UKChO

化学竞赛课程讲义

UK Chemistry Olympiad 英国化学奥林匹克竞赛

CHEMISTRY

Contents

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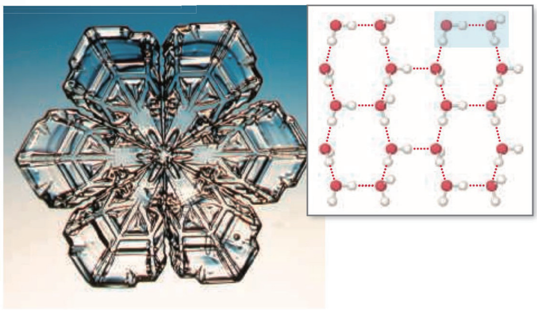
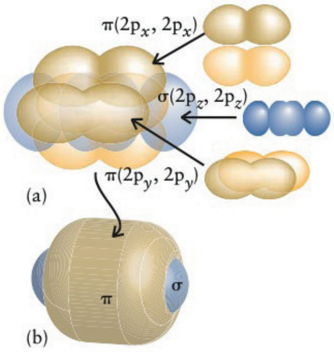
英国化学奥林匹克竞赛

Unit 1

Structural Chemistry





Unit 1

Structural Chemistry

1.Atomic structure & Atomic spectrum

2.Electron configuration

3.Periodicity

4.Chemical bond

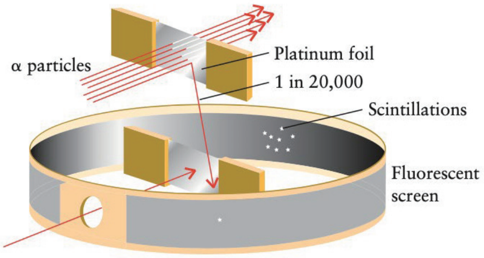
5.Molecular shape

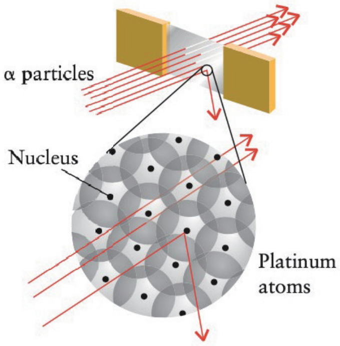
6.IMFs & Gas

7.Rrystal and unit cell

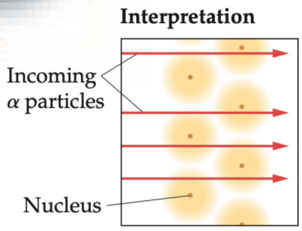
8.Phase change

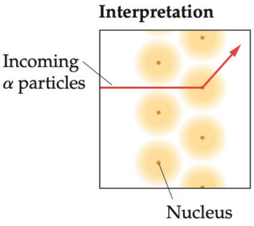
1.1 Atomic Structure

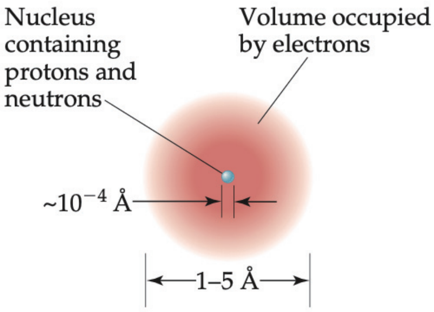




1.1.1 Atomic Structure







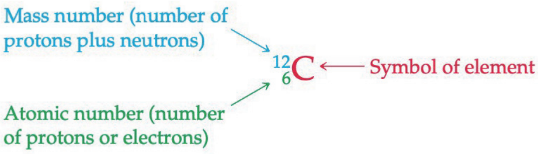
1.1.2 Elementary Particle

Comparison of the Proton, Neutron, and Electron

Particle	Charge	Mass (amu)
Proton	Positive (1+)	1.0073
Neutron	None (neutral)	1.0087
Electron	Negative (1−)	5.486×10^{-4}

1.1.3

Isotope



Mass number (number of protons plus neutrons)

$^{12}_{6}\text{C}$ ⟵ Symbol of element

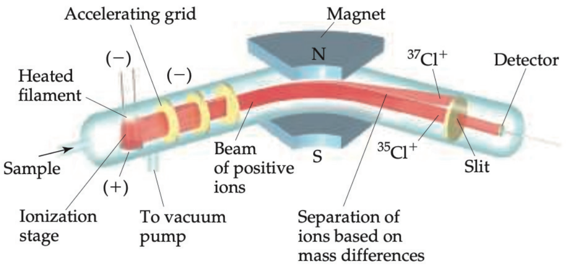
Atomic number (number of protons or electrons)

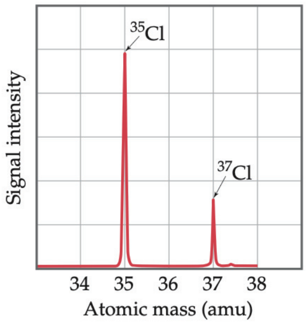
Atoms with identical atomic numbers but different mass numbers (that is, the same number of protons but different numbers of neutrons) are called **isotopes** of one another.

$$\text{Atomic weight} = \sum_{\substack{\text{over all}\\ \text{isotopes of}\\ \text{the element}}} [(\text{isotope mass}) \times (\text{fractional isotope abundance})]$$

1.1.4

Mass Spectrometer

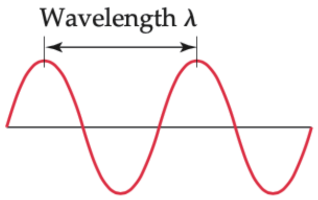




1.1.5

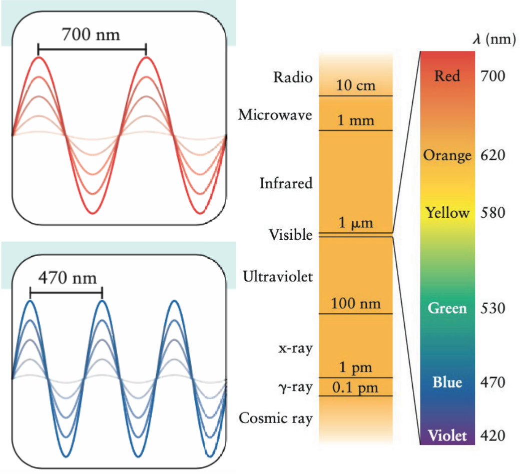
Wave-particle Dualism

$$\overbrace{\lambda}^{\text{wavelength}} \times \overbrace{\nu}^{\text{frequency}} = \overbrace{c}^{\text{speed of light}}$$



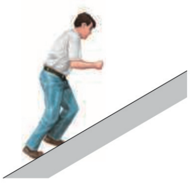
1.1.5 Wave-particle Dualism

Calculate red light & blue light frequency



1.1.6 Quantized Energy and Photons

$$E = h\nu$$

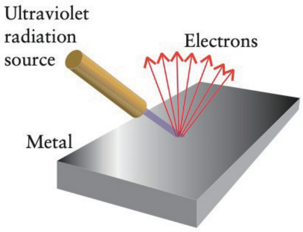


Potential energy of person walking up ramp increases in uniform, continuous manner

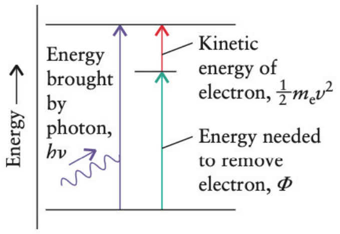
Planck's constant, has the value $6.626*10^{-34}$ J·s.

