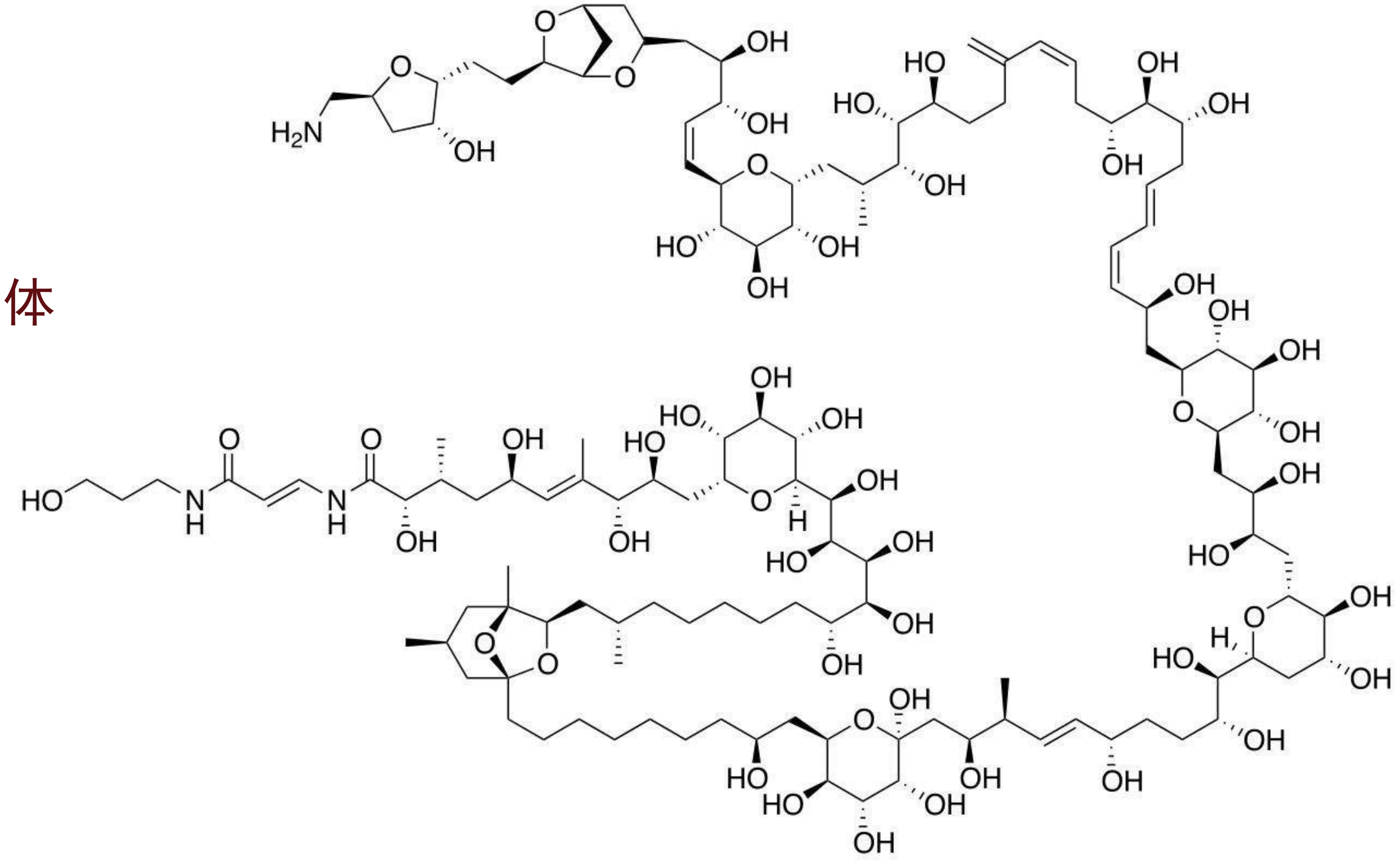
Organic Synthetic Chemistry

Physical Organic Chemistry

Natural Organic Chemistry

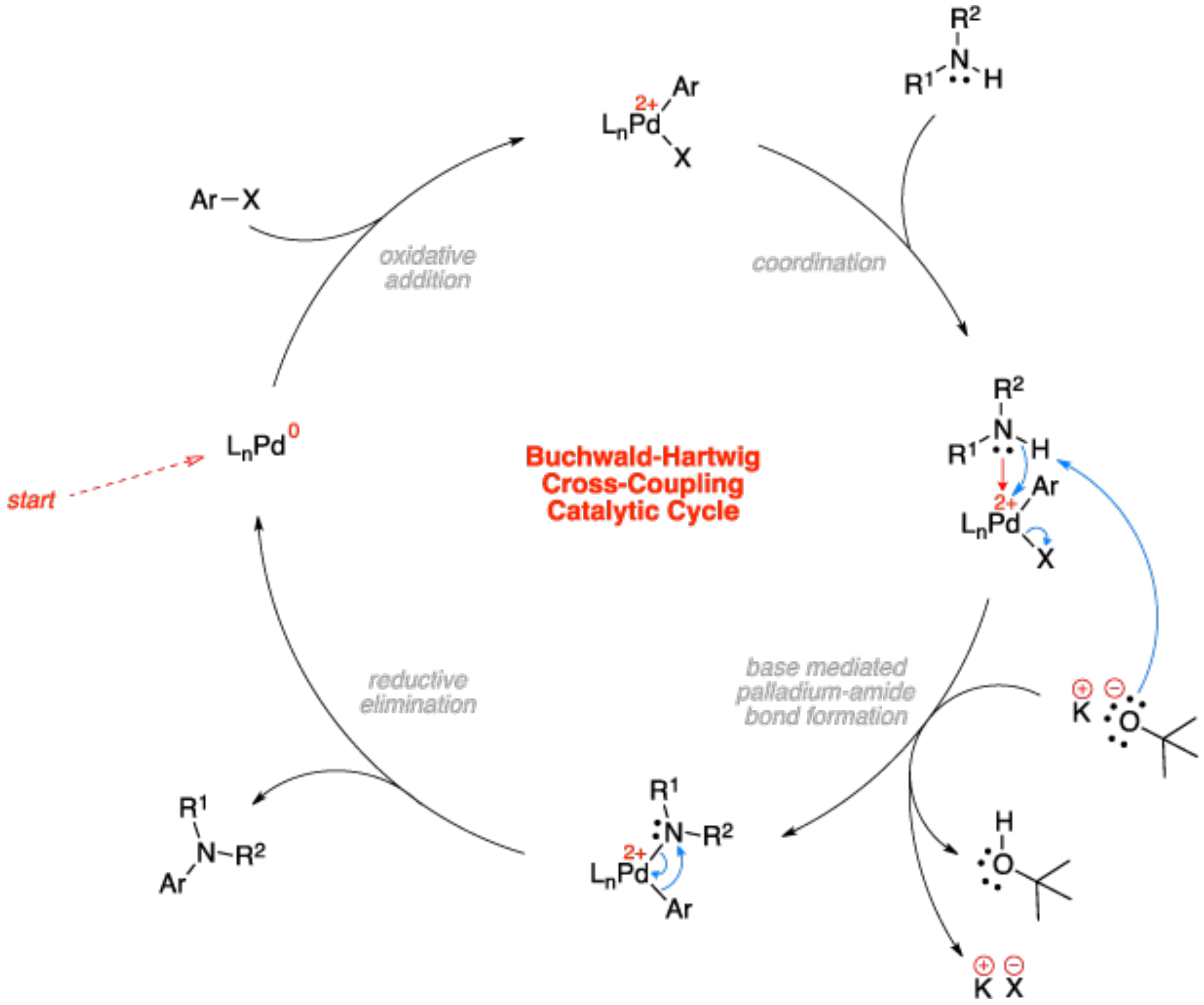
Today and... Future

- 海葵毒素
- 64个手性中心
- 7个双键
- 2^{71}个可能的异构体
- 1994年合成

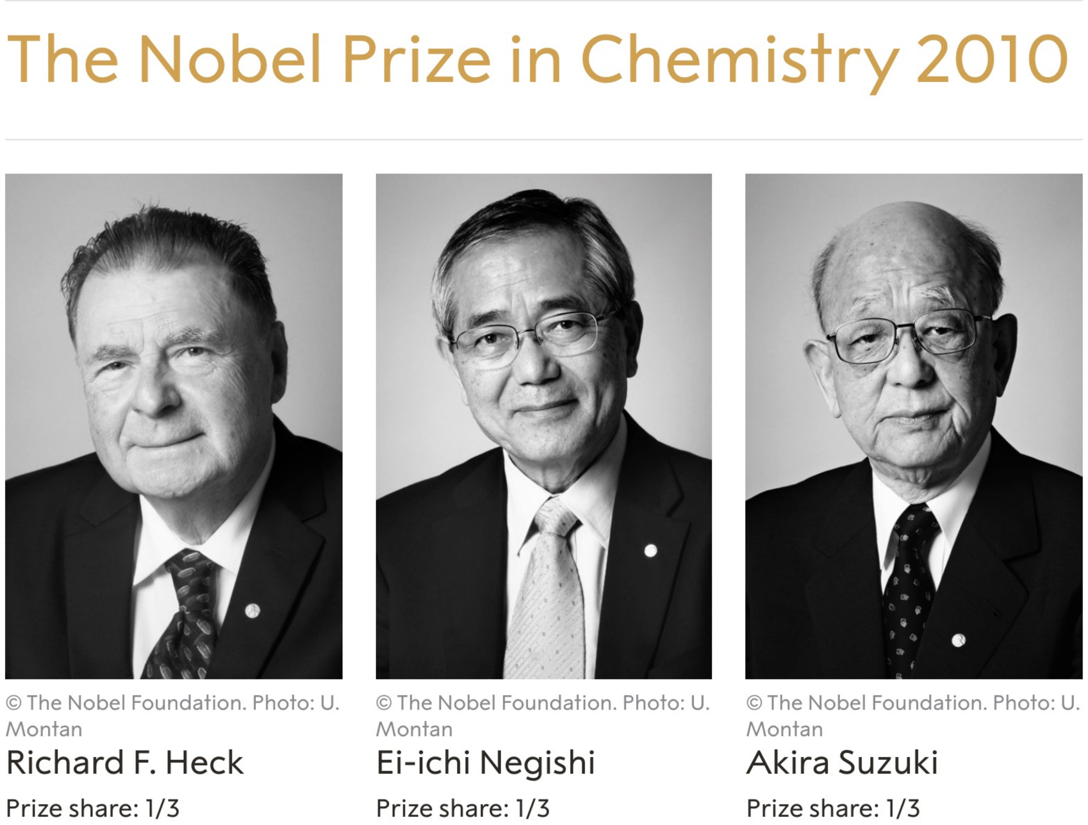


Today and… Future

John F. Hartwig
(1964-)



Stephen L. Buchwald
(1955-)



The Nobel Prize in Chemistry 2010

© The Nobel Foundation. Photo: U. Montan

Richard F. Heck

Prize share: 1/3

© The Nobel Foundation. Photo: U. Montan

Ei-ichi Negishi

Prize share: 1/3

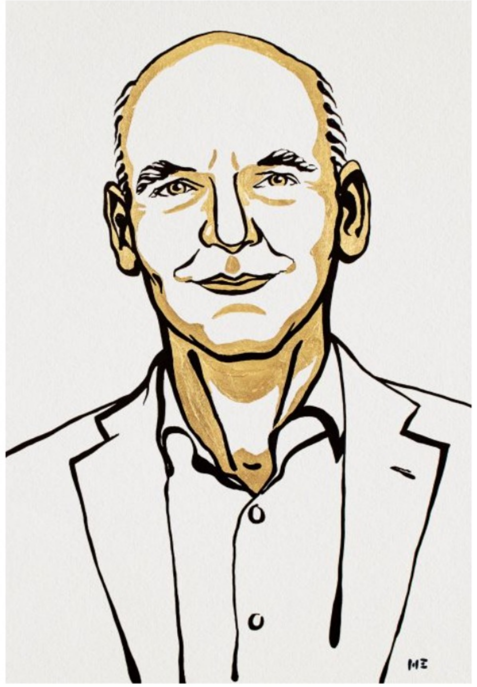
© The Nobel Foundation. Photo: U. Montan

Akira Suzuki

Prize share: 1/3

The Nobel Prize in Chemistry 2010 was awarded jointly to Richard F. Heck, Ei-ichi Negishi and Akira Suzuki "for palladium-catalyzed cross couplings in organic synthesis."

The Nobel Prize in Chemistry 2021



Ill. Niklas Elmehed © Nobel Prize Outreach.

Benjamin List

Prize share: 1/2

Ill. Niklas Elmehed © Nobel Prize Outreach.

David W.C. MacMillan

Prize share: 1/2

The Nobel Prize in Chemistry 2021 was awarded jointly to Benjamin List and David W.C. MacMillan "for the development of asymmetric organocatalysis."

Definition

What is Organic Chemistry?

Definition

- 有机化学是研究碳的化学

- 有机化学是研究碳氢化合物及其衍生物的化学

- 现代点r的？
  - 有机化合物：碳氢化合物及其衍生物
  - 有机化学：研究有机化合物的结构、性能与合成的科学

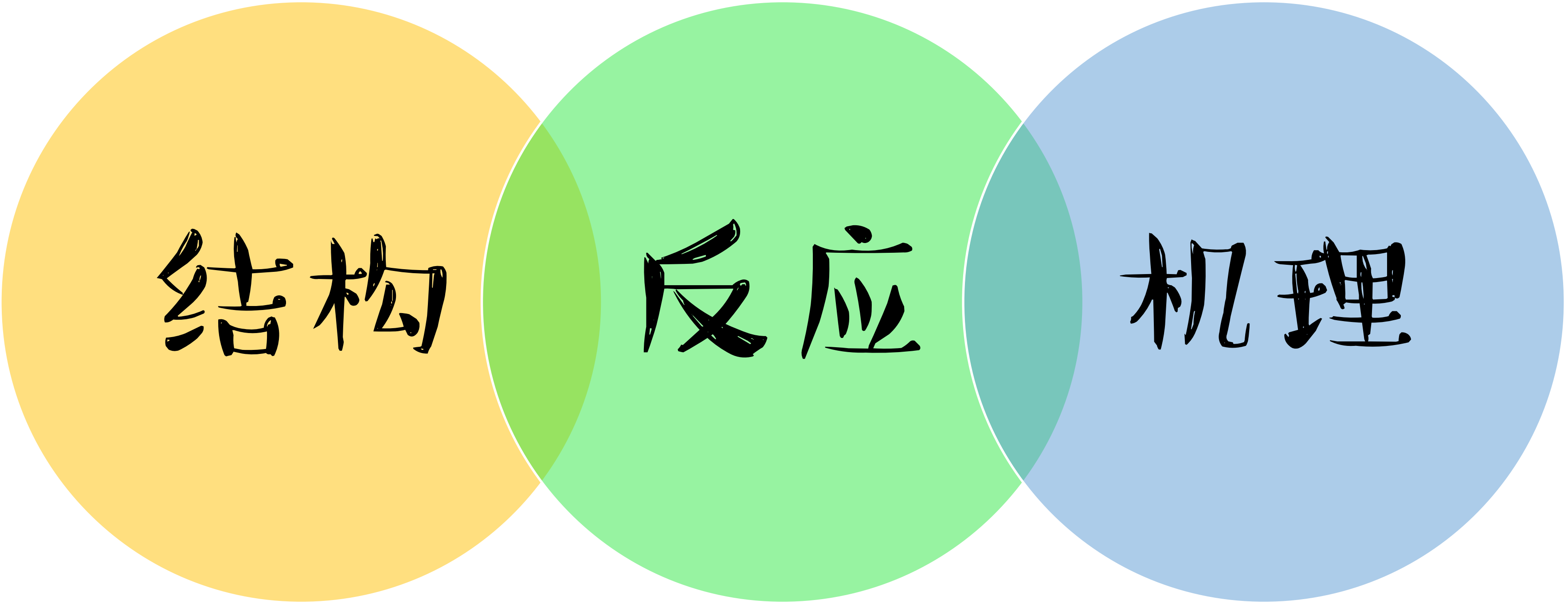
Definition

> “Organic chemistry is the study of the structure, properties, composition, reactions, and preparation of carbon-containing compounds, which include not only hydrocarbons but also compounds with any number of other elements, including hydrogen (most compounds contain at least one carbon–hydrogen bond), nitrogen, oxygen, halogens, phosphorus, silicon, and sulfur.”
>
> ——American Chemistry Society (ACS)

Properties

- 都含有碳原子（碳单质、碳的氧化物、碳酸、碳酸盐等除外）
- 种类繁多，约2000万以上；无机化合物虽遍布整张元素周期表，但却只有40-50万个（2019）
- 碳原子容易形成较稳定的共价键，包括单键、双键、三键等
- 物理性质：熔、沸点低，难溶于水，易挥发
- 化学性质：易燃烧，反应速率慢，副反应多

How to study?