Potential energy of person walking up steps increases in stepwise, quantized manner

1.1.7 The Photoelectric Effect and Photons



$$\underbrace{\tfrac{1}{2}m_e v^2}_{\text{Kinetic energy of an ejected electron}} = \underbrace{h\nu}_{\text{energy supplied by a photon}} - \underbrace{\Phi}_{\text{energy required to eject an electron (the work function)}}$$

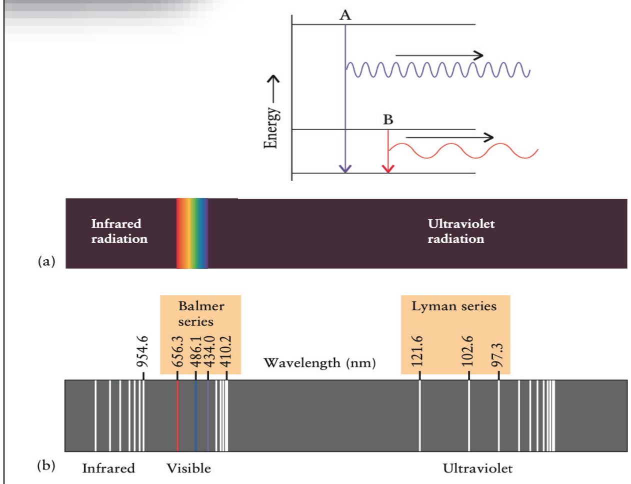


1.1.8 Bohr’s Model& & Atomic Spectra

Bohr based his model on three postulates:

1. Only orbits of certain radii, corresponding to certain specific energies, are permitted for the electron in a hydrogen atom.
2. An electron in a permitted orbit is in an “allowed” energy state. An electron in an allowed energy state does not radiate energy and, therefore, does not spiral into the nucleus.
3. Energy is emitted or absorbed by the electron only as the electron changes from one allowed energy state to another. This energy is emitted or absorbed as a photon that has energy $E = h\nu$.

1.1.8 Bohr’s Model & Atomic Spectra



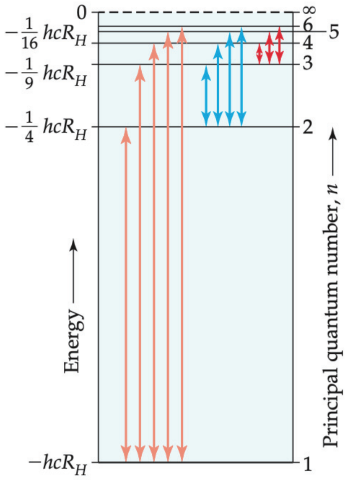
When an atom undergoes a transition from a state of higher energy to one of lower energy, it loses energy that is carried away as a photon. The greater the energy difference, the higher is the frequency (and the shorter the wavelength) of the radiation emitted. Compare the high frequency of the emission during a transition from state A to the ground state to that from state B to the ground state.

1.1.9 Atomic Spectra

$$E = (-hcR_{\mathrm{H}})\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18}\,\mathrm{J})\left(\frac{1}{n^2}\right)$$

h, *c*, and *R*H are the Planck constant, the speed of light, and the Rydberg constant

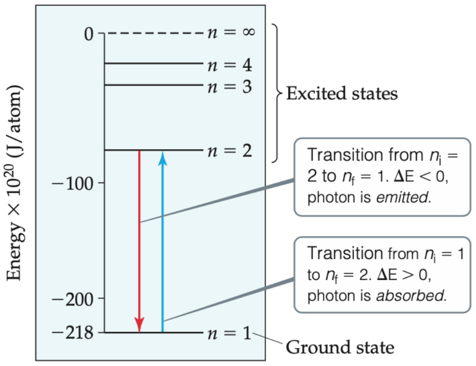
n principal quantum number.



1.1.9 Atomic Spectra

$$E = (-hcR_{\mathrm{H}})\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18}\,\mathrm{J})\left(\frac{1}{n^2}\right)$$

$$\Delta E = E_{\mathrm{f}} - E_{\mathrm{i}} = (-2.18 \times 10^{-18}\,\mathrm{J})\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2}\right)$$



Transition from n_i = 2 to n_f = 1. ΔE < 0, photon is *emitted.*

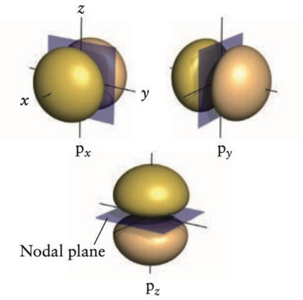
Transition from n_i = 1 to n_f = 2. ΔE > 0, photon is *absorbed.*

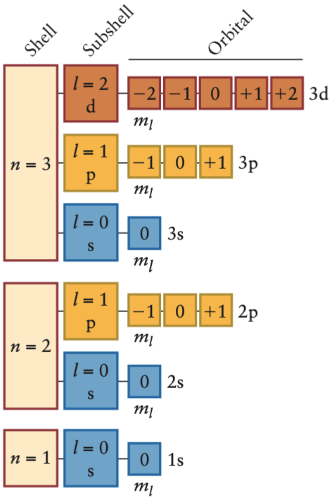
1.1 Summary & Practice

1. Concept

2. Example

1.2 Electron Configuration





1.2.1 Quantum Numbers

$$E = (-hcR_{\mathrm{H}})\left(\frac{1}{n^2}\right) = (-2.18 \times 10^{-18}\,\mathrm{J})\left(\frac{1}{n^2}\right)$$

1. The principal quantum number, n, can have positive integral values 1, 2, 3, ... As n increases, the orbital becomes larger, and the electron spends more time farther from the nucleus. An increase in n also means that the electron has a higher energy and is therefore less tightly bound to the nucleus. For the hydrogen atom, $E_n = -(2.18 \times 10^{-18}\,\mathrm{J})(1/n^2)$, as in the Bohr model.

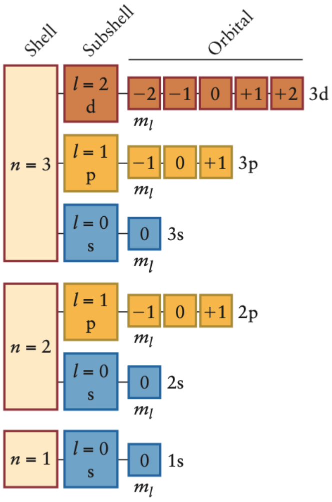
1.2.1 Quantum Numbers

2. Angular momentum quantum number

Value of *l*	0	1	2	3
Letter used	*s*	*p*	*d*	*f*

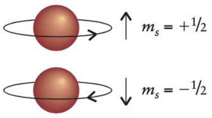
3.Magnetic quantum number

between -*l* and *l*, including zero.



1.2.1 Quantum Numbers

4.spin magnetic quantum number, is denoted *ms* (the subscript *s* stands for *spin*). Two possible values are allowed for *m*.



1.2.1

Summary of Quantum Numbers

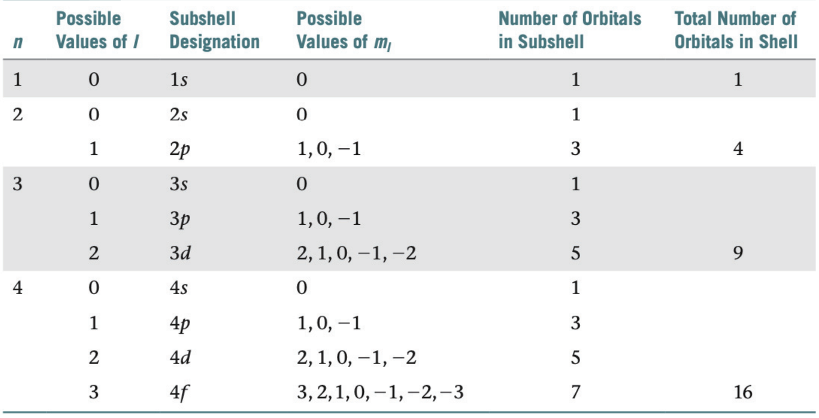
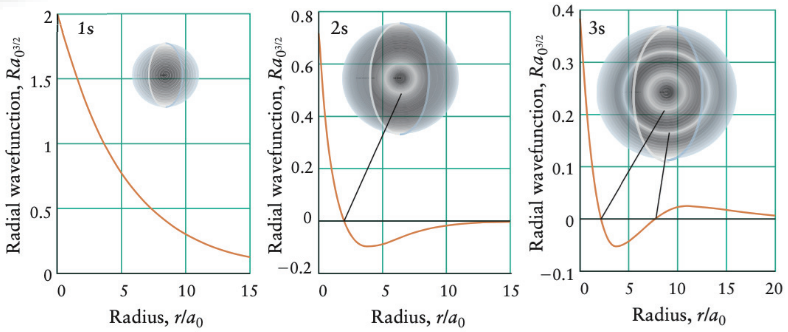


TABLE 6.2 **Relationship among Values of n, l, and m_l through $n = 4$**

n	Possible Values of l	Subshell Designation	Possible Values of m_l	Number of Orbitals in Subshell	Total Number of Orbitals in Shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	
	1	2*p*	1, 0, −1	3	4
3	0	3*s*	0	1	
	1	3*p*	1, 0, −1	3	
	2	3*d*	2, 1, 0, −1, −2	5	9
4	0	4*s*	0	1	
	1	4*p*	1, 0, −1	3	
	2	4*d*	2, 1, 0, −1, −2	5	
	3	4*f*	3, 2, 1, 0, −1, −2, −3	7	16

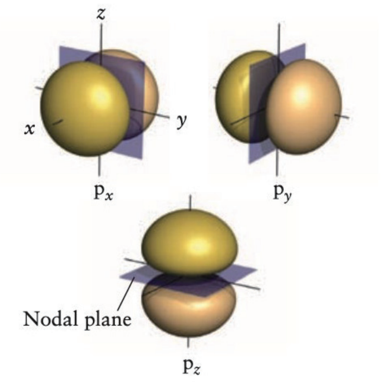
1.2.2

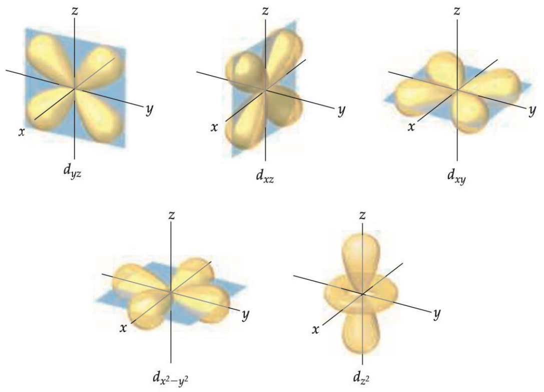
Contour Representations of Orbital



1.2.2

Contour Representations of Orbital





1.2.3

Pauli Exclusion Principle & Hund's Rule

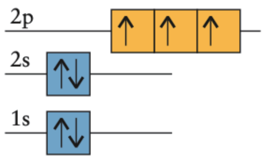
Pauli exclusion principle states that *no two electrons in an atom can have the same set of four quantum numbers* n, l, ml, *and* m_s.

An orbital can hold a maximum of two electrons and they must have opposite spins.

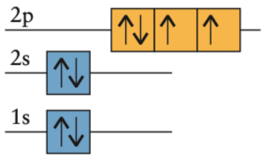
Hund's rule *states that that when filling degenerate orbitals the lowest energy is attained when the number of electrons having the same spin is maximized.*