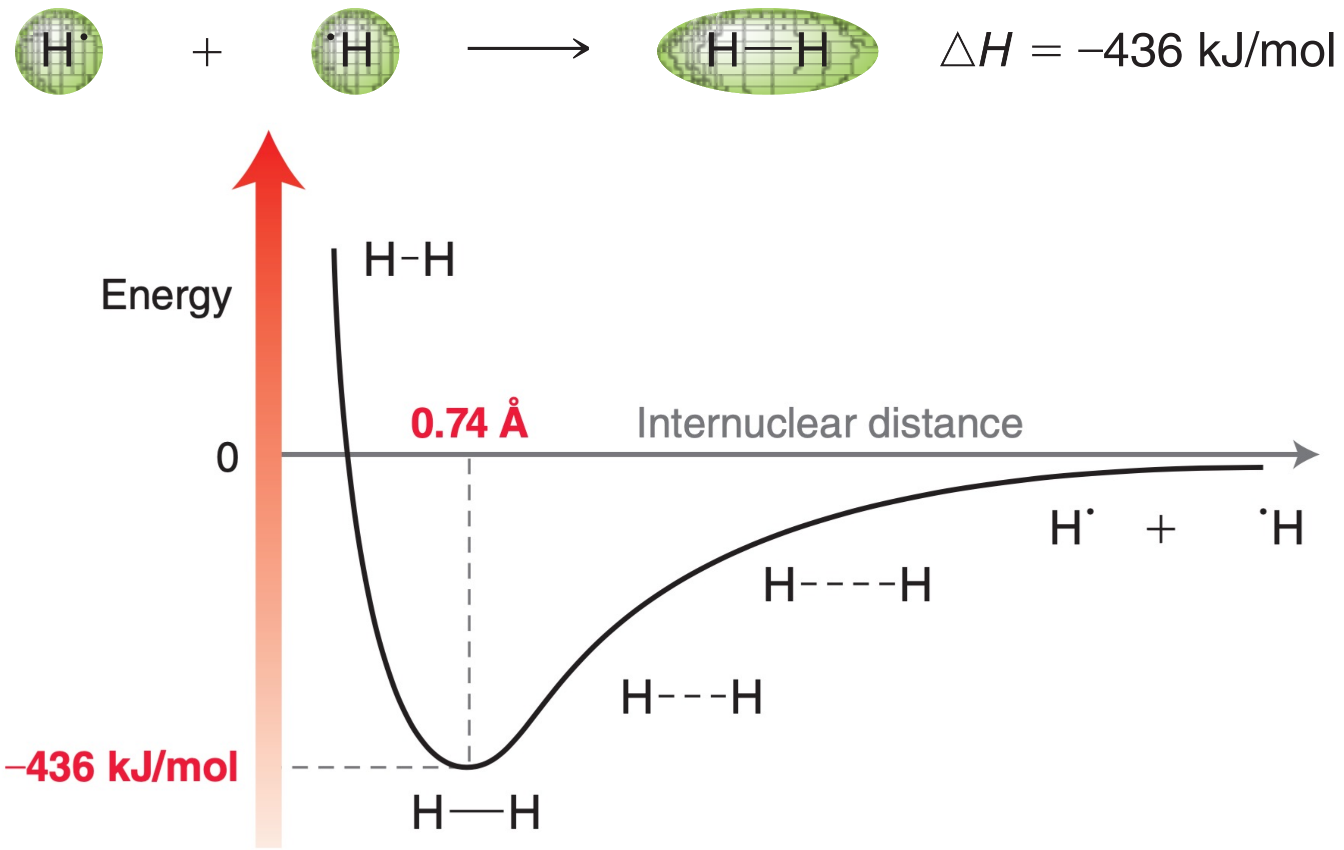


结构 反应 机理

Chem Principle Review

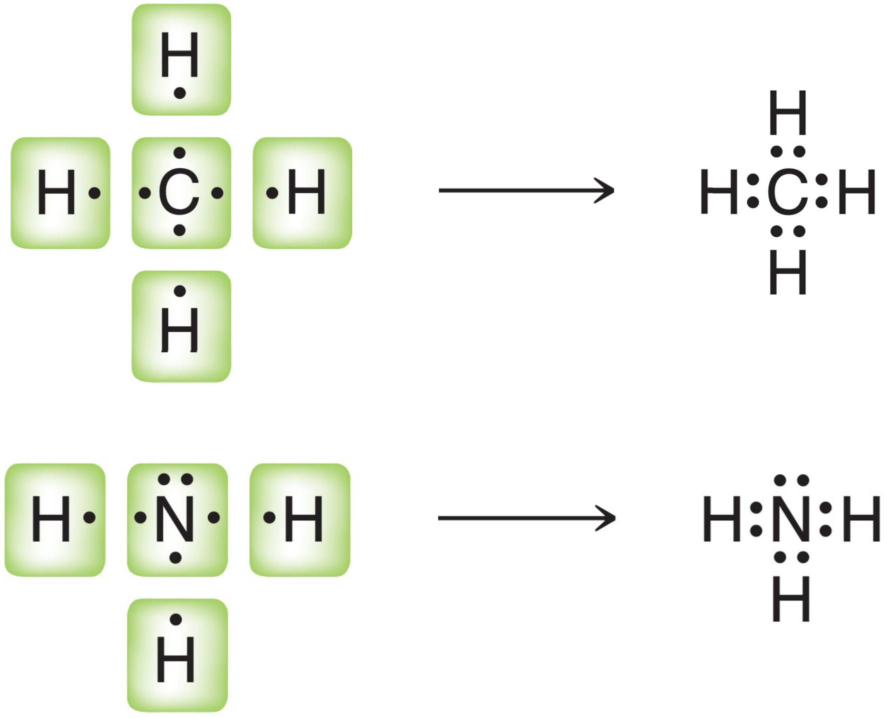
Structure, Thermodynamics & Kinetics, Acid & Base

- Covalent bond: share of electrons

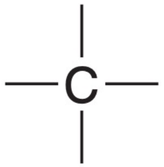


Lewis Structure

- Octet Rule

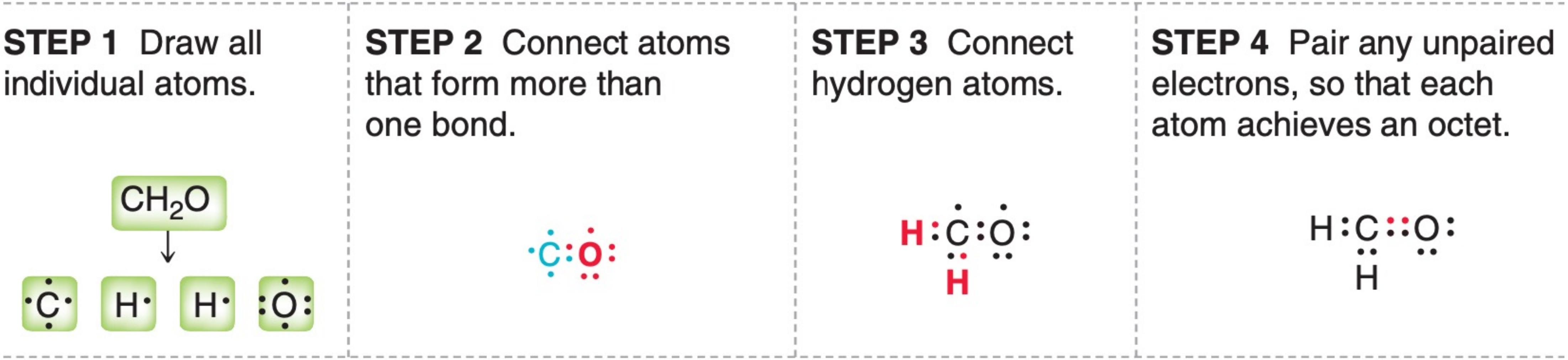


Lewis Structure

Tetravalent	*Trivalent*	*Divalent*	*Monovalent*
 $-\overset{\vert}{\underset{\vert}{C}}-$ Carbon generally forms ***four*** bonds.	 $-\underset{\vert}{N}-$ Nitrogen generally forms ***three*** bonds.	$-O-$ Oxygen generally forms ***two*** bonds.	$H-$ $X-$ (where X = F, Cl, Br, or I) Hydrogen and halogens generally form ***one*** bond.

Lewis Structure

- Practice: draw the Lewis structure of CH_2O



STEP 1 Draw all individual atoms.

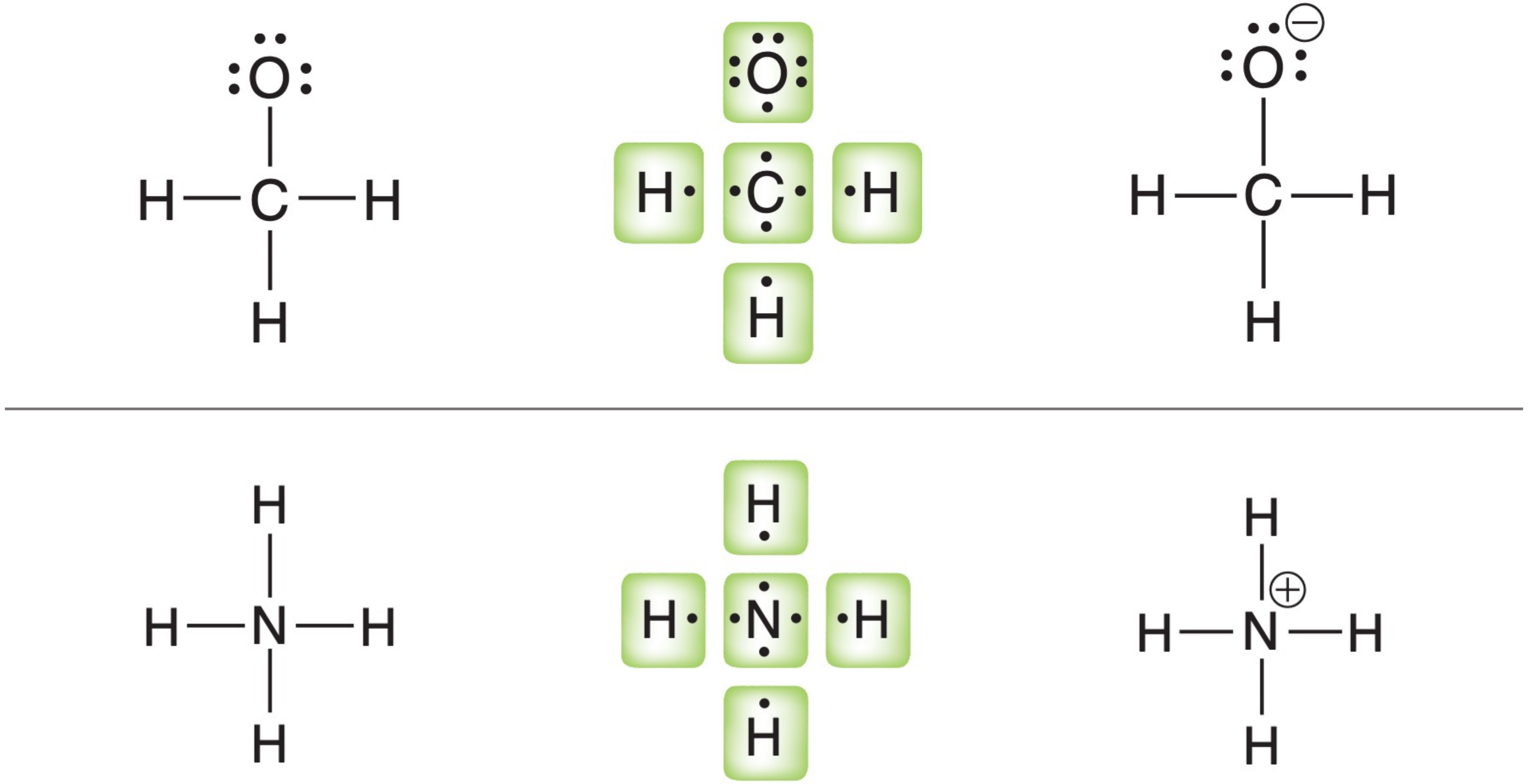
STEP 2 Connect atoms that form more than one bond.

STEP 3 Connect hydrogen atoms.

STEP 4 Pair any unpaired electrons, so that each atom achieves an octet.

Formal Charge

- Formal charge: atoms which have unusual # valance electrons



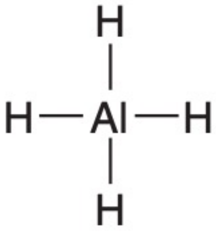
Formal Charge

- Take a look at the group number
- The group number indicates valance electron numbers
- Homolyze all bonds
- Determine whether the current electron number of the atom is equal to the original valence electron number
- More electrons (-); less electrons (+)

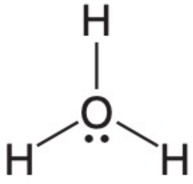
Formal Charge

- Practice: identify any formal charges in the structures below

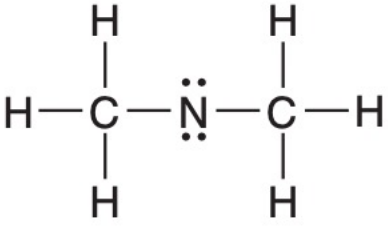
(a)



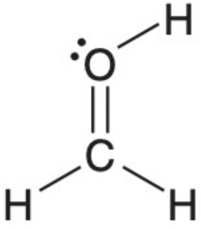
(b)



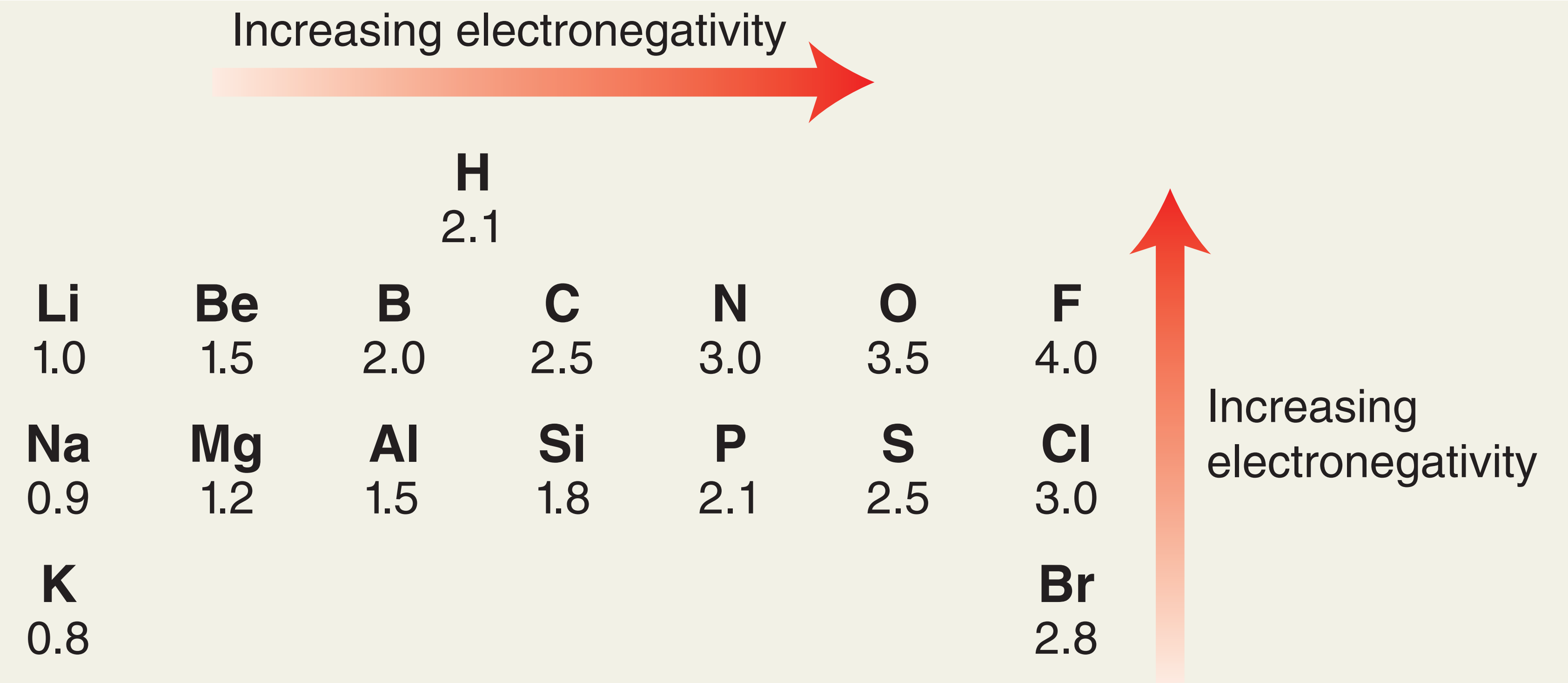
(c)



(d)



- Electronegativity



Increasing electronegativity

H
2.1

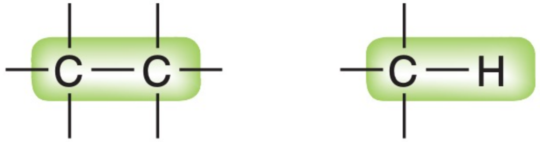
Li	**Be**	**B**	**C**	**N**	**O**	**F**
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K						**Br**
0.8						2.8