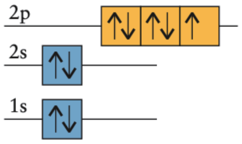
1.2.3

Pauli Exclusion Principle & Hund's Rule

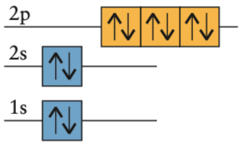


7 N $1s^22s^22p^3$, [He]$2s^22p^3$





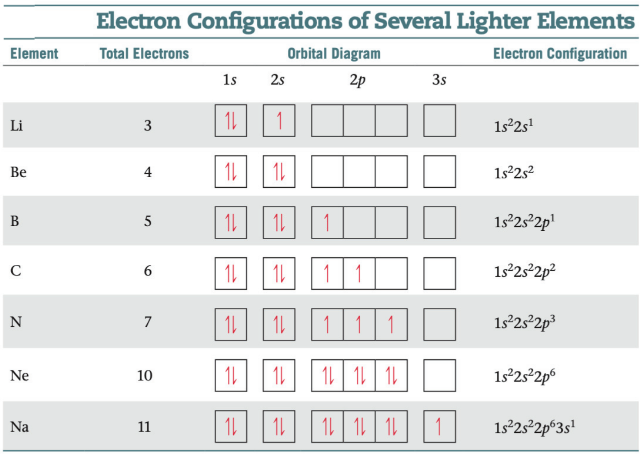
9 F $1s^22s^22p^5$, [He]$2s^22p^5$



10 Ne $1s^22s^22p^6$, [He]$2s^22p^6$

1.2.3

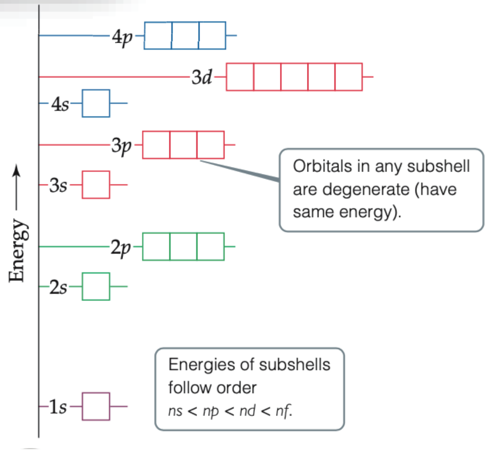
Configuration Principle



Electron Configurations of Several Lighter Elements

Element	Total Electrons	Orbital Diagram 1s	2s	2p	3s	Electron Configuration
Li	3	↑↓	↑			$1s^22s^1$
Be	4	↑↓	↑↓			$1s^22s^2$
B	5	↑↓	↑↓	↑		$1s^22s^22p^1$
C	6	↑↓	↑↓	↑ ↑		$1s^22s^22p^2$
N	7	↑↓	↑↓	↑ ↑ ↑		$1s^22s^22p^3$
Ne	10	↑↓	↑↓	↑↓ ↑↓ ↑↓		$1s^22s^22p^6$
Na	11	↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	$1s^22s^22p^63s^1$

1.2.4 Energy Level Overlap

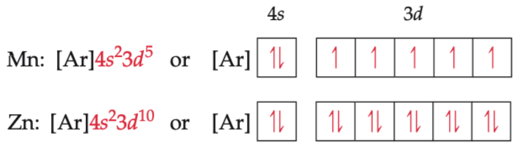


Orbitals in any subshell are degenerate (have same energy).

Energies of subshells follow order $ns < np < nd < nf$.

(n-2)f > (n-1)d > ns

1.2.5 Transition Metals



Mn: $[Ar]4s^2 3d^5$ or [Ar] ⥮ ↿ ↿ ↿ ↿ ↿

Zn: $[Ar]4s^2 3d^{10}$ or [Ar] ⥮ ⥮ ⥮ ⥮ ⥮ ⥮

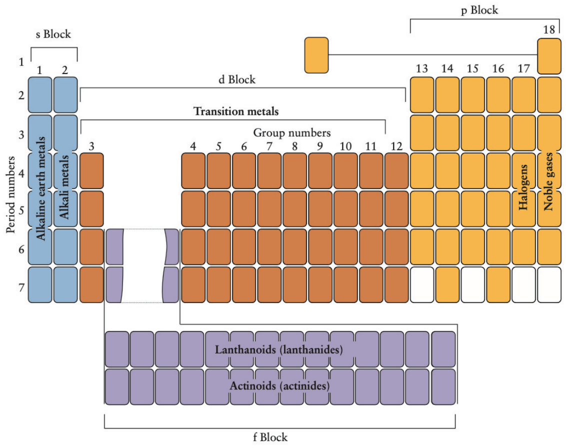
Cu?
Cr ?

1.2.6 The Lanthanides and Actinides

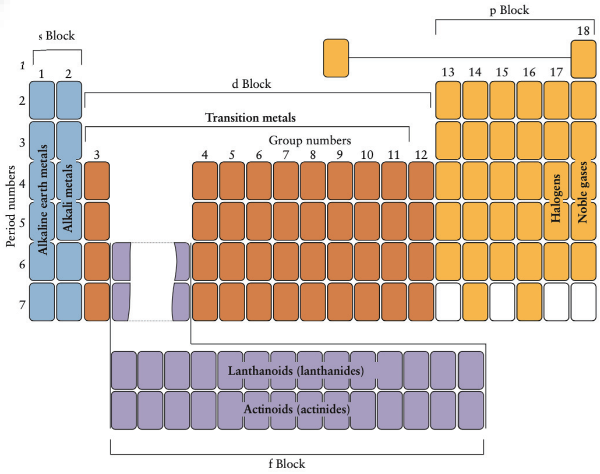
$[Xe]6s^2 5d^1$
Lanthanum

$[Xe]6s^2 5d^1 4f^1$
Cerium

$[Xe]6s^2 4f^3$
Praseodymium



1.2.7 Electron Configuration and Periodic Table

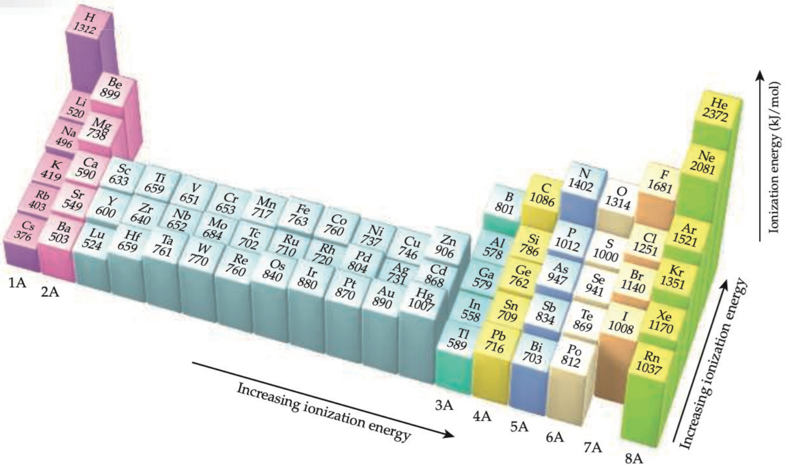


1.2 Summary & Practice

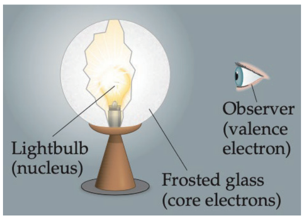
1.Concept

2.Example

1.3 Periodicity

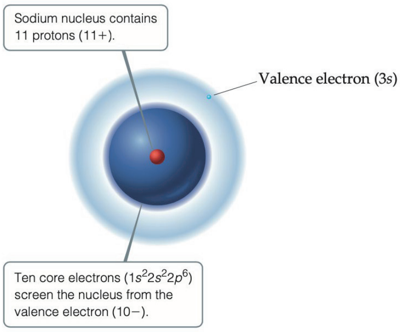


1.3.1 Effective Nuclear Charge



We call this partially screened nuclear charge the **effective nuclear charge**, *Z*eff. Because the full attractive force of the nucleus has been decreased by the electron repulsions, we see that the effective nuclear charge is always less than the *actual* nuclear charge (*Z*eff < *Z*)

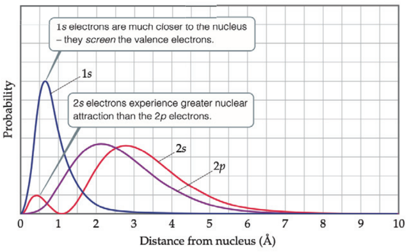
$$Z_{\text{eff}} = Z - S$$



Sodium nucleus contains 11 protons (11+).