Increasing electronegativity

Bond Polarity

- Nonpolar/weak polar covalent bond

$$\Delta\chi \leq 0.5$$



- Polar covalent bond

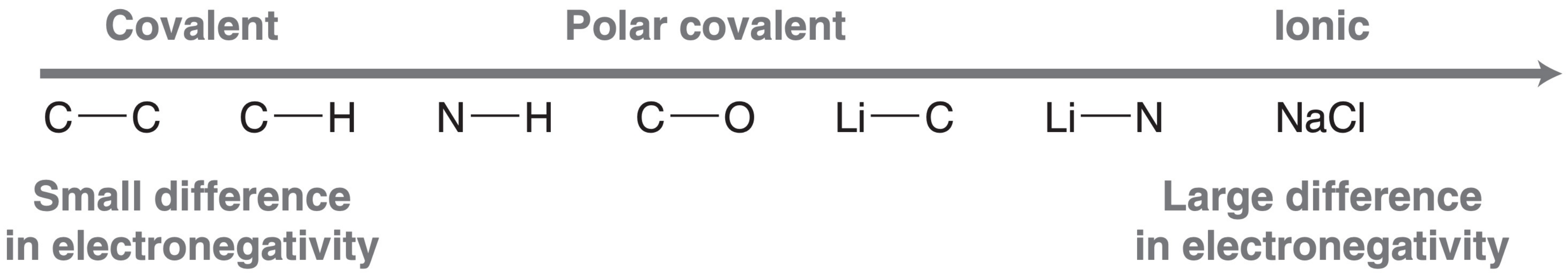
$$0.5 < \Delta\chi \leq 1.7$$

- Ionic bond

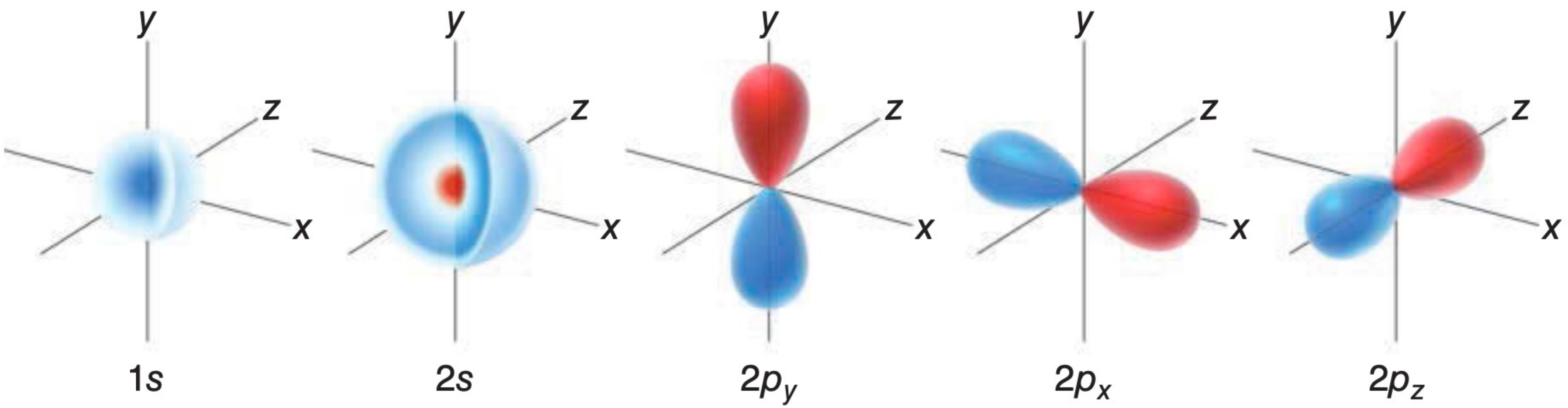
$$1.7 < \Delta\chi$$

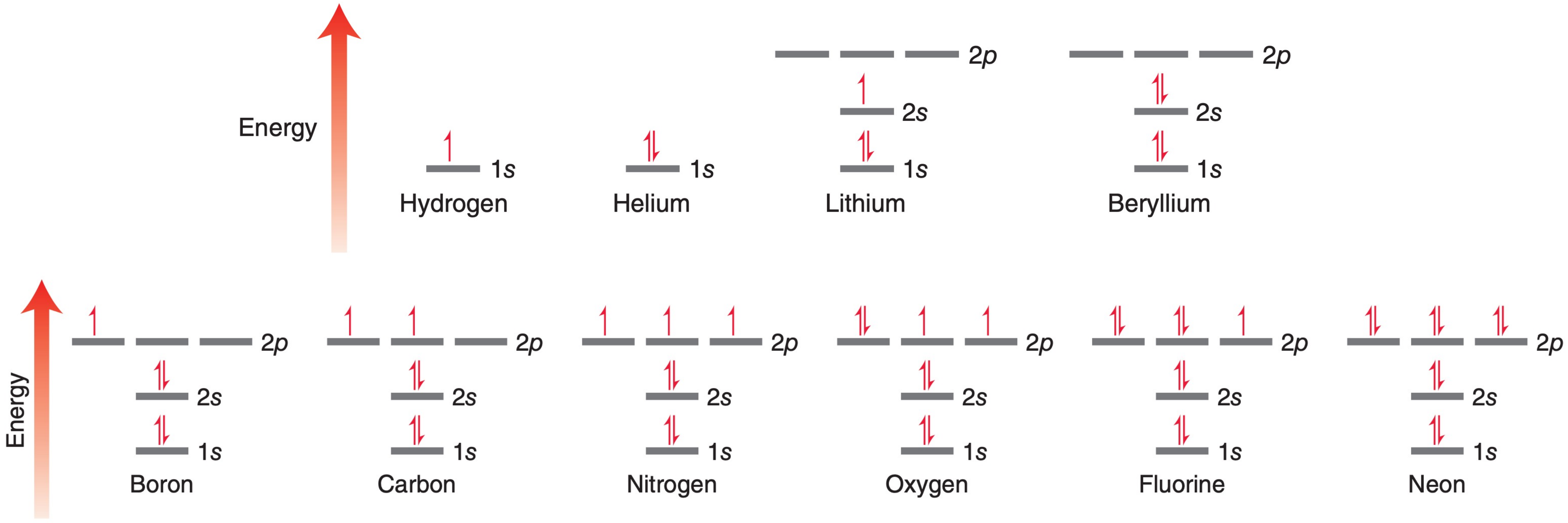
Bond Polarity

- Bonds can be *both covalent & ionic*

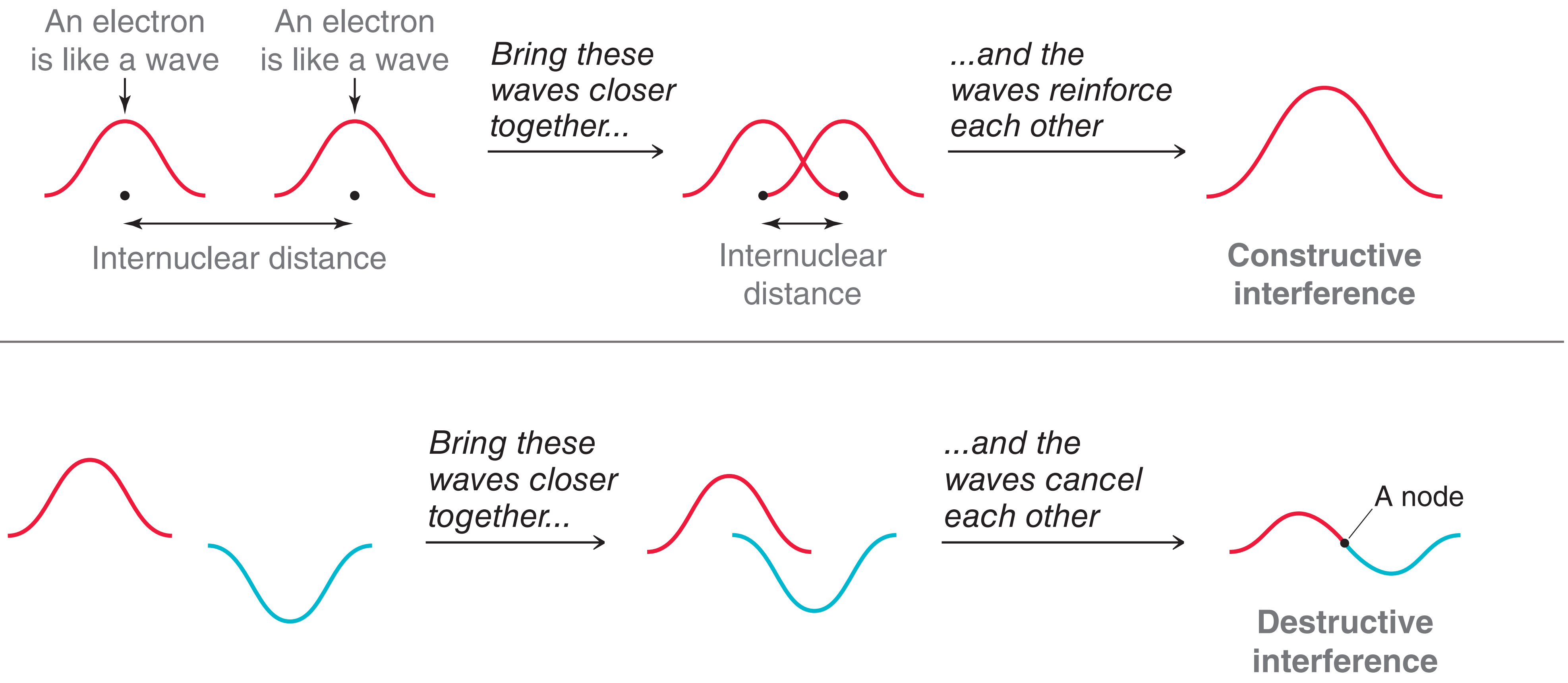


Atomic Orbitals





Valence Bond Theory



An electron is like a wave

An electron is like a wave

Bring these waves closer together...

...and the waves reinforce each other

Internuclear distance

Internuclear distance

Constructive interference

Bring these waves closer together...

...and the waves cancel each other

A node

Destructive interference

Valence Bond Theory

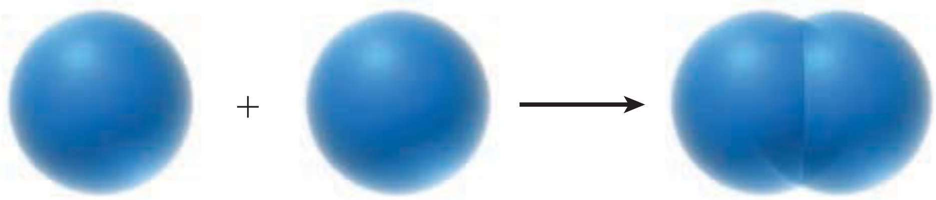


FIGURE 1.13
The overlap of the 1s atomic orbitals of two hydrogen atoms, forming molecular hydrogen (H_2).

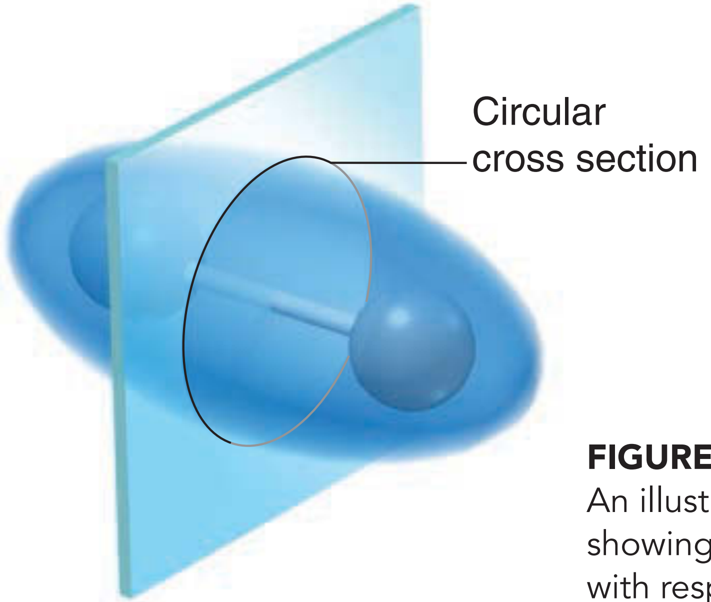
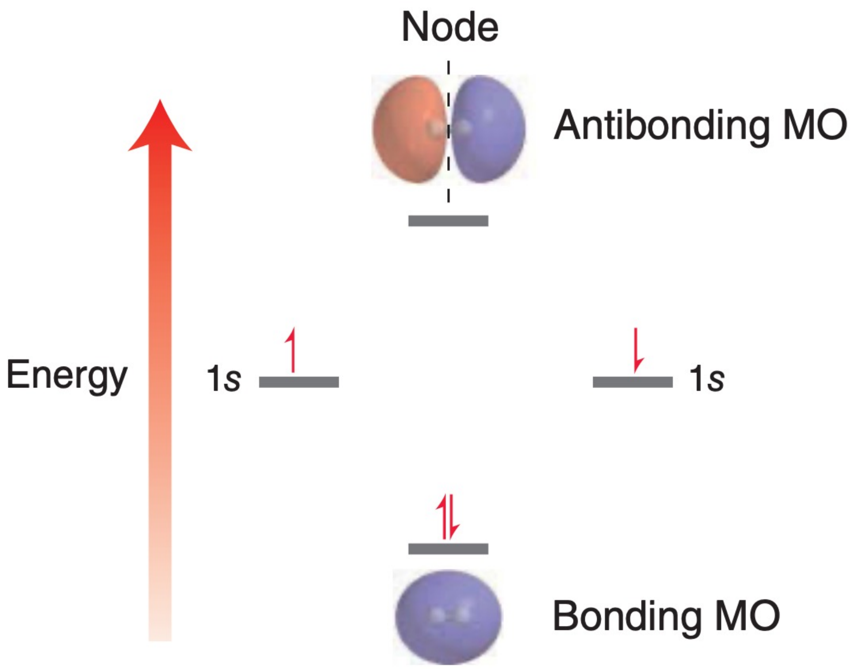
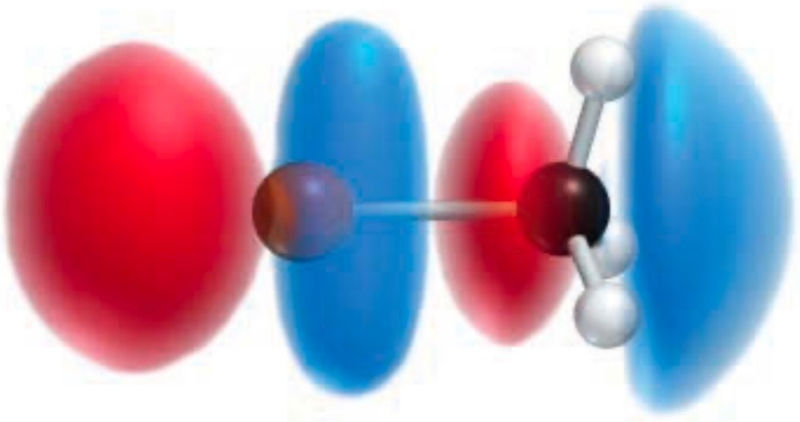


FIGURE 1.14
An illustration of a sigma bond, showing the circular symmetry with respect to the bond axis.

- Molecular orbital theory (MO)

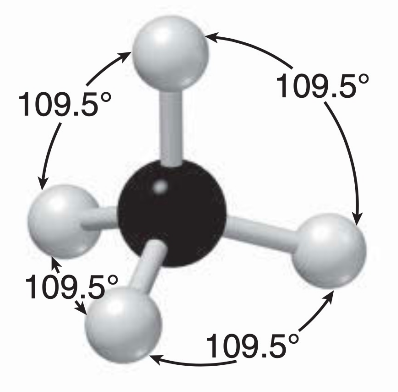




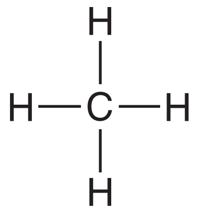
Lowest Unoccupied Molecular Orbital (LUMO) of CH_3Br

HOMO

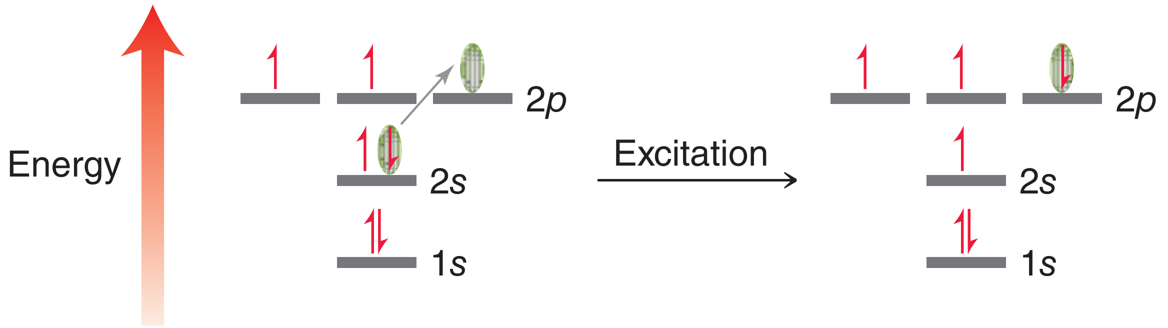
Hybrid Orbital Theory

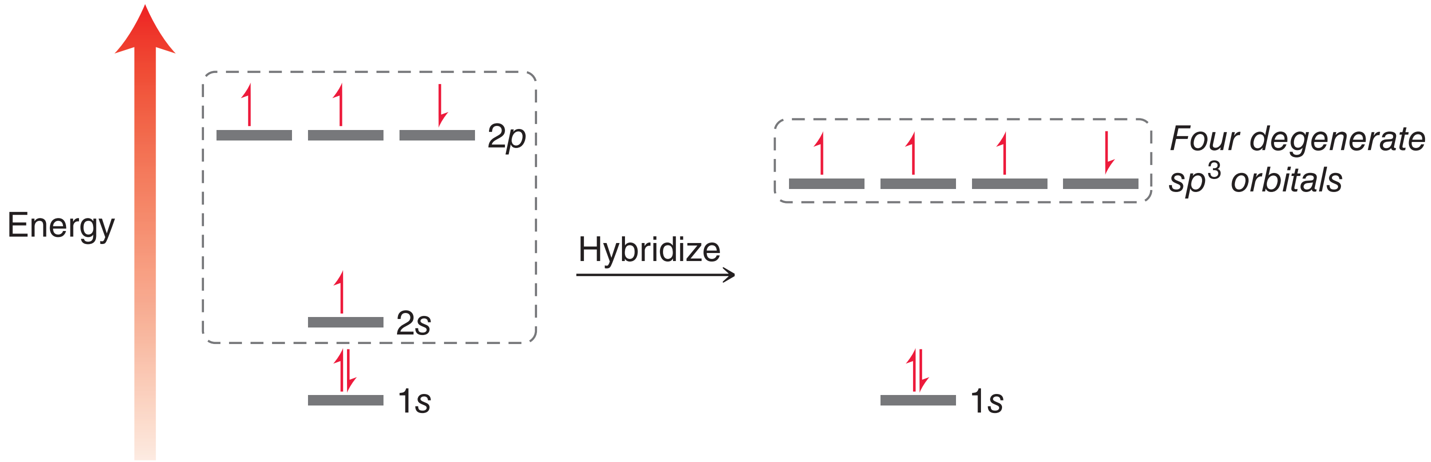


- sp^3 hybrid: tetrahedral



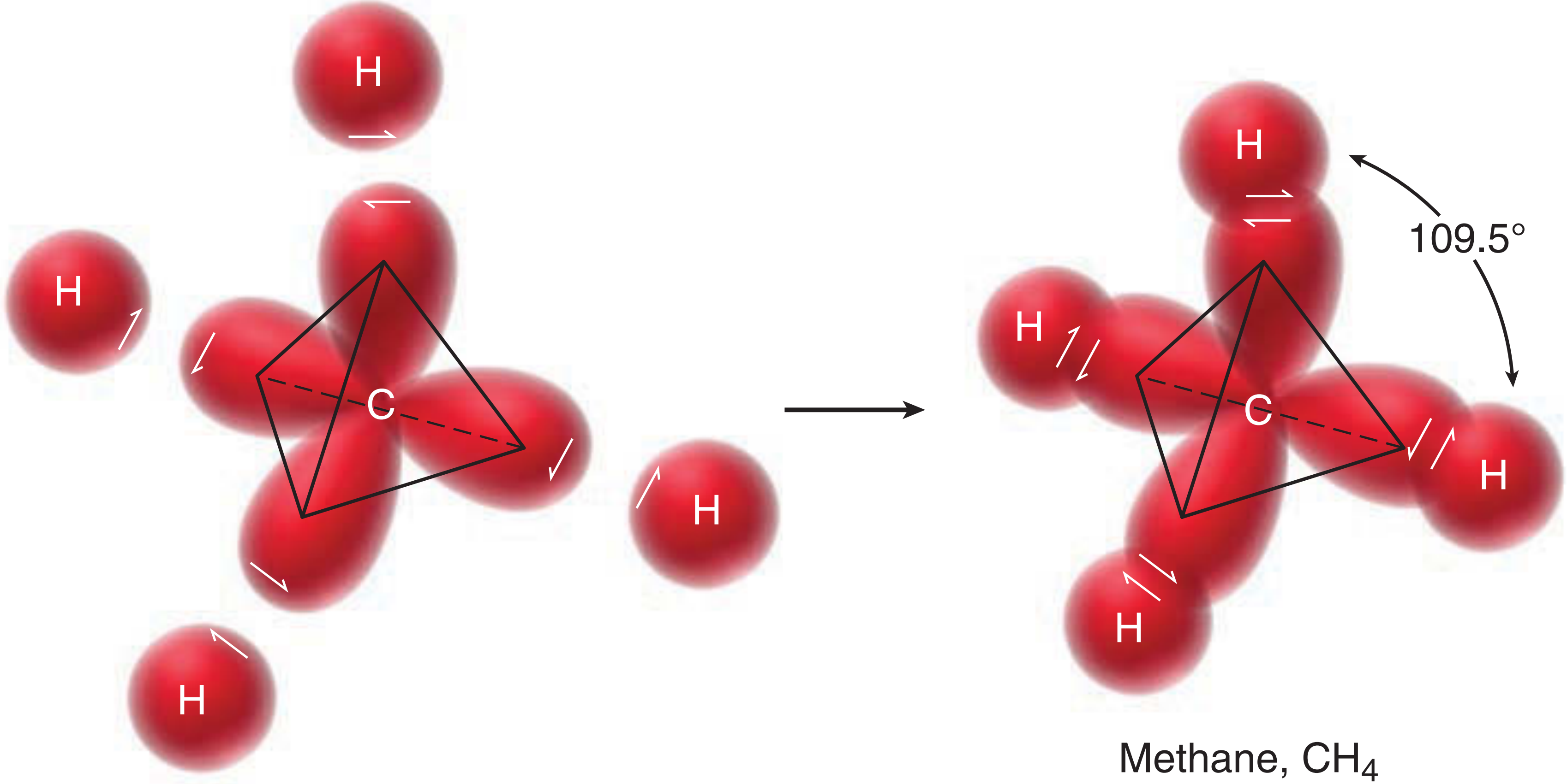
Methane





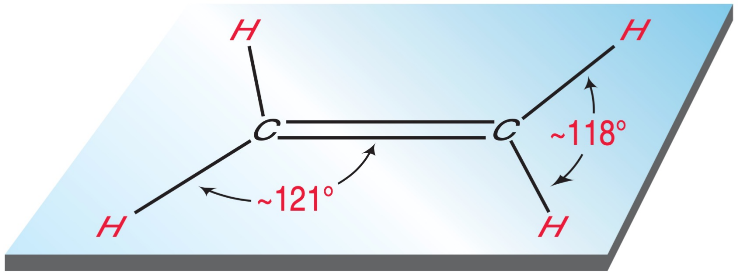
Hybrid Orbital Theory

sp^3 hybrid orbital

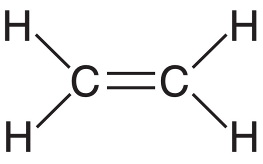


Methane, CH_4

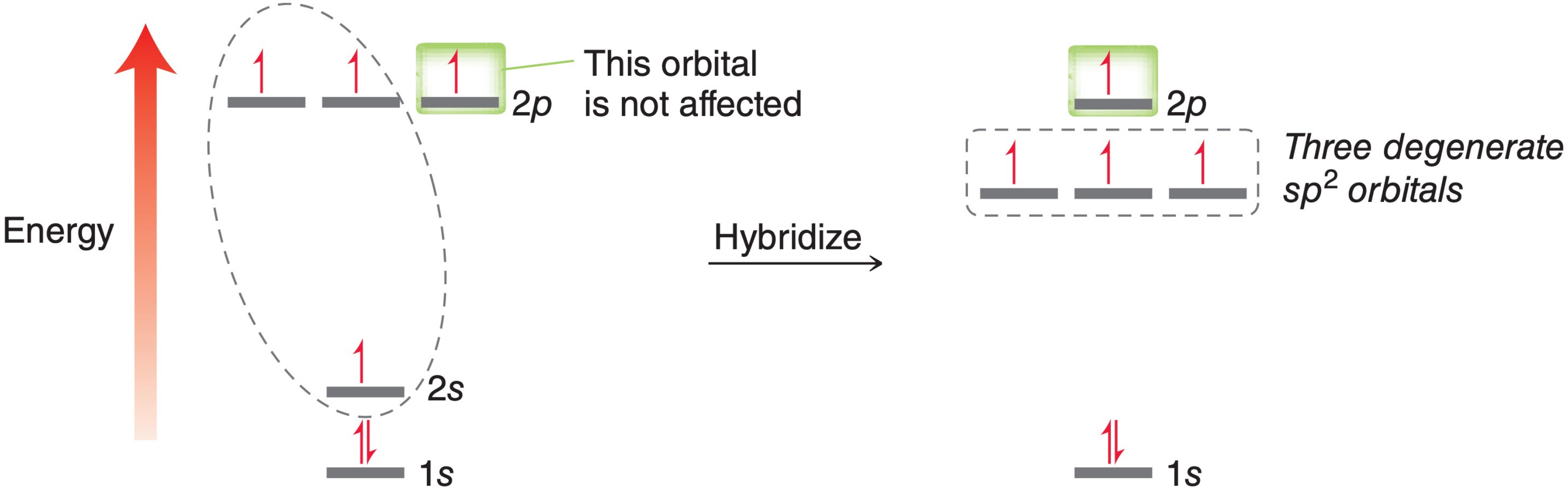
Hybrid Orbital Theory



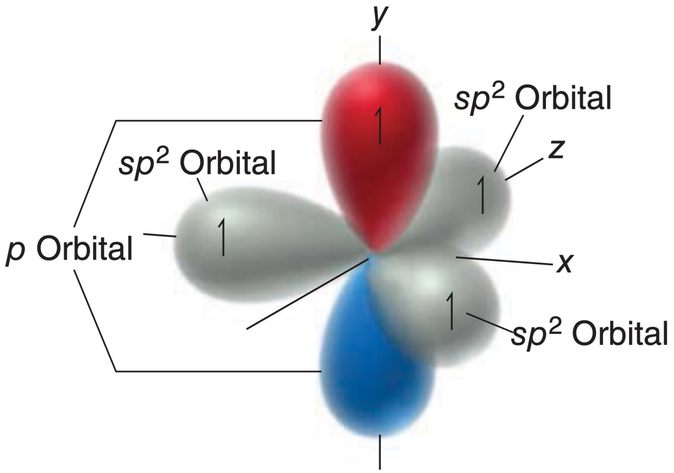
- sp^2 hybrid: trigonal planar

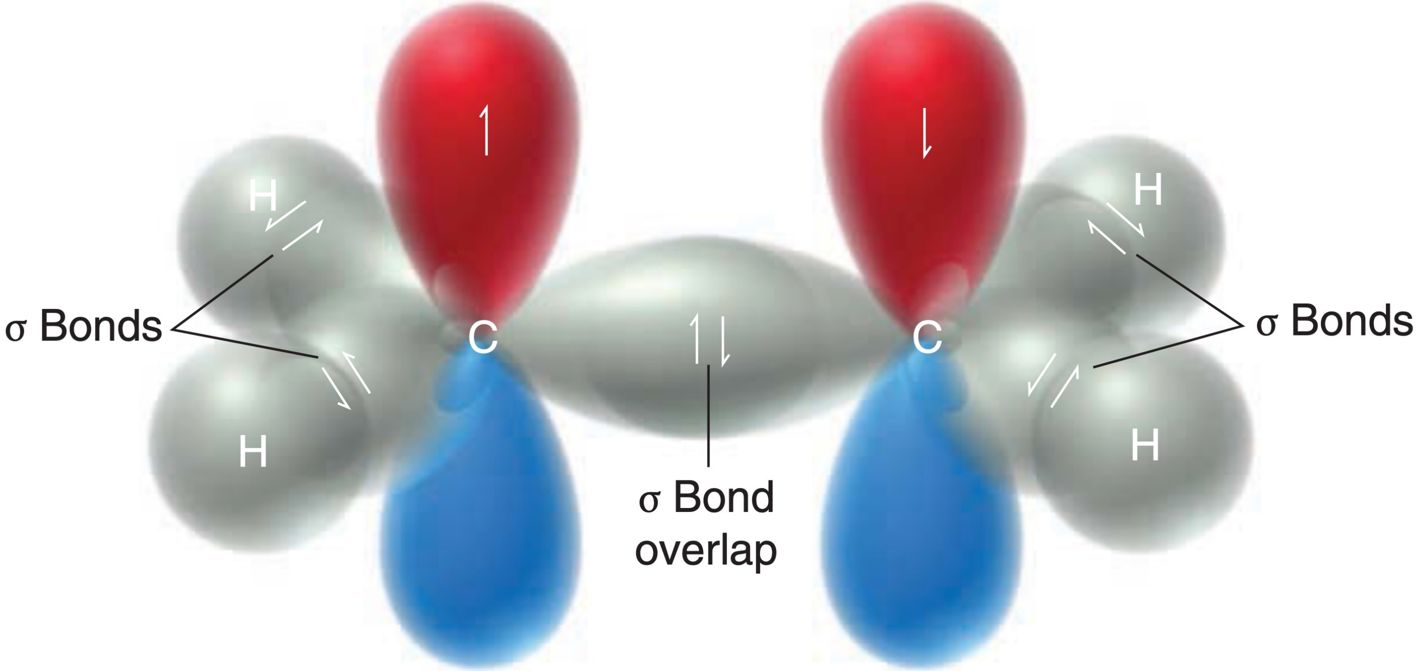


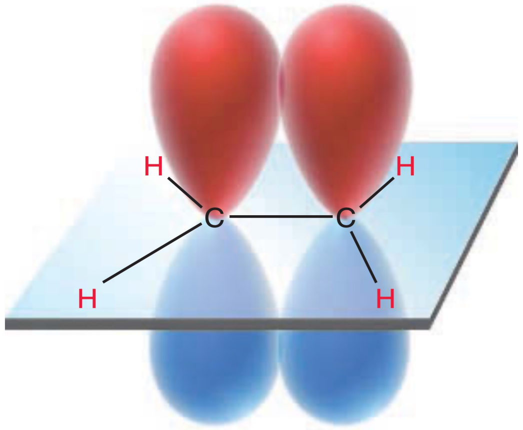
Ethylene



Hybrid Orbital Theory





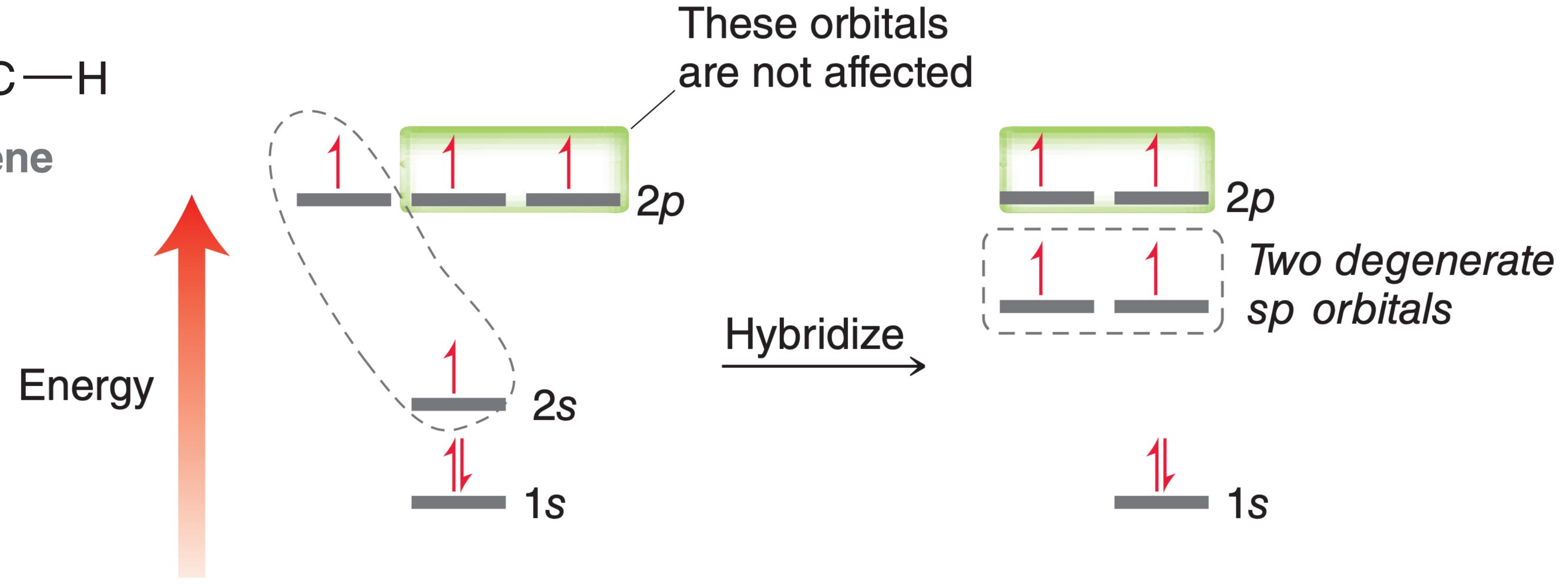


π Bond

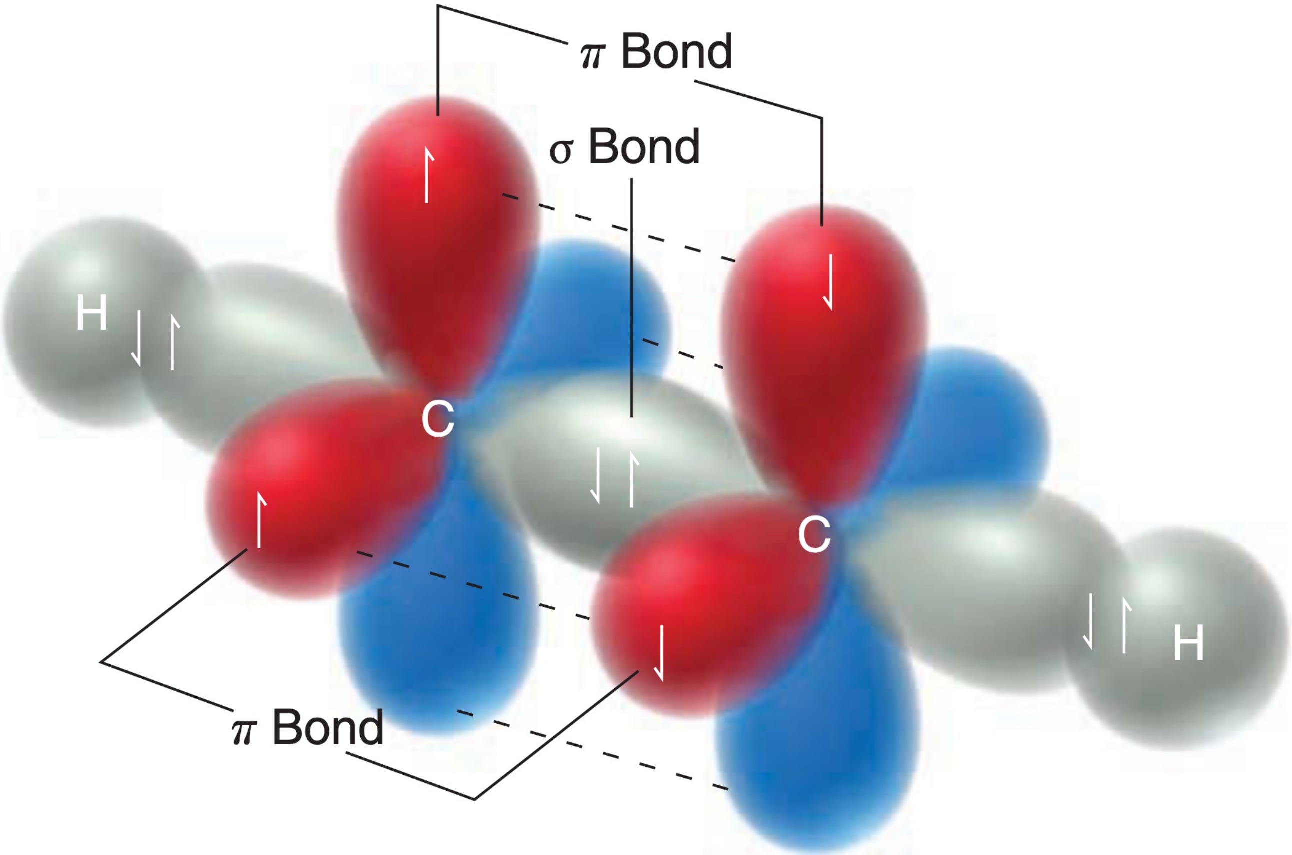
- sp hybrid: linear

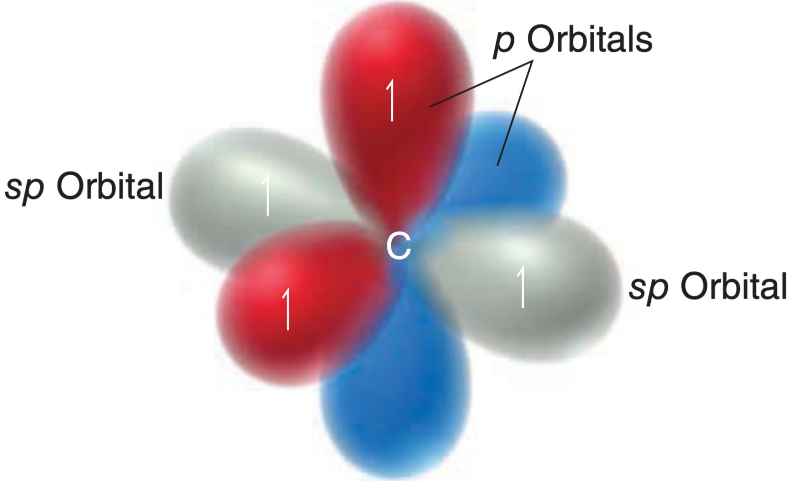
H—C≡C—H

Acetylene

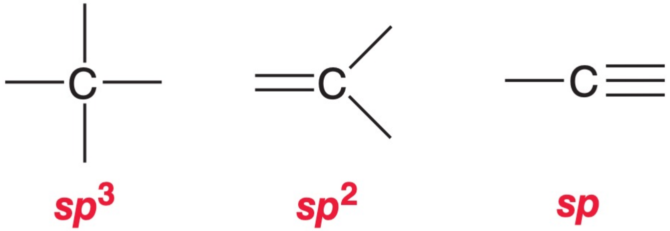


Hybrid Orbital Theory

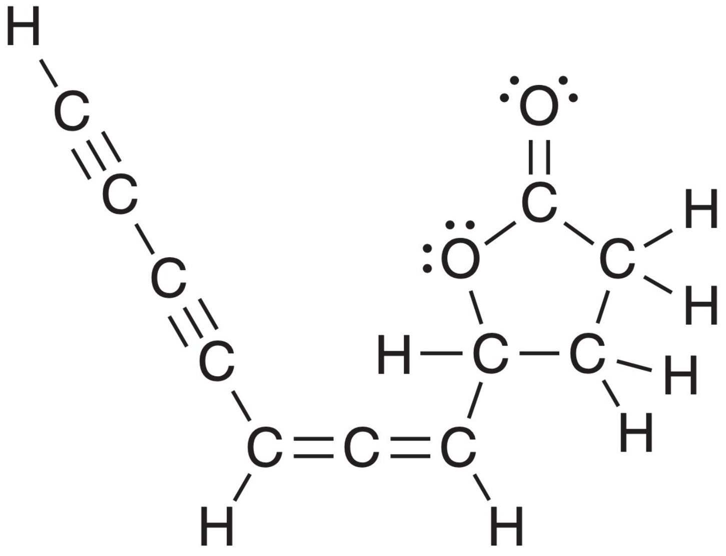




To determine the hybridization state of *an uncharged carbon atom*, simply count the number of σ bonds and π bonds:

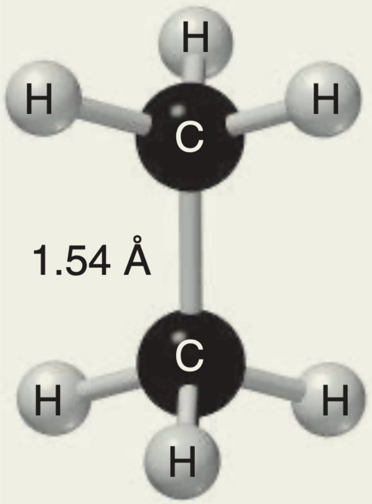
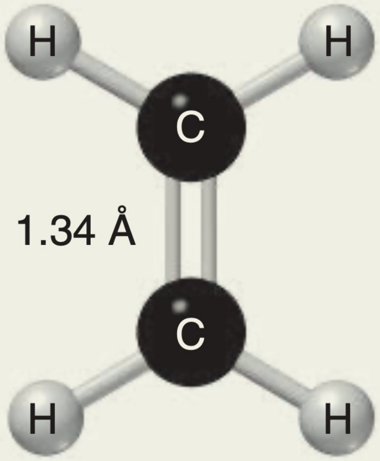
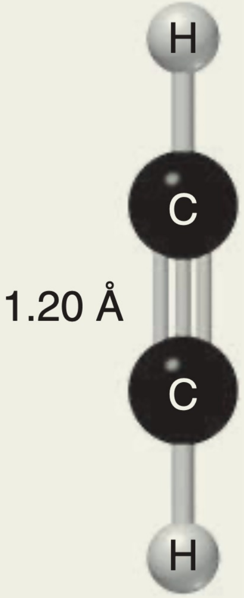


- Practice **1.25** Nemotin is a compound that was first isolated from the fungi *Poria tenuis* and *Poria corticola* in the 1940s and was shown to possess potent antibacterial activity. However, its structure was not verified until it was made in the laboratory much more recently.[7] Determine the hybridization state of each carbon atom in nemotin.