Ten core electrons ($1s^2 2s^2 2p^6$) screen the nucleus from the valence electron (10−).

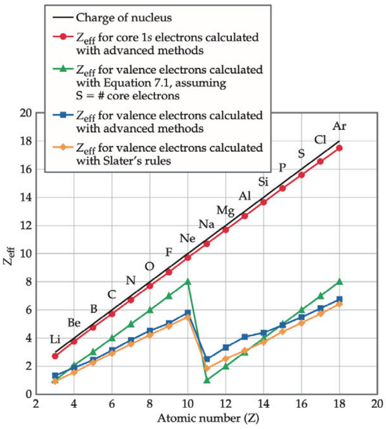
1.3.1 Effective Nuclear Charge



1*s* electrons are much closer to the nucleus – they *screen* the valence electrons.

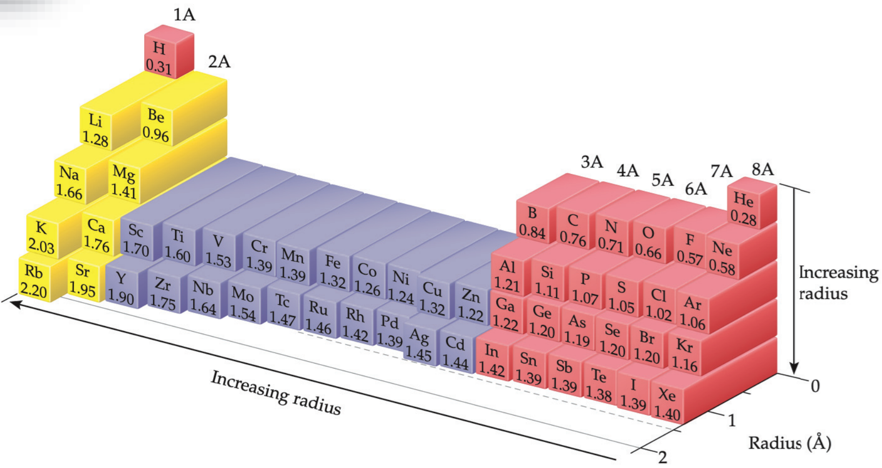
2*s* electrons experience greater nuclear attraction than the 2*p* electrons.

The effective nuclear charge increases from left to right across any period of the periodic table.

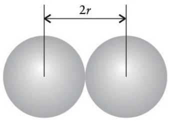


Which would you expect to experience a greater effective nuclear charge, a 2*p* electron of a Ne atom or a 3*s* electron of a Na atom?

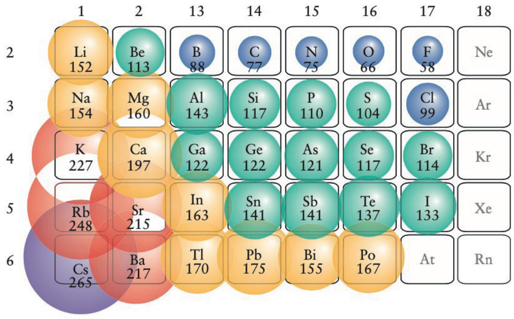
1.3.2 Radius



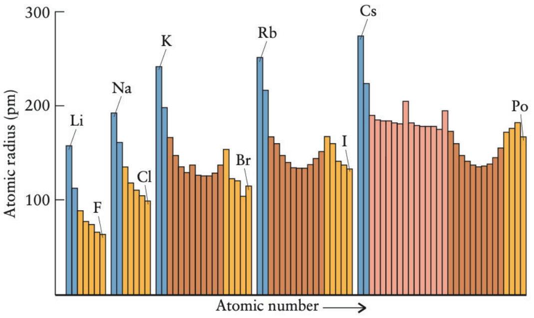
1.3.2 Radius(atom)



11 Atomic radius

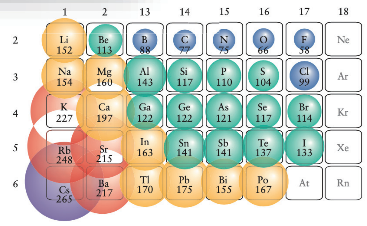


	1	2	13	14	15	16	17	18
2	Li 152	Be 113	B 88	C 77	N 75	O 66	F 58	Ne
3	Na 154	Mg 160	Al 143	Si 117	P 110	S 104	Cl 99	Ar
4	K 227	Ca 197	Ga 122	Ge 122	As 121	Se 117	Br 114	Kr
5	Rb 248	Sr 215	In 163	Sn 141	Sb 141	Te 137	I 133	Xe
6	Cs 265	Ba 217	Tl 170	Pb 175	Bi 155	Po 167	At	Rn

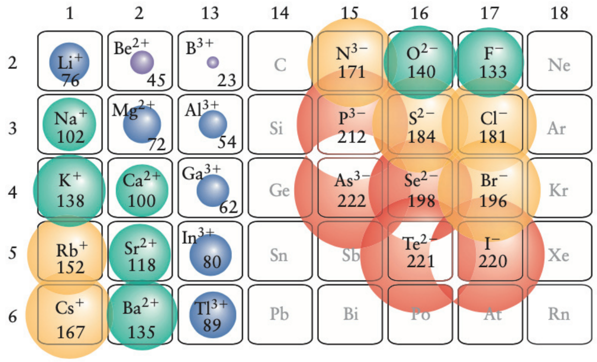


1.3.2 Radius(ION)

ATOM



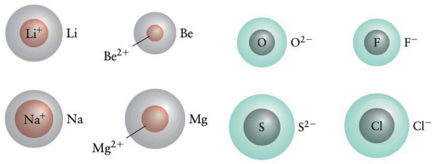
	1	2	13	14	15	16	17	18
2	Li 152	Be 113	B 88	C 77	N 75	O 66	F 58	Ne
3	Na 154	Mg 160	Al 143	Si 117	P 110	S 104	Cl 99	Ar
4	K 227	Ca 197	Ga 122	Ge 122	As 121	Se 117	Br 114	Kr
5	Rb 248	Sr 215	In 163	Sn 141	Sb 141	Te 137	I 133	Xe
6	Cs 265	Ba 217	Tl 170	Pb 175	Bi 155	Po 167	At	Rn



	1	2	13	14	15	16	17	18
2	Li^+ 76	Be^{2+} 45	B^{3+} 23	C	N^{3-} 171	O^{2-} 140	F^- 133	Ne
3	Na^+ 102	Mg^{2+} 72	Al^{3+} 54	Si	P^{3-} 212	S^{2-} 184	Cl^- 181	Ar
4	K^+ 138	Ca^{2+} 100	Ga^{3+} 62	Ge	As^{3-} 222	Se^{2-} 198	Br^- 196	Kr
5	Rb^+ 152	Sr^{2+} 118	In^{3+} 80	Sn	Sb	Te^{2-} 221	I^- 220	Xe
6	Cs^+ 167	Ba^{2+} 135	Tl^{3+} 89	Pb	Bi	Po	At	Rn