Nemotin

Bond Length

	ETHANE	ETHYLENE	ACETYLENE
Structure			
C—C bond length	1.54 Å	1.34 Å	1.20 Å
Bond energy	368 kJ/mol	632 kJ/mol	820 kJ/mol

sp^3 sp^2 sp

VSEPR Theory

- VSEPR theory: repulsion maximizes the distance between electron pairs in space
- Used to predict molecular geometries

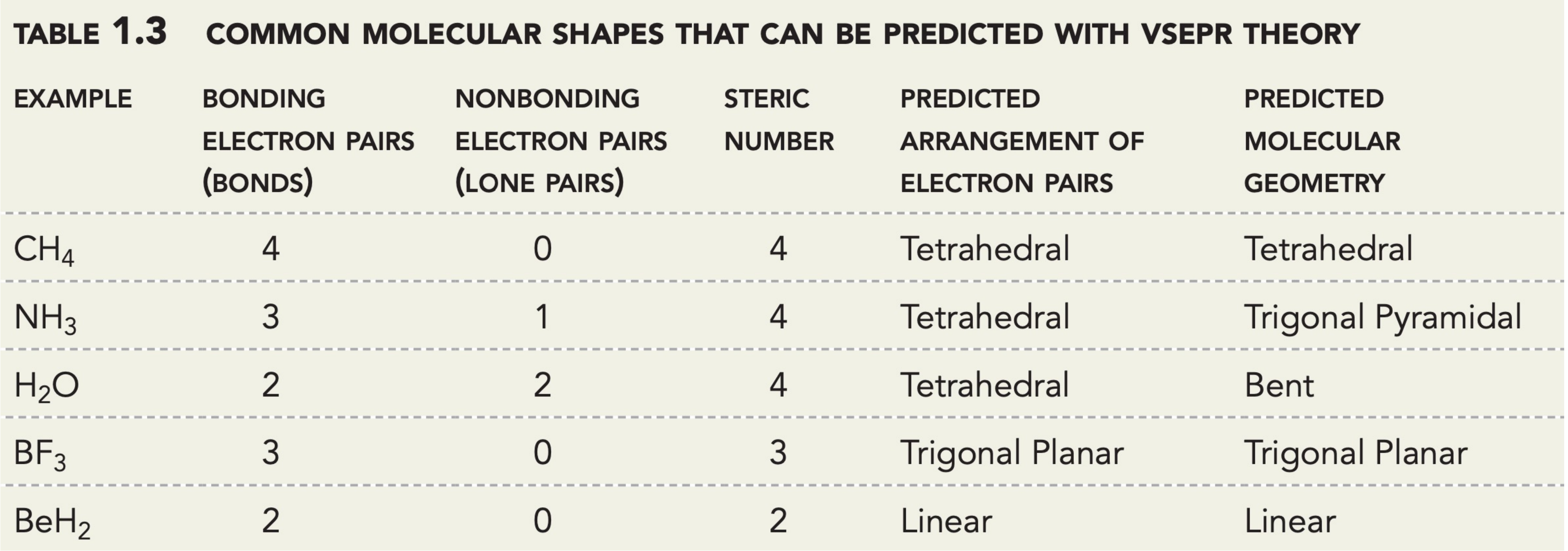
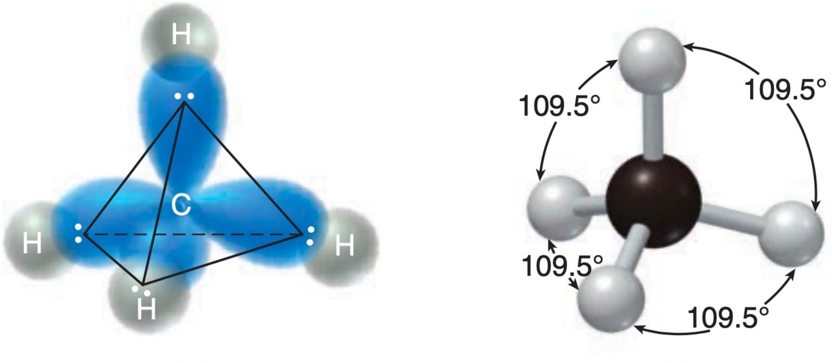


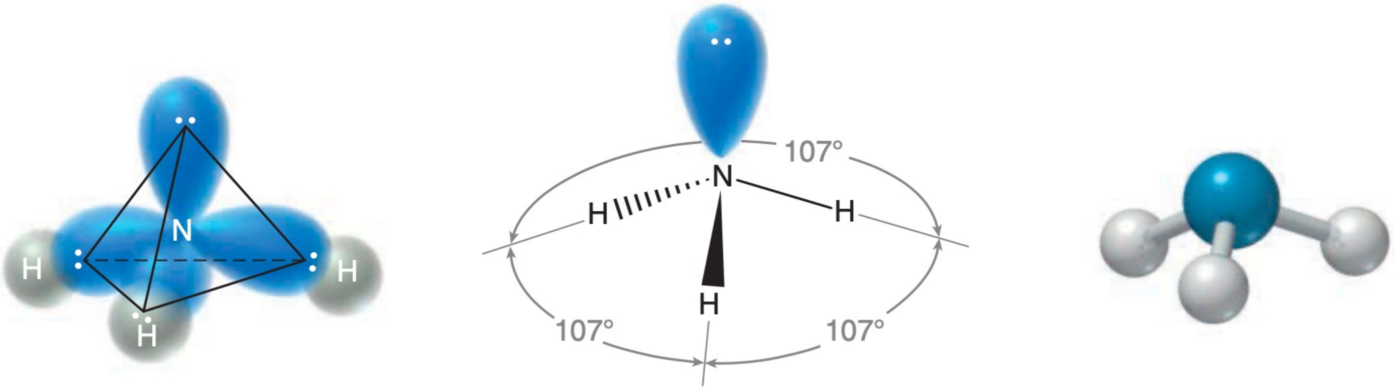
TABLE 1.3 COMMON MOLECULAR SHAPES THAT CAN BE PREDICTED WITH VSEPR THEORY

EXAMPLE	BONDING ELECTRON PAIRS (BONDS)	NONBONDING ELECTRON PAIRS (LONE PAIRS)	STERIC NUMBER	PREDICTED ARRANGEMENT OF ELECTRON PAIRS	PREDICTED MOLECULAR GEOMETRY
CH_4	4	0	4	Tetrahedral	Tetrahedral
NH_3	3	1	4	Tetrahedral	Trigonal Pyramidal
H_2O	2	2	4	Tetrahedral	Bent
BF_3	3	0	3	Trigonal Planar	Trigonal Planar
BeH_2	2	0	2	Linear	Linear

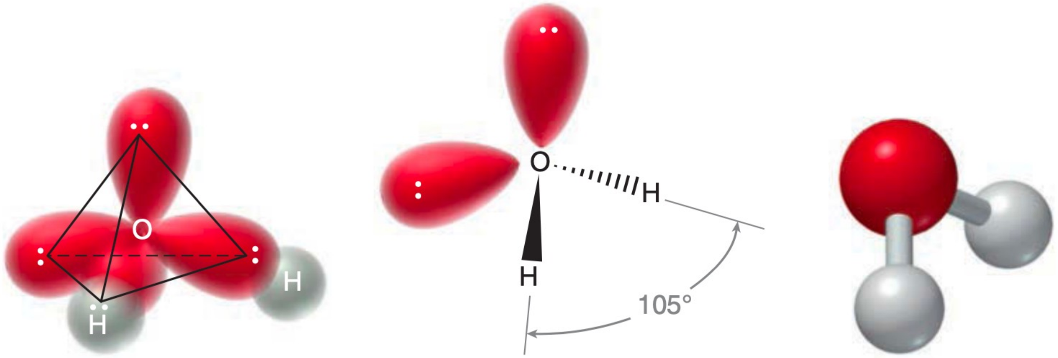
VSEPR Theory



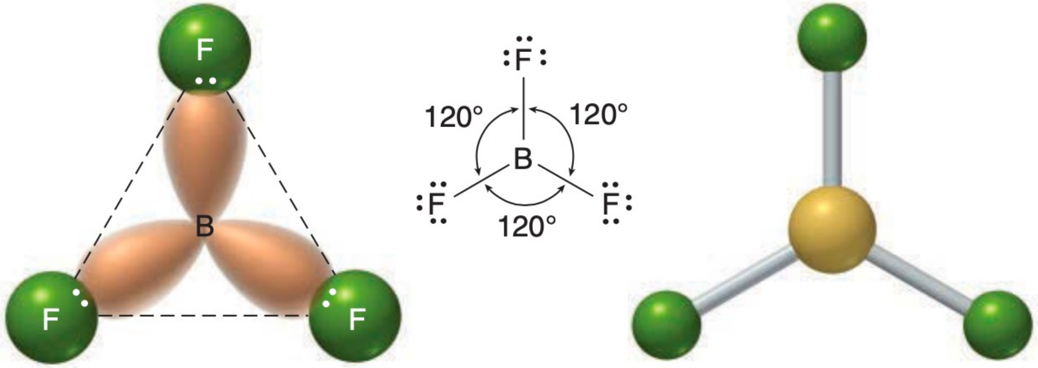
(a) (b)



(a) (b) (c)

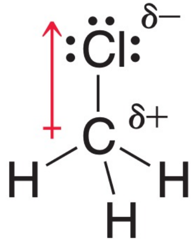


(a) (b) (c)

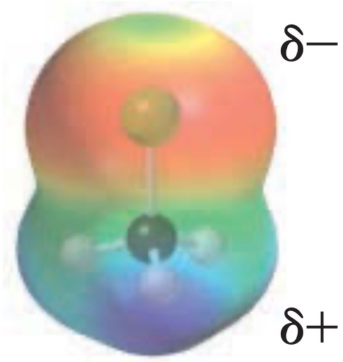


Linear geometry of BeH_2

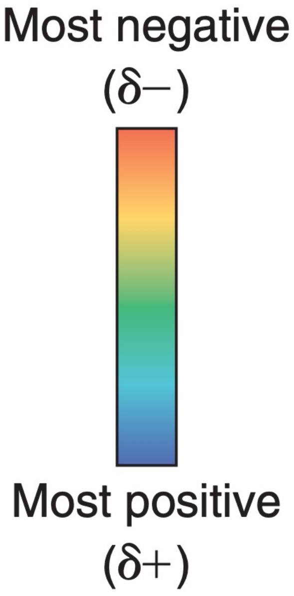
- Electrostatic Potential Map



Chloromethane



Electrostatic potential map of chloromethane



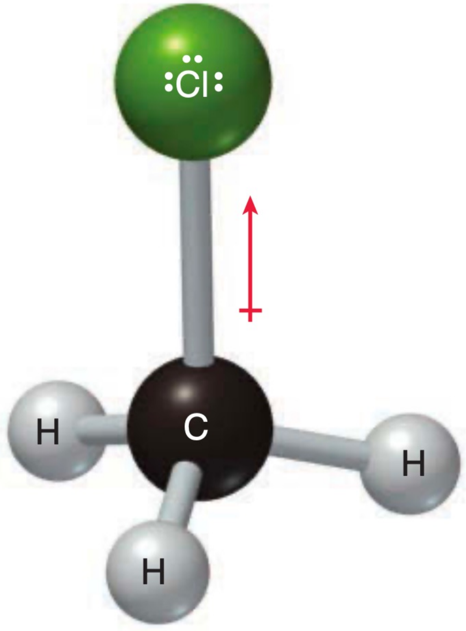
Color scale

Molecular Polarity

- Dipole moment (μ): an indicator of polarity

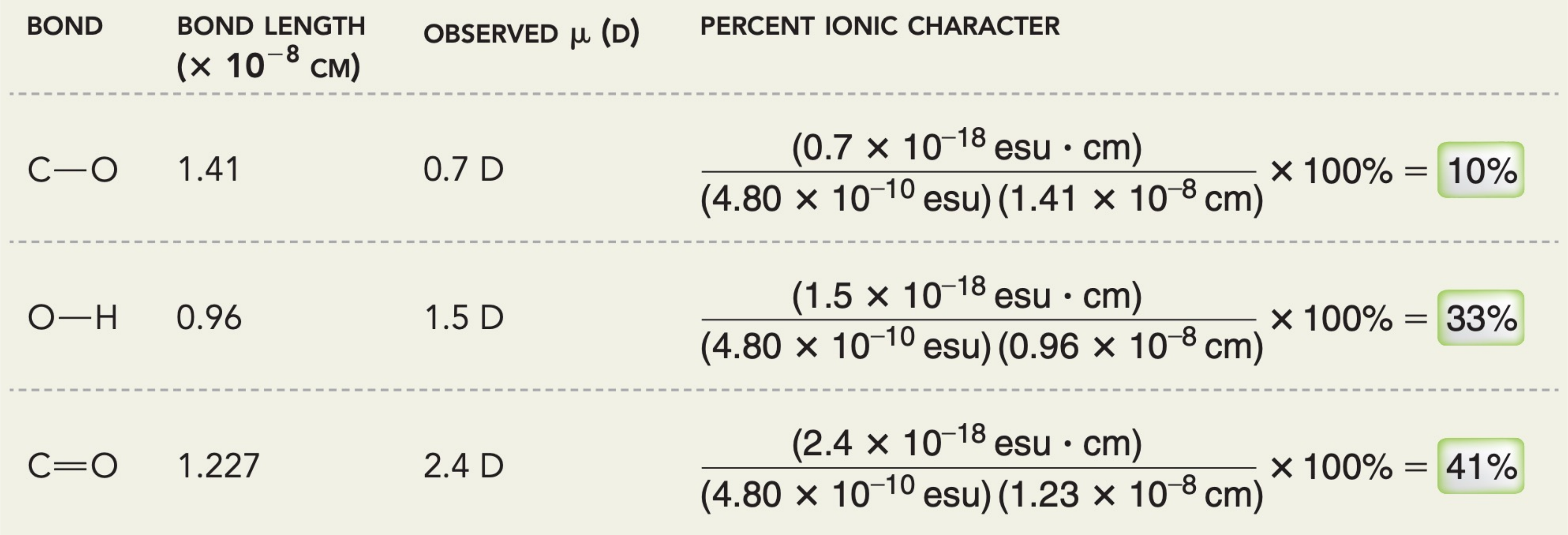
$$\mu = \delta \times d$$

$$1 \text{ Debye} = 10^{-18} \text{ esu} \cdot \text{cm}$$



$\mu = 1.87$ D

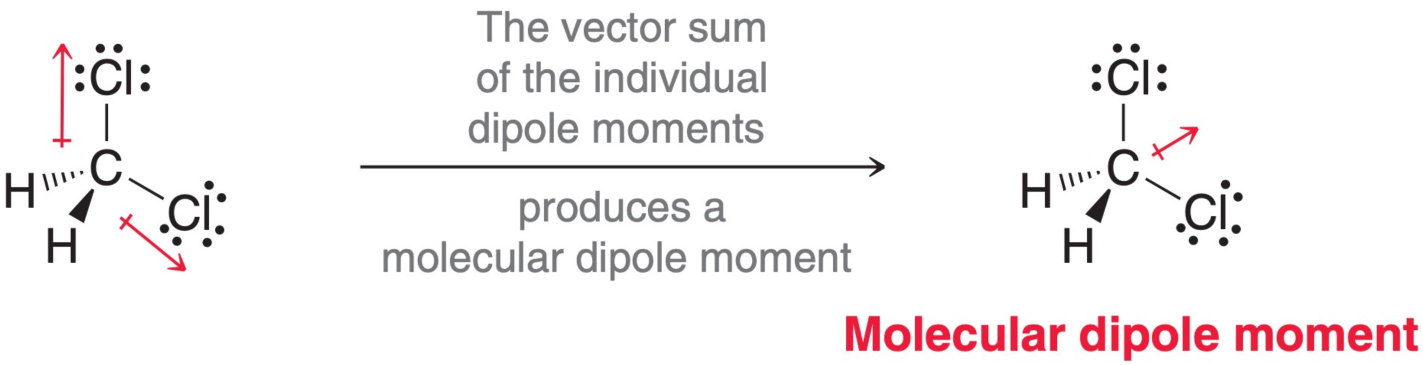
- Measuring % *ionic characteristics*

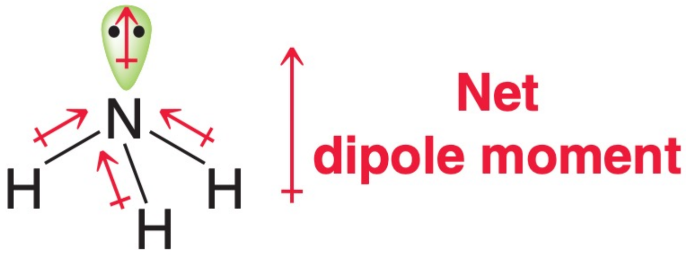


BOND	BOND LENGTH ($\times 10^{-8}$ CM)	OBSERVED μ (D)	PERCENT IONIC CHARACTER
C—O	1.41	0.7 D	$\frac{(0.7 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})(1.41 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{10\%}$
O—H	0.96	1.5 D	$\frac{(1.5 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})(0.96 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{33\%}$
C═O	1.227	2.4 D	$\frac{(2.4 \times 10^{-18}\ \text{esu} \cdot \text{cm})}{(4.80 \times 10^{-10}\ \text{esu})(1.23 \times 10^{-8}\ \text{cm})} \times 100\% = \boxed{41\%}$

Molecular Polarity

- Molecular dipole moment: vector sum of bond dipole moments





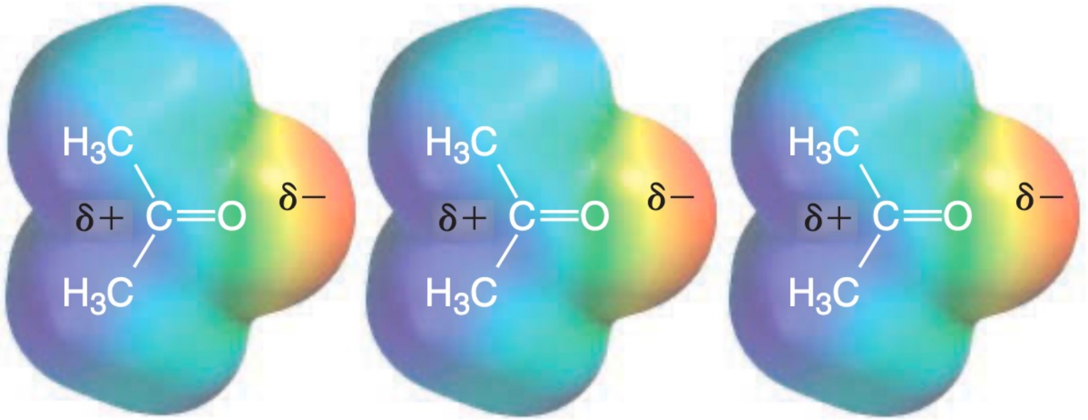
Molecular Polarity

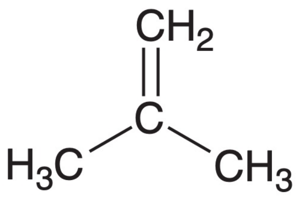
- Practice

Identify whether each of the following compounds exhibits a molecular dipole moment. If so, indicate the direction of the net molecular dipole moment:

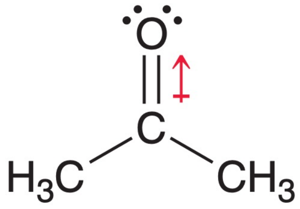
(a) $CH_3CH_2OCH_2CH_3$ **(b)** CO_2

- Dipole-Dipole Interactions





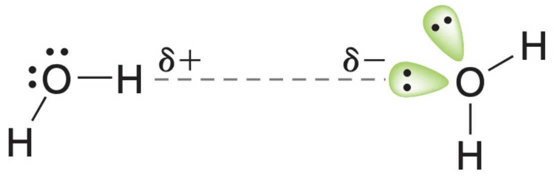
Isobutylene
Melting point = –140.3°C
Boiling point = –6.9°C



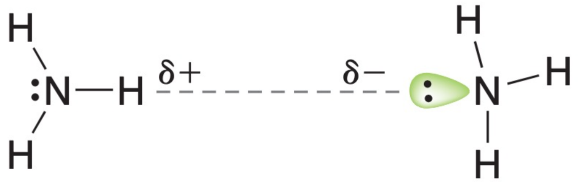
Acetone
Melting point = –94.9°C
Boiling point = 56.3°C