CATION

ANION



1.3.3 Ionization Energy

$$X(g) \longrightarrow X^+(g) + e^-(g) \qquad I = E(X^+) - E(X)$$

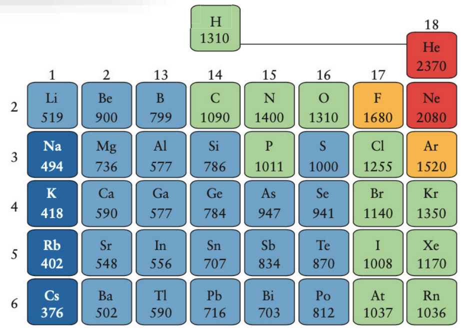
I, is the minimum energy needed to remove an electron from an atom in the gas phase

first ionization energy, I_1 $Cu(g) \longrightarrow Cu^+(g) + e^-(g)$ energy required = I_1 (7.73 eV, 746 kJ·mol^{-1})

second ionization energy, I_2 $Cu^+(g) \longrightarrow Cu^{2+}(g) + e^-(g)$ energy required = I_2 (20.29 eV, 1958 kJ·mol^{-1})

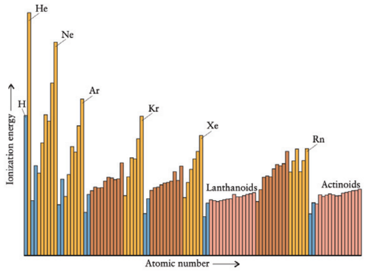
THINKING POINT Why is the second ionization energy of an atom always higher than its first ionization energy?

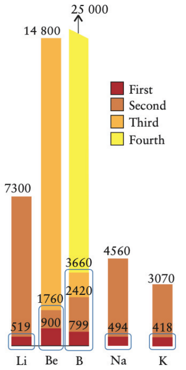
1.3.3 Ionization Energy



	1	2	13	14	15	16	17	18
				H 1310				He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

- First ionization energies typically decrease down a group.
- First ionization energies generally increase across a period.





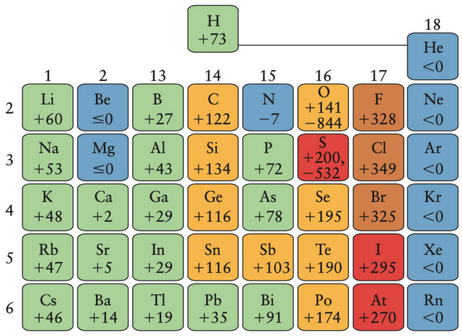
Why first ionization energy of Be greater than B?
N>O?

1.3.4 Electron Affinity

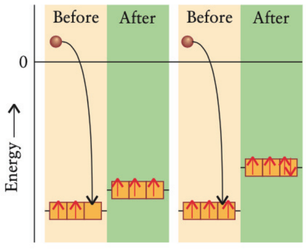
$$X(g) + e^-(g) \longrightarrow X^-(g) \qquad E_{ea}(X) = E(X) - E(X^-)$$

The **electron affinity** (E_{ea}) of an element is the energy released when an electron is added to a gas-phase atom.

Electron affinities are highest toward the right of the periodic table.



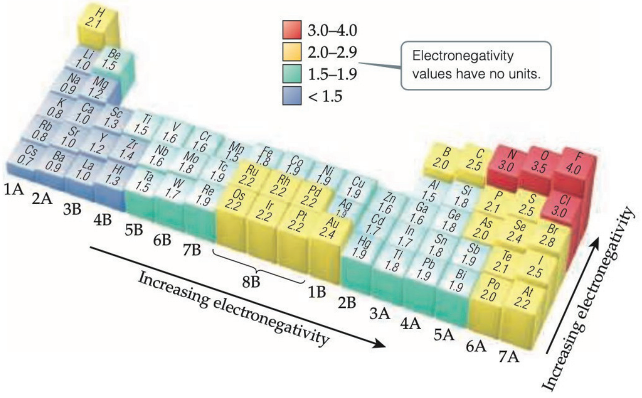
	1	2	13	14	15	16	17	18
				H +73				He <0
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200, −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6	Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0



(a) Carbon (b) Nitrogen

1.3.5 Electronegativity

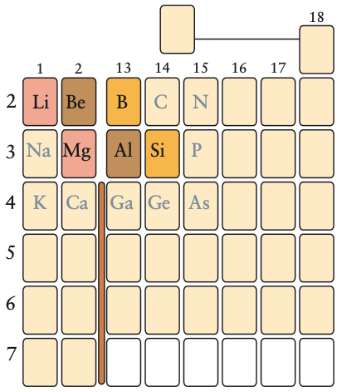
Electronegativity is defined as the ability of an atom *in a molecule* to attract electrons to itself.



Electronegativity values have no units.

1.3.6 Diagonal Relationship

A **diagonal relationship** is a similarity in properties between diagonal neighbors in the main groups of the periodic table



Diagonally related pairs of elements often show similar chemical properties.

Boron (top) and silicon (bottom) have a diagonal relationship. Both are brittle solids with high melting points. They also show a number of chemical similarities.

1.3.7 The General Properties of the Elements

TABLE 2.3 Characteristics of Metals and Nonmetals

Metals	Nonmetals
Physical properties	
good conductors of electricity	poor conductors of electricity
malleable	not malleable
ductile	not ductile
lustrous	not lustrous
typically: solid; high melting point; good conductors of heat	typically: solid, liquid, or gas; low melting point; poor conductors of heat
Chemical properties	
react with acids	do not react with acids
form basic oxides (which react with acids)	form acidic oxides (which react with bases)
form cations	form anions
form ionic halides	form covalent halides

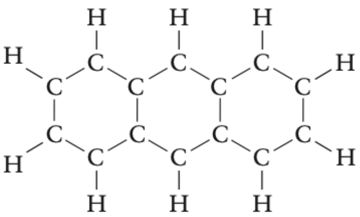
All elements in the s-block are reactive metals that form basic oxides. The p-block elements tend to gain electrons to complete closed shells; they range from metals through metalloids to nonmetals. All d-block elements are metals with properties between those of s-block and p-block metals. Many d-block elements form cations in more than one oxidation state.

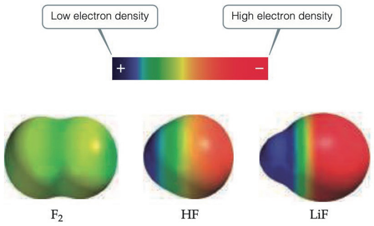
1.3 Summary & Practice

1.Concept

2.Example

1.4 Chemical Bond

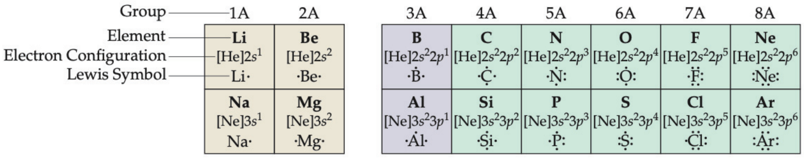




1.4.1 Lewis Symbols

Lewis represented each **valence electron** as a dot and arranged the dots around the symbol of the element.
A single dot represents an electron alone in an orbital.
A pair of dots represents two paired electrons sharing an orbital.

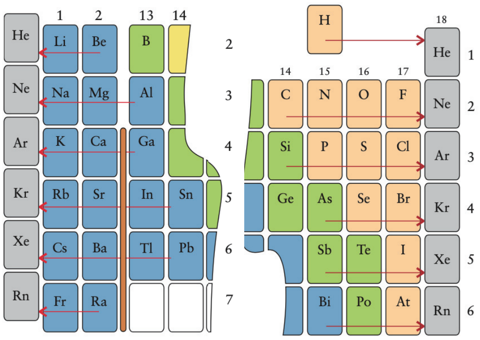
H· He: :Ṇ̇· ·Ö̤· :C̤̈l· K· Mg:



Group	1A	2A	3A	4A	5A	6A	7A	8A
Element	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Electron Configuration	[He]$2s^1$	[He]$2s^2$	[He]$2s^22p^1$	[He]$2s^22p^2$	[He]$2s^22p^3$	[He]$2s^22p^4$	[He]$2s^22p^5$	[He]$2s^22p^6$
Lewis Symbol	Li·	·Be·	·Ḃ·	·Ċ̣·	·Ṇ̇:	:Ọ̇:	·F̤̈:	:N̤̈e:
	Na	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**Ar**
	[Ne]$3s^1$	[Ne]$3s^2$	[Ne]$3s^23p^1$	[Ne]$3s^23p^2$	[Ne]$3s^23p^3$	[Ne]$3s^23p^4$	[Ne]$3s^23p^5$	[Ne]$3s^23p^6$
	Na·	·Mg·	·Ȧl·	·Ṩi·	·Ṗ̣:	:Ṩ:	·C̤̈l:	:Ä̤r:

1.4.2 The Octet Rule

Atoms tend to gain, lose, or share electrons until they are surrounded by **eight valence electrons**.



Atom	Configuration	Ion	Configuration
Li	[He]$2s^1$	Li^+	[He] ($1s^2$)
Be	[He]$2s^2$	Be^{2+}	[He]
Na	[Ne]$3s^1$	Na^+	[Ne] ([He]$2s^22p^6$)
Mg	[Ne]$3s^2$	Mg^{2+}	[Ne]
Al	[Ne]$3s^23p^1$	Al^{3+}	[Ne]
N	[He]$2s^22p^3$	N^{3-}	[Ne]
O	[He]$2s^22p^4$	O^{2-}	[Ne]
F	[He]$2s^22p^5$	F^-	[Ne]
S	[Ne]$3s^23p^4$	S^{2-}	[Ar] ([Ne]$3s^23p^6$)
Cl	[Ne]$3s^23p^5$	Cl^-	[Ar]

1.4.3

Ionic Bonds

$\mathrm{Na(g)} \longrightarrow \mathrm{Na^+(g)} + \mathrm{e^-(g)}$ energy required = 494 $\mathrm{kJ{\cdot}mol^{-1}}$

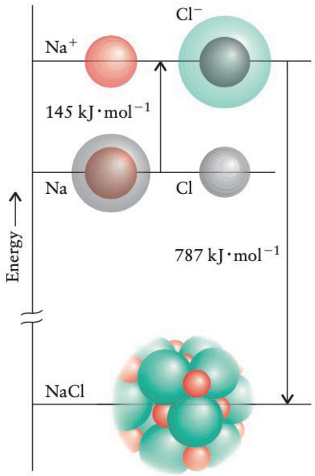
$\mathrm{Cl(g)} + \mathrm{e^-(g)} \longrightarrow \mathrm{Cl^-(g)}$ energy released = 349 $\mathrm{kJ{\cdot}mol^{-1}}$

$\mathrm{Na^+(g)} + \mathrm{Cl^-(g)} \longrightarrow \mathrm{NaCl(s)}$ energy released = 787 $\mathrm{kJ{\cdot}mol^{-1}}$

$$\mathrm{Na(g)} + \mathrm{Cl(g)} \longrightarrow \mathrm{NaCl(s)}$$

$$\mathrm{Na}\cdot + \cdot\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}: \longrightarrow \mathrm{Na}^+ + [:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:]^-$$

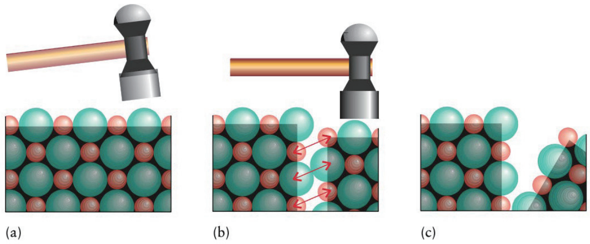
There is a net lowering of energy below that of the individual atoms, provided the net attraction between ions is greater than the energy needed to make them.



1.4.3

Ionic Bonds

$$E_{p,12} = \frac{\overbrace{(z_1e)}^{\text{charge of ion 1}} \times \overbrace{(z_2e)}^{\text{charge of ion 2}}}{4\pi\varepsilon_0 \underbrace{r_{12}}_{\text{separation}}} = \frac{z_1z_2e^2}{4\pi\varepsilon_0 r_{12}}$$



1.4.4

Lattice Energy

lattice energy is the energy required to completely separate one mole of a solid ionic compound into its gaseous ions.

$\mathrm{Na^+(g)} + \mathrm{Cl^-(g)} \longrightarrow \mathrm{NaCl(s)}$ energy released = 787 $\mathrm{kJ{\cdot}mol^{-1}}$

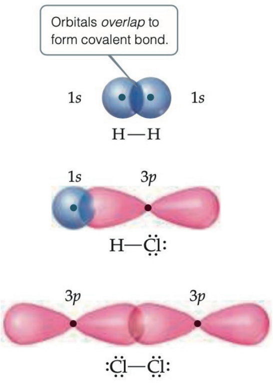
TABLE 8.1 Lattice Energies for Some Ionic Compounds