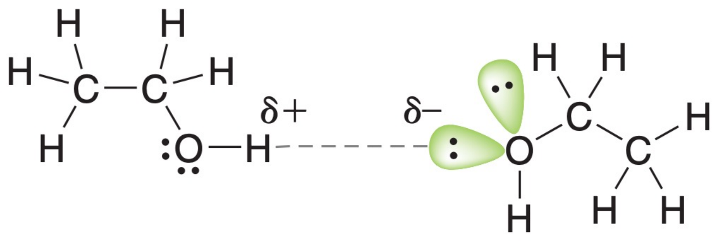
- Hydrogen Bonding

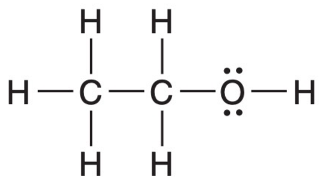
Hydrogen bond interaction between molecules of water



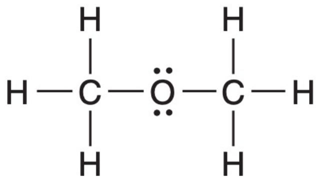
Hydrogen bond interaction between molecules of ammonia



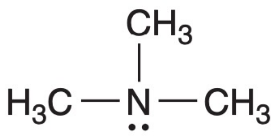




Ethanol
Boiling point = 78.4°C

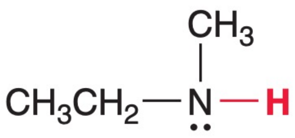


Methoxymethane
Boiling point = −23°C



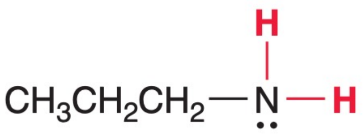
$H_3C-\overset{CH_3}{N}-CH_3$

Trimethylamine
Boiling point = 3.5°C



$CH_3CH_2-\overset{CH_3}{N}-H$

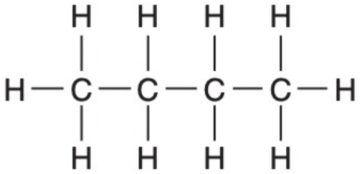
Ethylmethylamine
Boiling point = 37°C



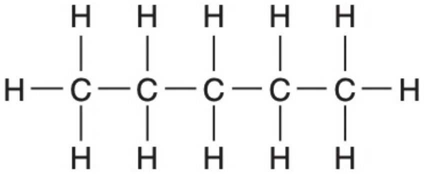
$CH_3CH_2CH_2-\overset{H}{N}-H$

Propylamine
Boiling point = 49°C

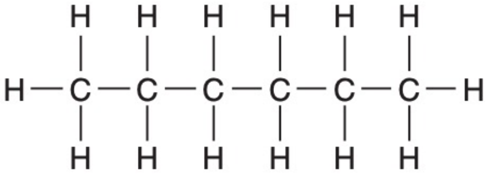
- London Dispersion Forces



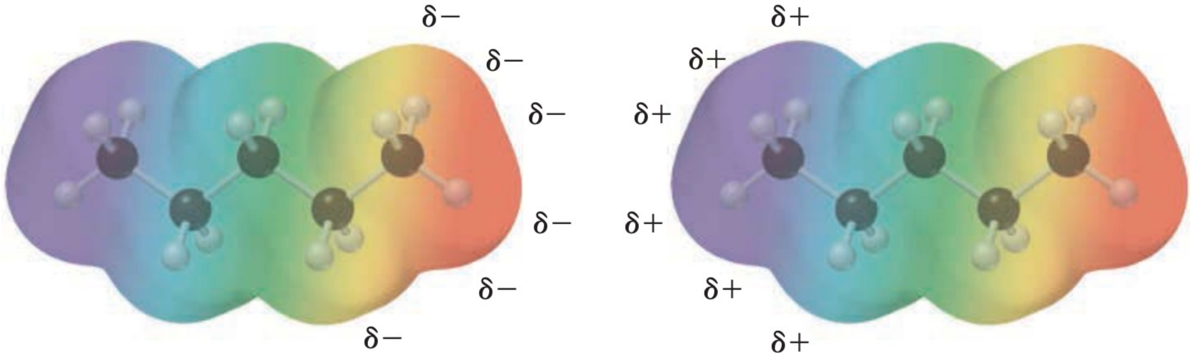
Butane
(C_4H_{10})
Boiling point = 0°C

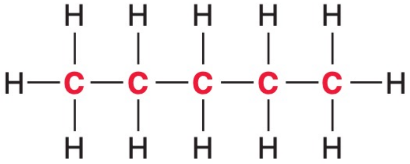


Pentane
(C_5H_{12})
Boiling point = 36°C

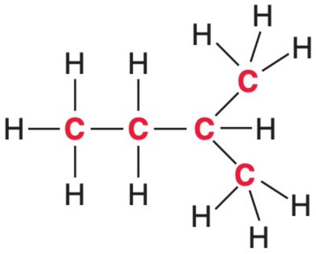


Hexane
(C_6H_{14})
Boiling point = 69°C

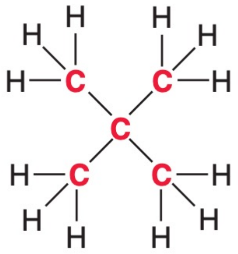




Pentane
Boiling point = 36°C



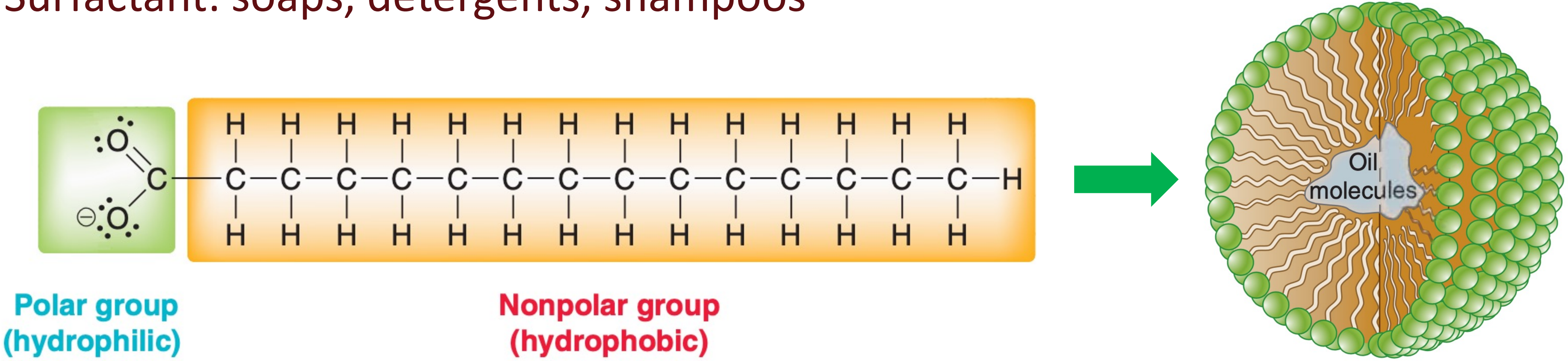
2-Methylbutane
Boiling point = 28°C



2,2-Dimethylpropane
Boiling point = 10°C

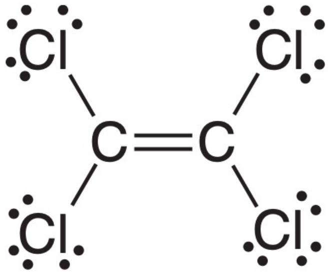
Solubility

- "Like dissolve like"
  - Polar compounds dissolve in polar solvents
  - Nonpolar compounds dissolve in nonpolar solvents
- Surfactant: soaps, detergents, shampoos



- Dry-cleaning

Unlike using water, dry cleaning uses non-polar solvents, such as tetrachloroethylene, to clean clothes, which can ensure that clothes are not damaged by water.



Tetrachloroethylene

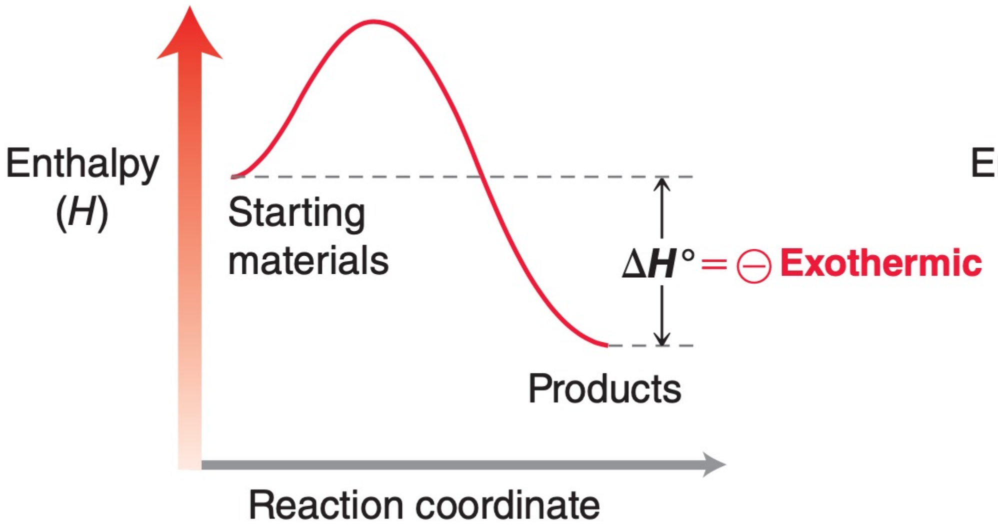
Chem Principle Review

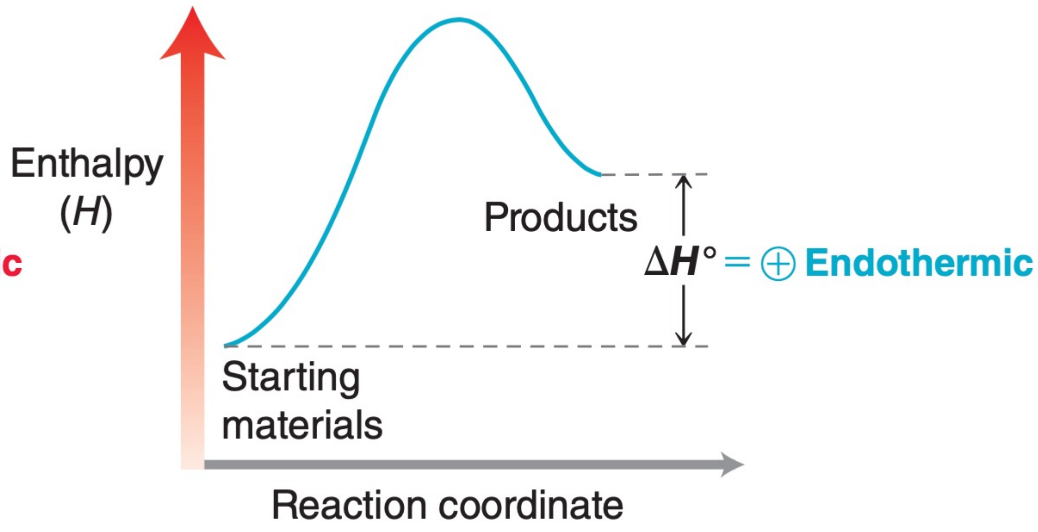
Structure, Thermodynamics & Kinetics, Acid & Base

- State functions
- Example: H (enthalpy), S (entropy), G (Gibbs free energy)
- The change of the state function only depends on the **initial state** and the **final state** of the system

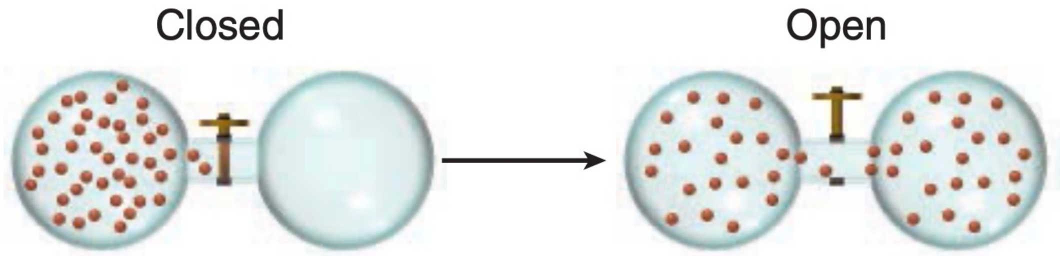
- Enthalpy

$$\Delta H = q \quad \text{(at constant pressure)}$$





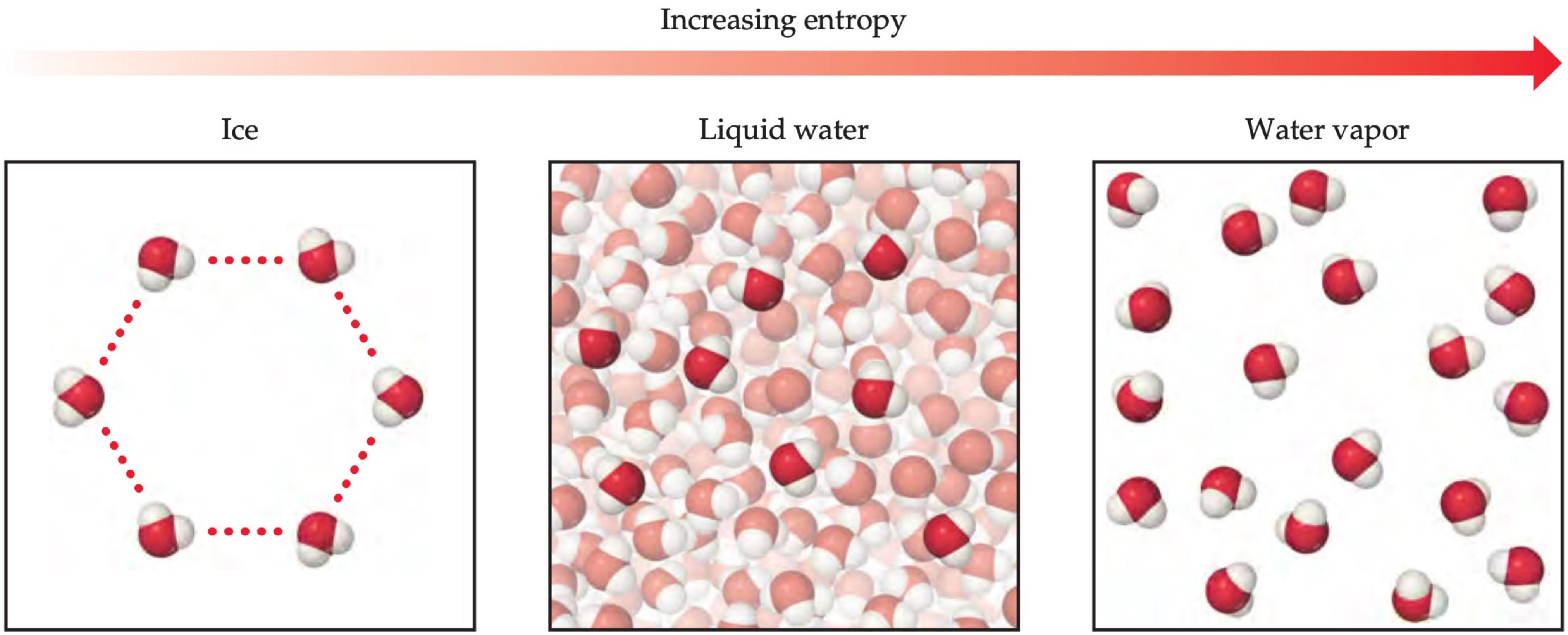
- Entropy: a measurement of system *chaos*



The Second Law: the entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$$

$$\Delta S = \frac{q_{rev}}{T} \qquad \underline{(\text{constant } T)}$$



Rigid, crystalline structure

Motion restricted to **vibration** only

Smallest number of microstates

Increased freedom with respect to **translation**

Free to **vibrate** and **rotate**

Larger number of microstates

Molecules spread out, essentially independent of one another

Complete freedom for **translation**, **vibration**, and **rotation**

Largest number of microstates

- Gibbs free energy: the spontaneity of reactions

$$\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$$

$$\Delta H = q \quad \text{(at constant pressure)}$$

$$\Rightarrow \quad \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T}$$

- Deriving Gibbs free energy from ΔS_{tot}

$$\Delta S_{\boxed{\text{surr}}} = -\frac{\Delta H_{\boxed{\text{sys}}}}{T}$$

$$\Delta S_{\text{tot}} = \left(-\frac{\Delta H_{\text{sys}}}{T}\right) + \Delta S_{\text{sys}}$$

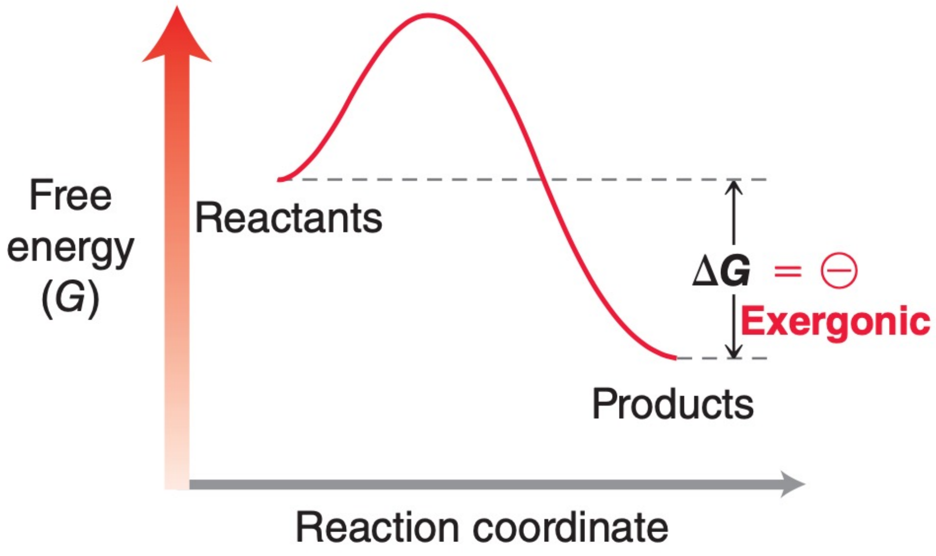
$$\begin{tikzcd}
\boxed{-T\Delta S_{\text{tot}}} \arrow[d] & = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \\
\boxed{\Delta G} &
\end{tikzcd}$$

$$\Delta G = \boxed{\Delta H} - \boxed{T\Delta S}$$

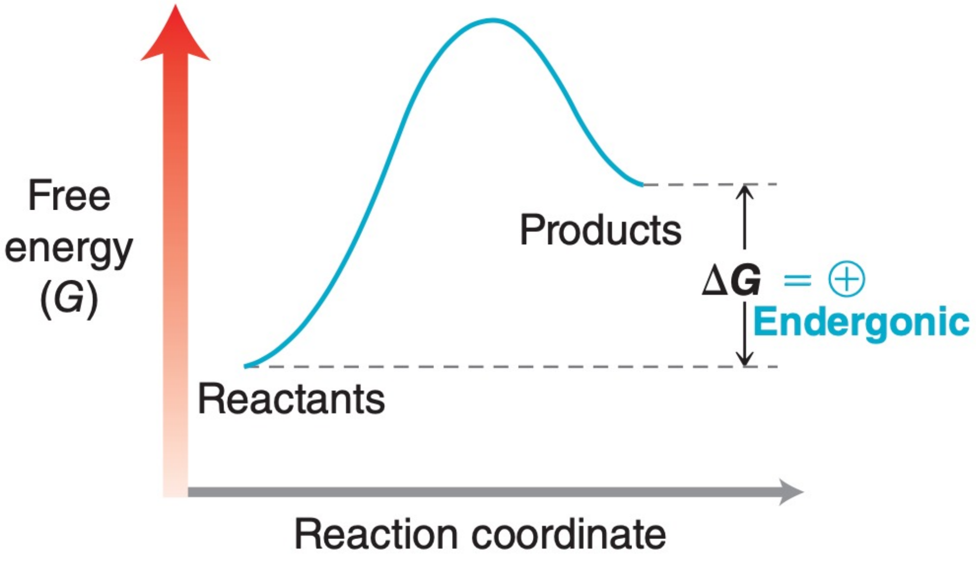
$\swarrow$ **Associated with the change in entropy of the surroundings**

$\searrow$ **Associated with the change in entropy of the system**

Thermodynamics

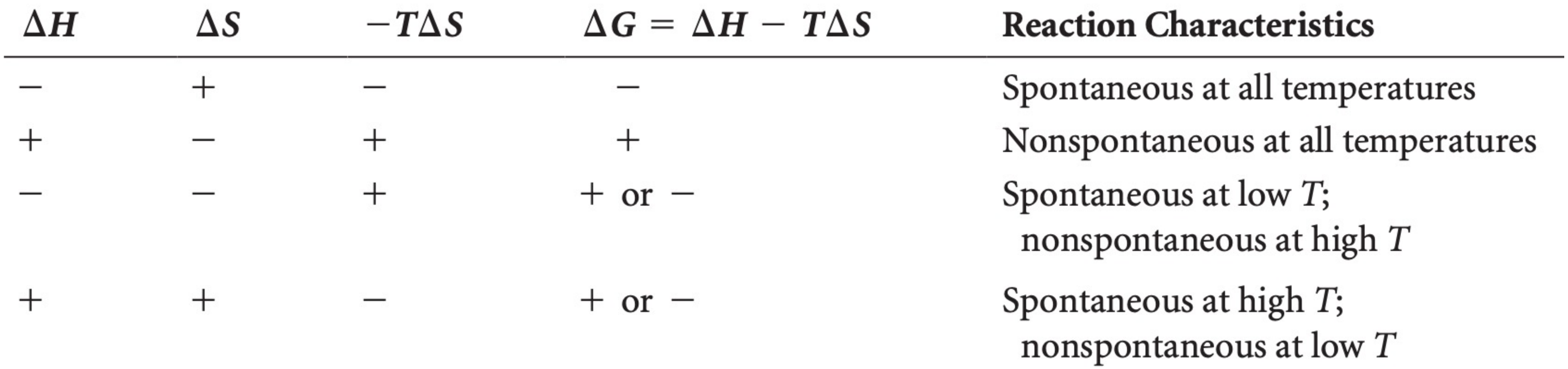


spontaneous



nonspontaneous

- Spontaneity and different state functions

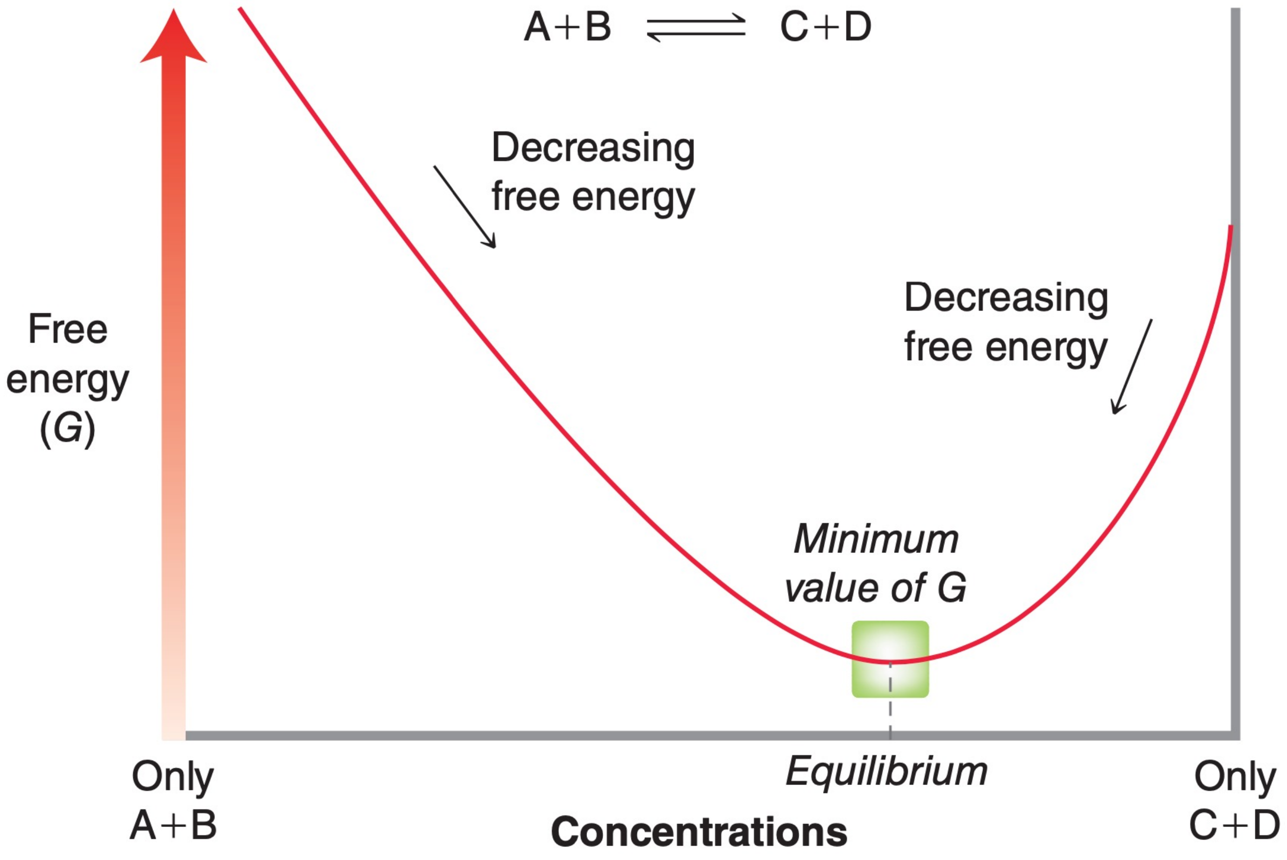


ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	**Reaction Characteristics**
−	+	−	−	Spontaneous at all temperatures
+	−	+	+	Nonspontaneous at all temperatures
−	−	+	+ or −	Spontaneous at low *T*; nonspontaneous at high *T*
+	+	−	+ or −	Spontaneous at high *T*; nonspontaneous at low *T*

- Chemical equilibrium

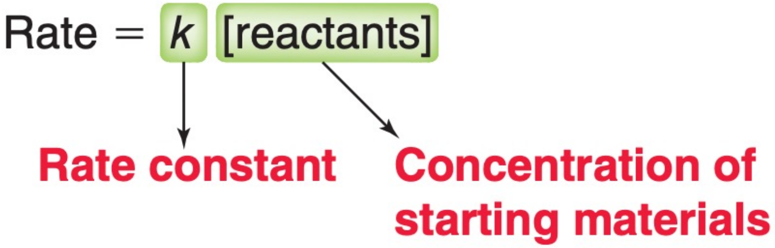
$$K_{\mathrm{eq}} = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$$

$$\Delta G = -RT \ln K_{\mathrm{eq}}$$



Kinetics

- Kinetics: the speed of reactions



$$\text{Rate} = k\,[\text{reactants}]$$

Rate constant

Concentration of starting materials

$$\text{Rate} = k\,[\text{A}]^{x}\,[\text{B}]^{y}$$

$$\text{Rate} = k\,[\text{A}]$$

First order

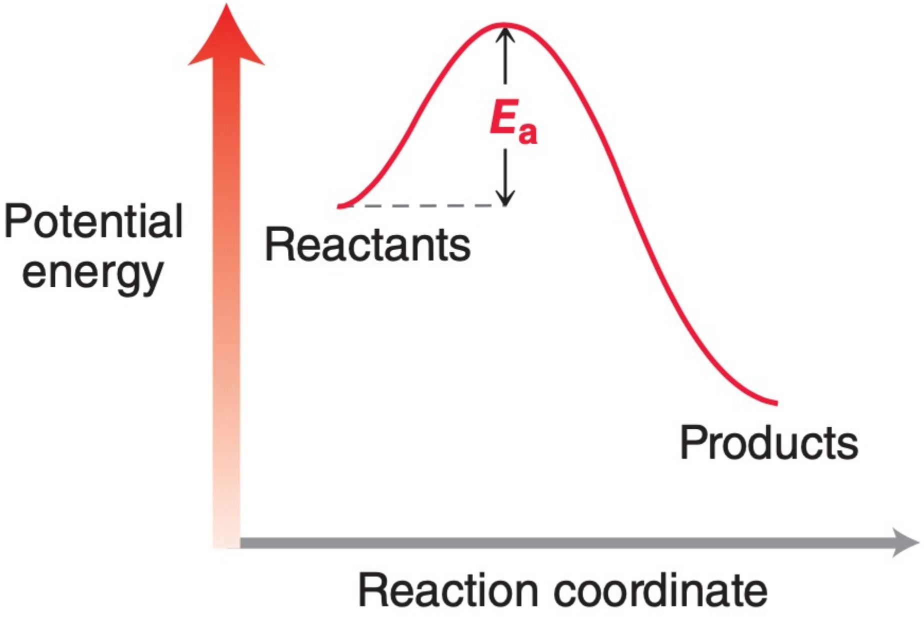
$$\text{Rate} = k\,[\text{A}]\,[\text{B}]$$

Second order

$$\text{Rate} = k\,[\text{A}]^{2}\,[\text{B}]$$

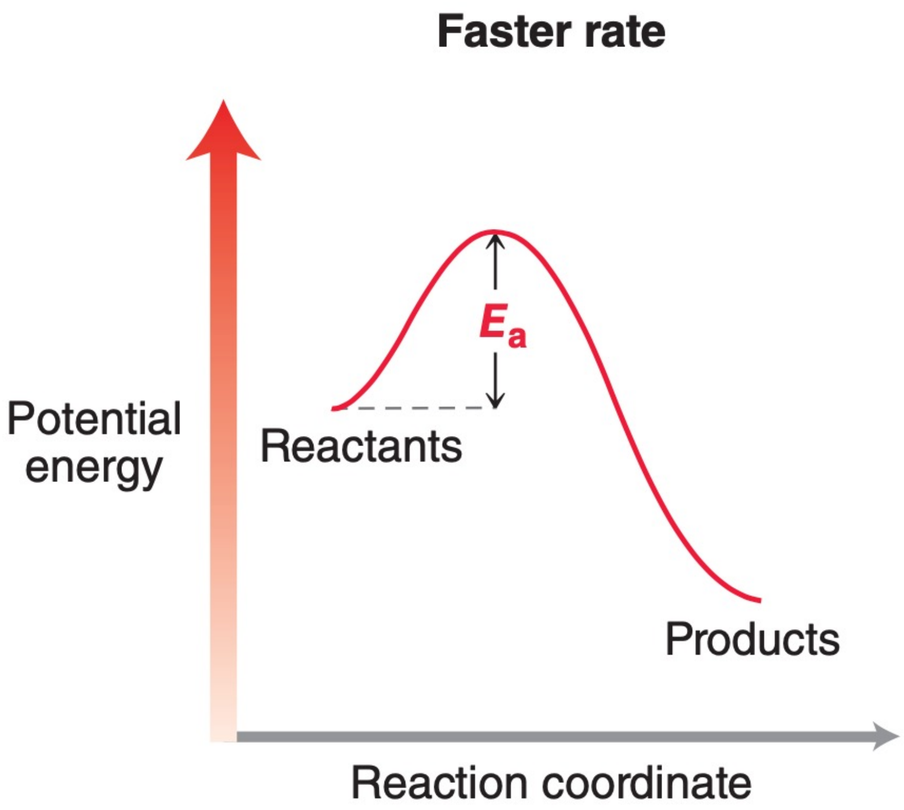
Third order

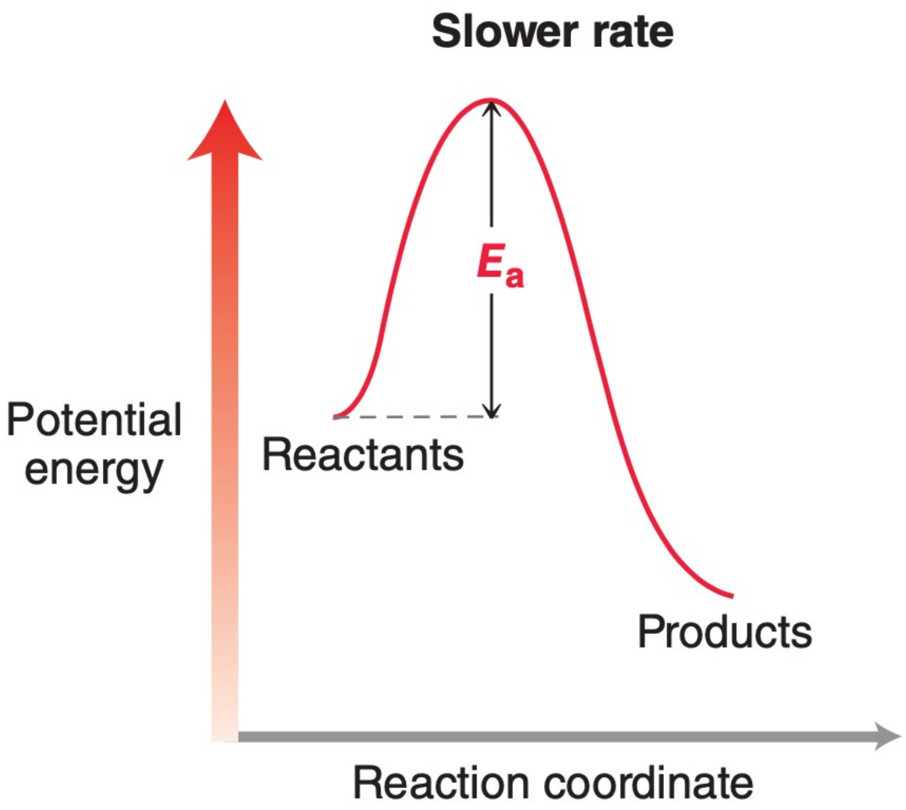
- Activation energy (E_a) & reaction rates



$$\text{Rate} = \boxed{k}\,[A]^x\,[B]^y$$

Kinetics


Faster rate


Slower rate

- Factors affecting reaction rate

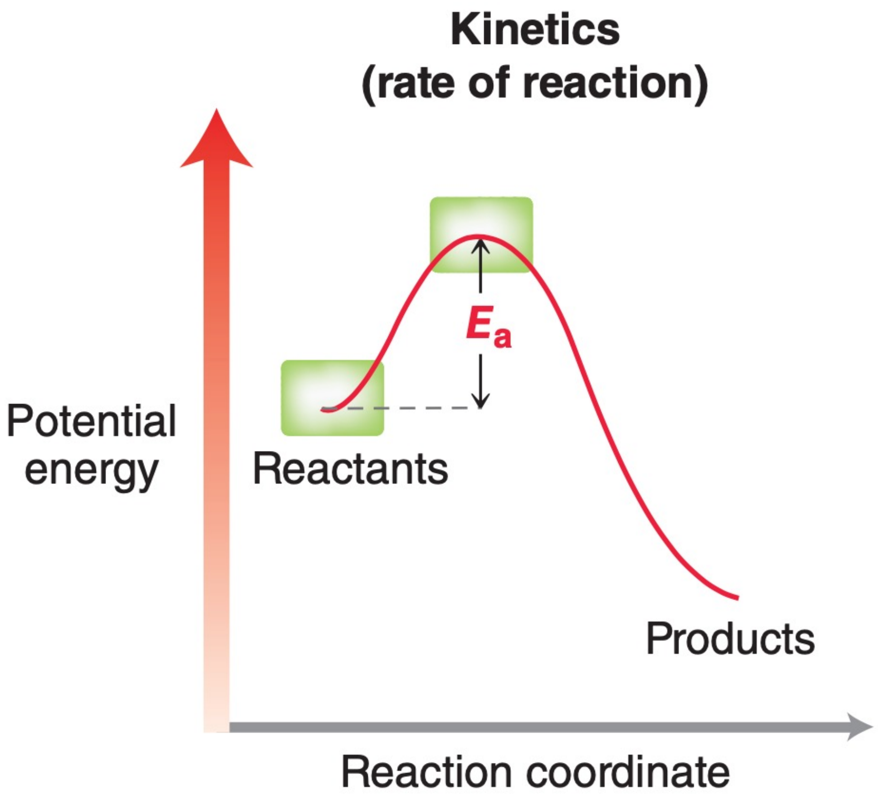
1. Temperature
2. Concentration (liquid phase reaction)
3. Pressure (gaseous phase reaction)
4. Surface area, structures
5. Catalyst

$$k = Ae^{-\frac{E_a}{RT}}$$

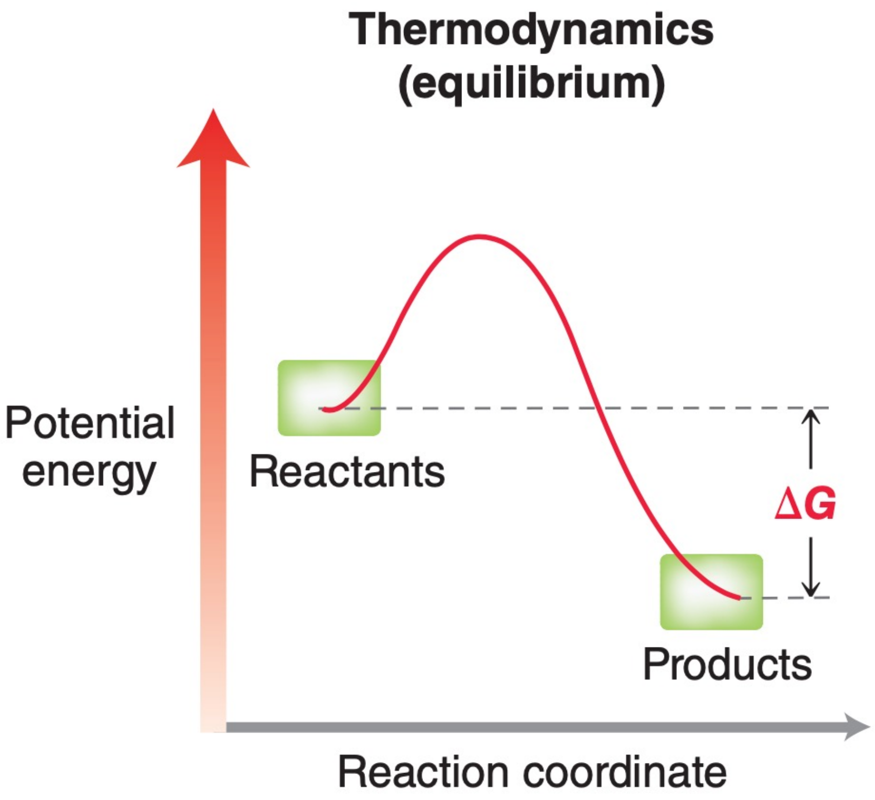
Arrhenius equation

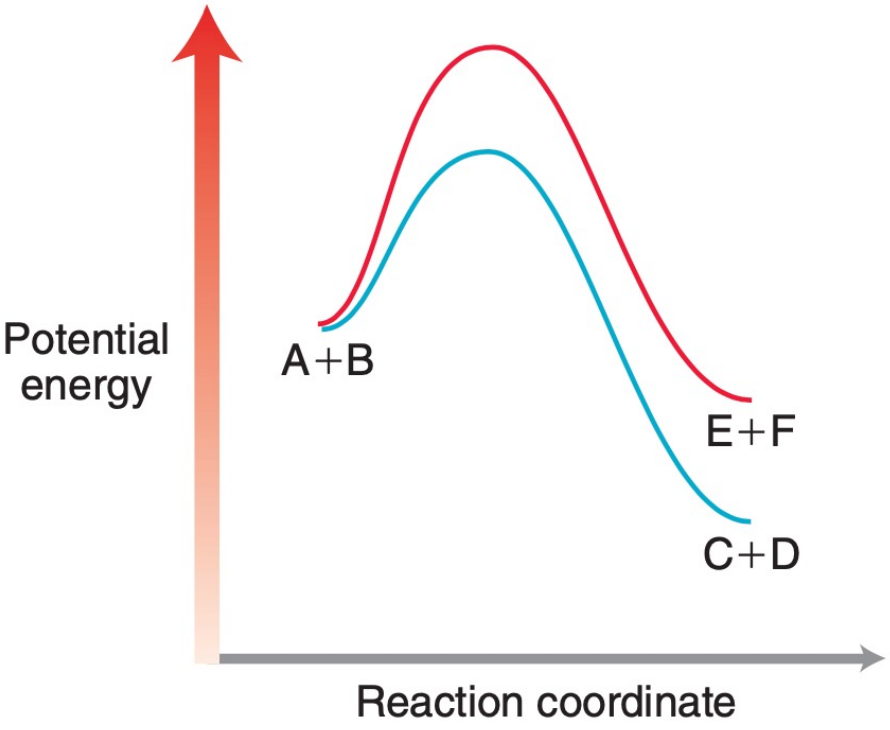
Comparison between T& K

the essence of kinetics: rate

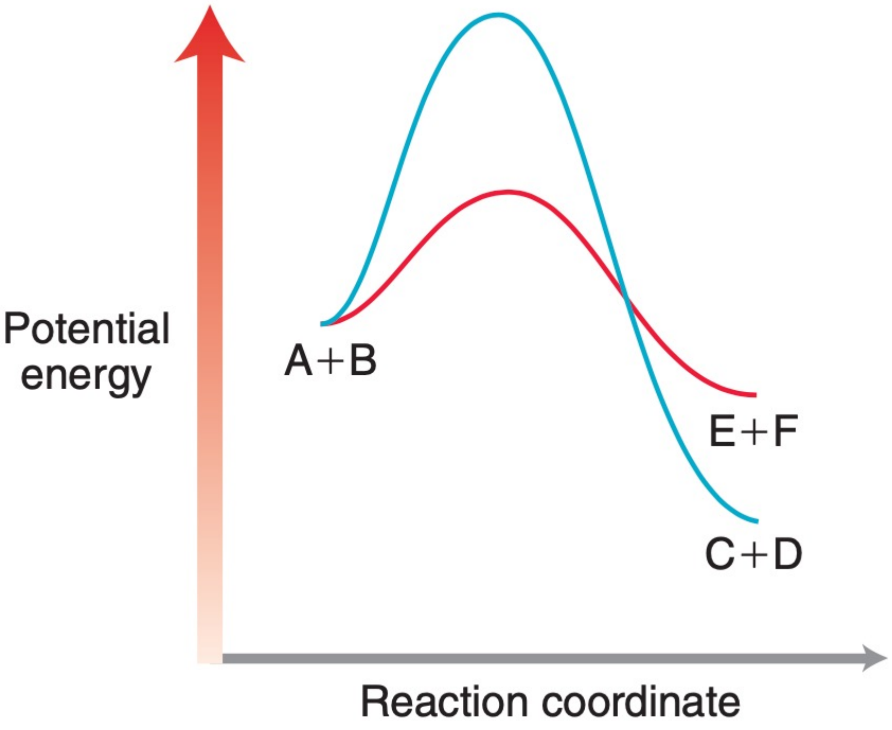


the essence of thermodynamics: equilibrium





thermodynamics: C+D favors
kinetics: C+D favors



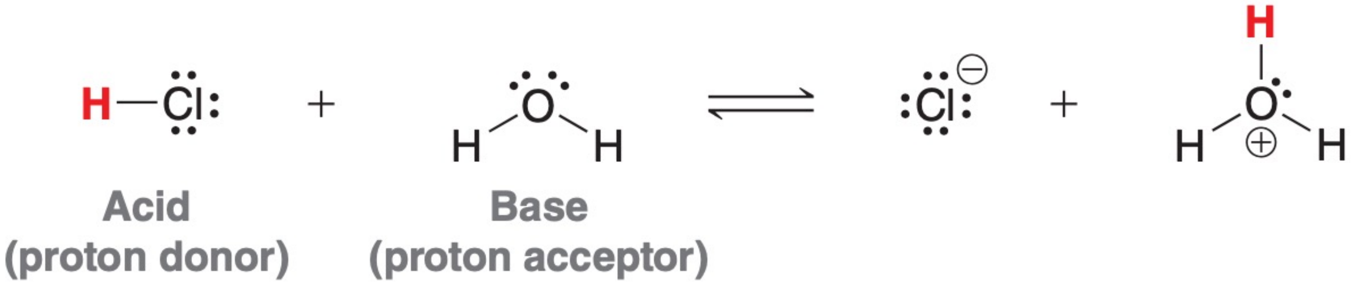
thermodynamics: C+D favors
kinetics: E+F favors

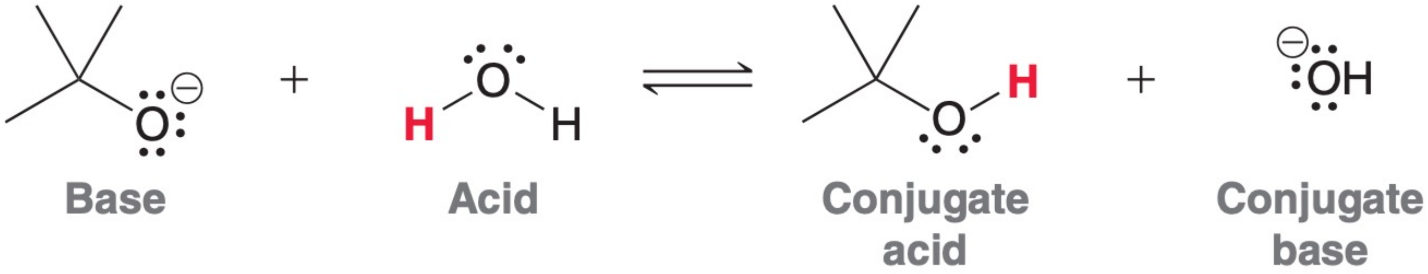
Chem Principle Review

Structure, Thermodynamics & Kinetics, Acid & Base

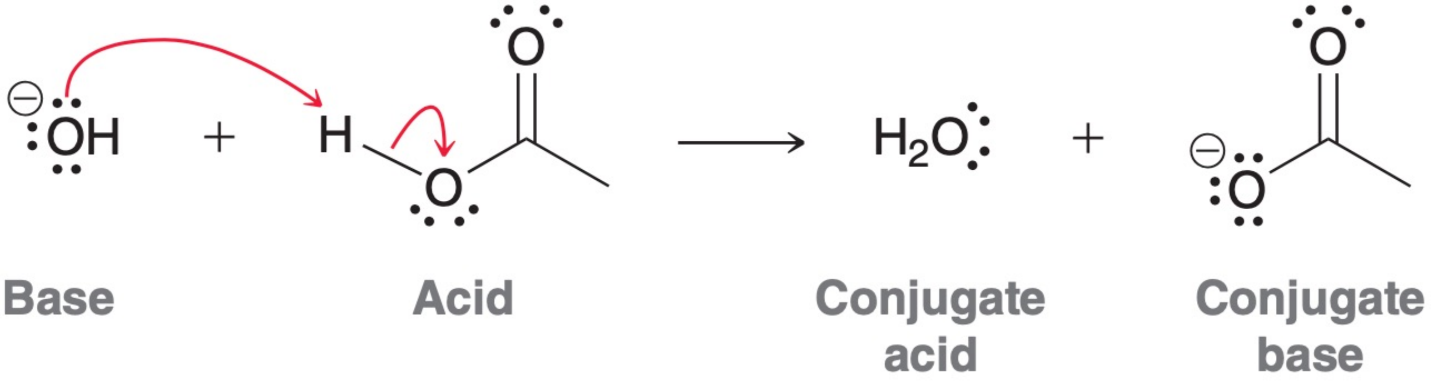
Brønsted-Lowry Acid & Base

- Brønsted-Lowry acid & base theory

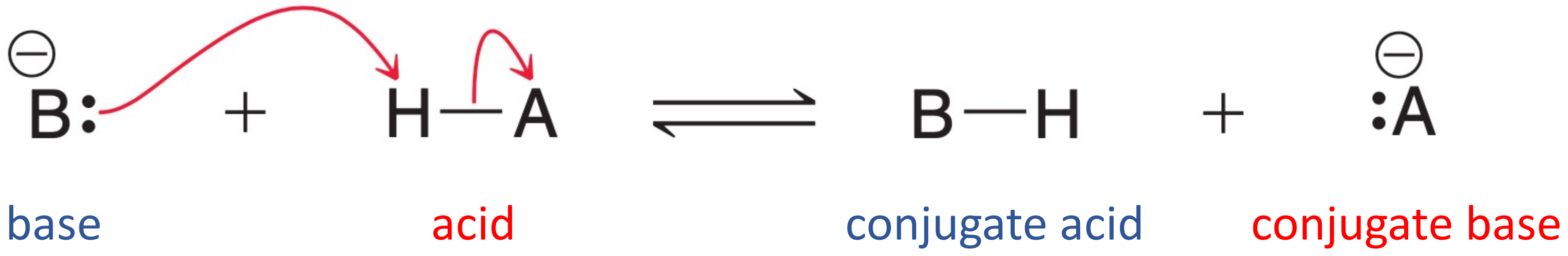




- Arrow-pushing

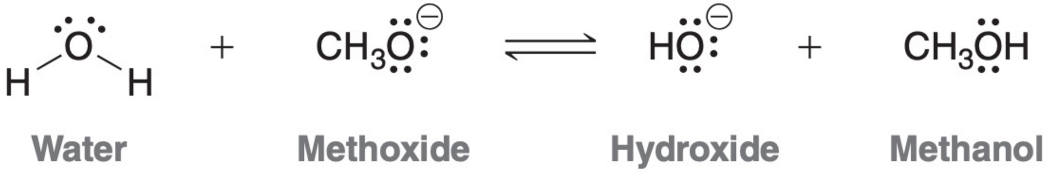


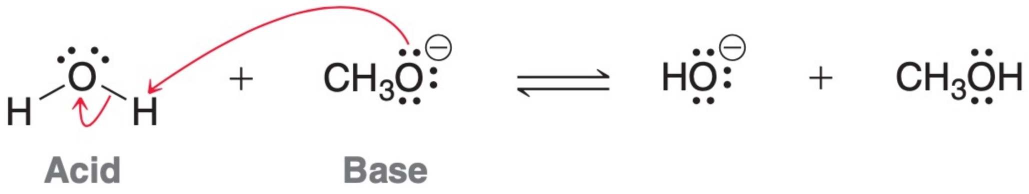
- Direction of arrow – flowing of electrons



- Practice

Draw a mechanism for the following acid-base reaction. Label the acid, base, conjugate acid, and conjugate base:





- Measurement of acidity: pK_a

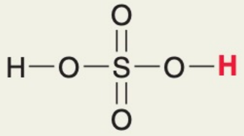
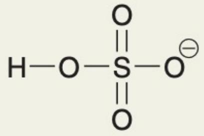
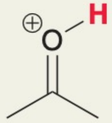
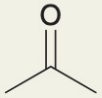
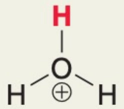
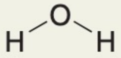
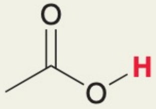
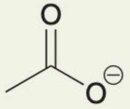
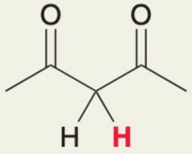
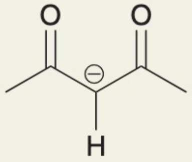
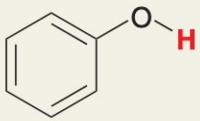
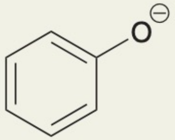
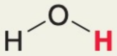
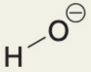
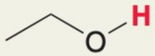
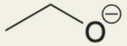
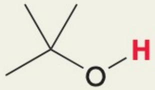
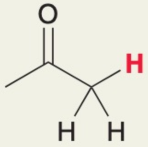
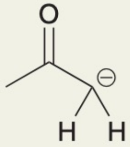
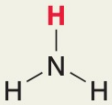
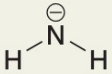
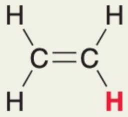
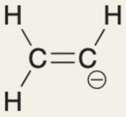
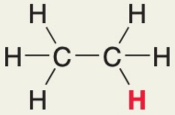
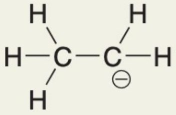
$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

$$K_{eq} = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K_a = K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

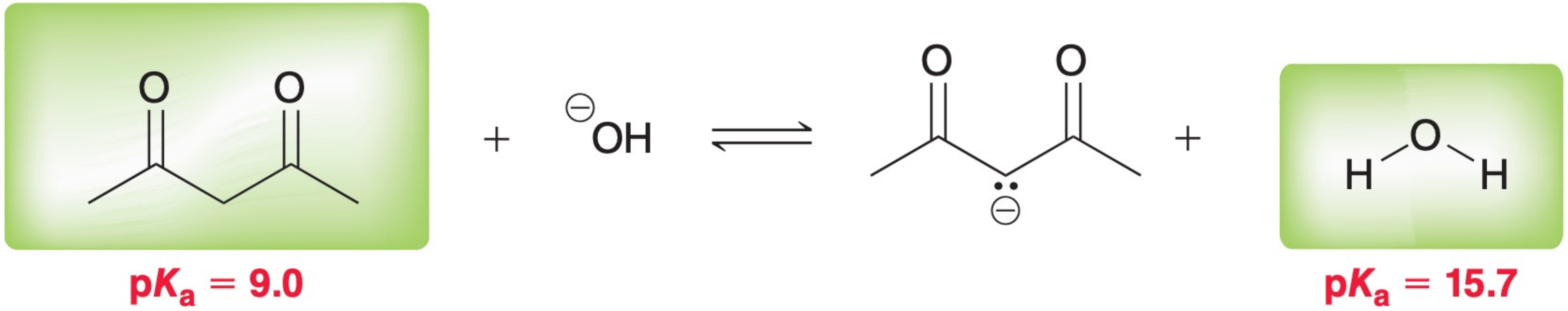
$$pK_a = -\log K_a$$

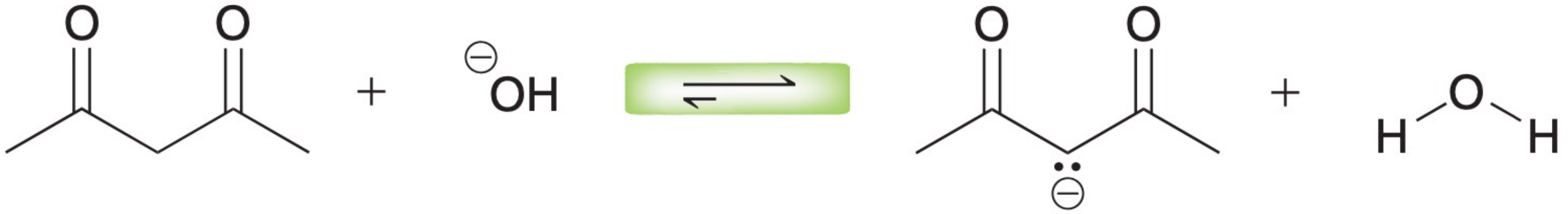
Acidity and pK_a

Acid	pK_a	Conjugate Base
	−9	
	−7.3	
Cl—**H**	−7	$Cl^{\ominus}$
	−1.74	
	4.75	
	9.0	
	9.9	
	15.7	
	16	
	18	
	19.2	
H—C≡C—**H**	25	$H{-}C{\equiv}C^{\ominus}$
	38	
	44	
	50	

Acidity and pK_a

- pK_a can be used to determine the direction of acid-base reactions

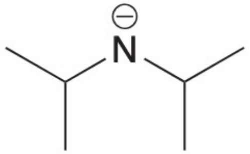


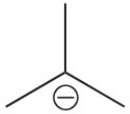
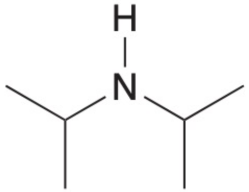


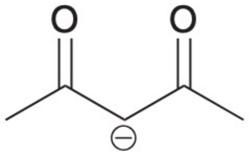
the reaction goes forward

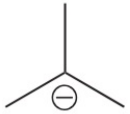
- Practice

3.29 In each of the following cases, identify whether the reagent shown is suitable to accomplish the task described. Explain why or why not:

(a) To protonate  using H_2O

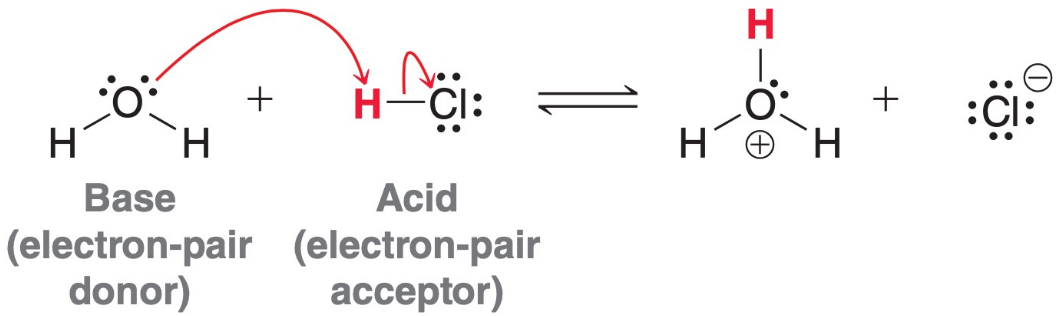
(b) To protonate  using 

(d) To protonate  using H_2O

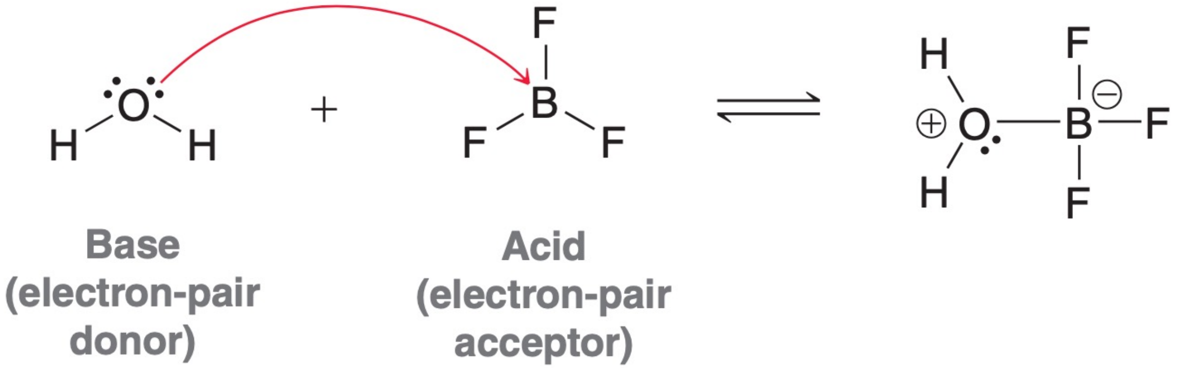
(e) To protonate  using H_2O

- Lewis acid & base theory

proton acid & base reaction



non-proton acid & base reaction



- Practice

Identify the Lewis acid and the Lewis base in the reaction between BH_3 and THF.