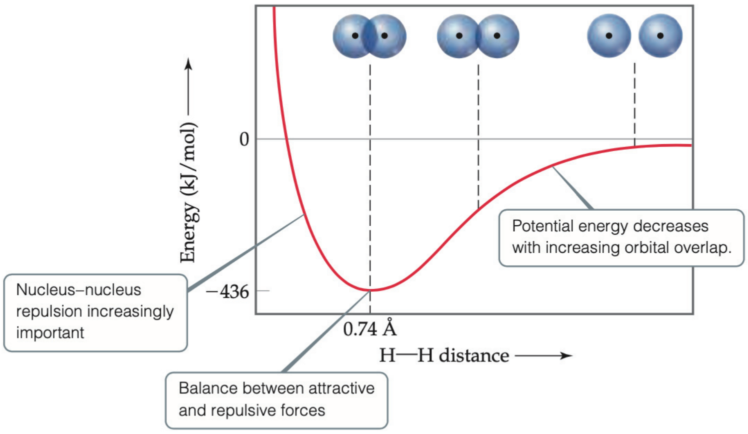
Compound	Lattice Energy (kJ/mol)	Compound	Lattice Energy (kJ/mol)
LiF	1030	$MgCl_2$	2526
LiCl	834	$SrCl_2$	2127
LiI	730		
NaF	910	MgO	3795
NaCl	788	CaO	3414
NaBr	732	SrO	3217
NaI	682		
KF	808	ScN	7547
KCl	701		
KBr	671		
CsCl	657		
CsI	600		

1.4.5

Covalent Bonds

Valence-bond theory is the description of covalent bonding in terms of atomic orbitals


Orbitals *overlap* to form covalent bond.



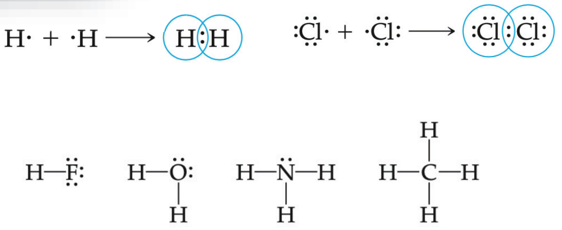
Nucleus–nucleus repulsion increasingly important

Potential energy decreases with increasing orbital overlap.

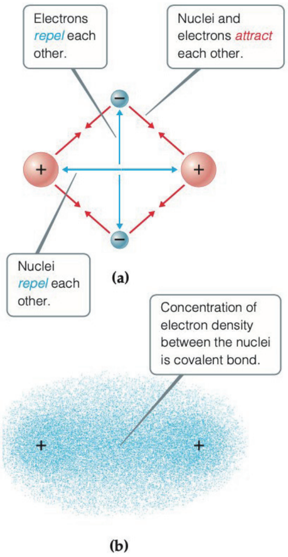
Balance between attractive and repulsive forces

1.4.5

Covalent Bonds



In covalent bond formation, atoms go as far as possible toward completing their octets by sharing electron pairs.


Electrons *repel* each other.

Nuclei and electrons *attract* each other.

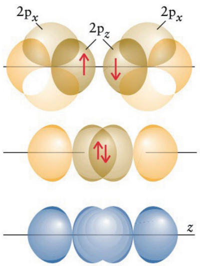
Nuclei *repel* each other.

Concentration of electron density between the nuclei is covalent bond.

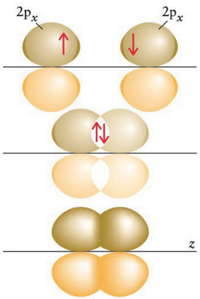
1.4.6

Sigma and Pi Bonds

Sigma bond is cylindrically symmetrical (the same in all directions around the long axis of the bond), with no nodal planes containing the internuclear axis.
Pi bond has a single nodal plane containing the internuclear axis.



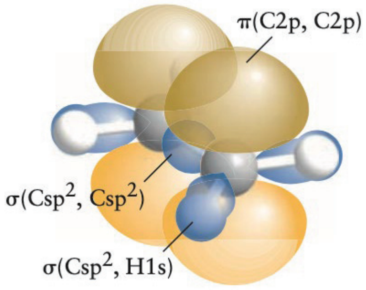
σ-bond

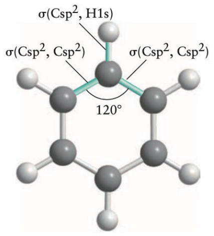


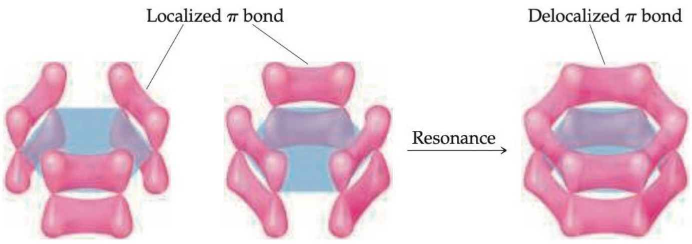
π-bond

A **single bond** is a σ-bond.
A **double bond** is a σ-bond plus one π-bond.
A **triple bond** is a σ-bond plus two π-bonds.

1.4.7 Multiple Bonds







1.4.7 Multiple Bonds

In covalent bond formation, atoms go as far as possible toward completing their octets by sharing electron pairs.

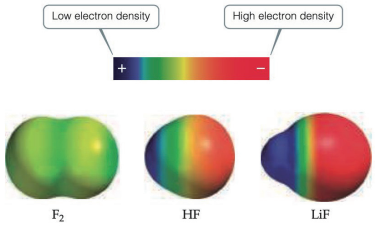
$$:\ddot{\underset{\cdot\cdot}{O}}: + \cdot\dot{\underset{\cdot}{C}}\cdot + :\ddot{\underset{\cdot\cdot}{O}}: \longrightarrow \ddot{\underset{\cdot\cdot}{O}}::C::\ddot{\underset{\cdot\cdot}{O}} \quad (\text{or } \ddot{\underset{\cdot\cdot}{O}}{=}C{=}\ddot{\underset{\cdot\cdot}{O}})$$

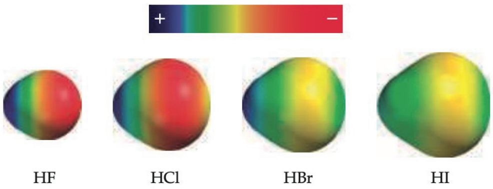
$$:\dot{\underset{\cdot}{N}}\cdot + \cdot\dot{\underset{\cdot}{N}}: \longrightarrow :N:::N: \quad (\text{or } :N{\equiv}N:)$$

N—N	N═N	N≡N
1.47 Å	1.24 Å	1.10 Å

1.4.8 Bond Polarity

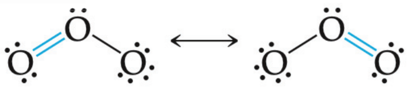
	F_2	HF	LiF
Electronegativity difference	4.0 − 4.0 = 0	4.0 − 2.1 = 1.9	4.0 − 1.0 = 3.0
Type of bond	Nonpolar covalent	Polar covalent	Ionic

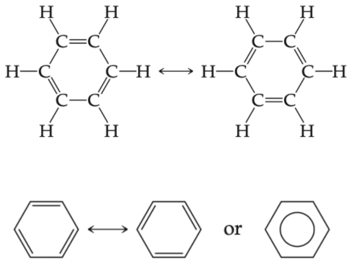


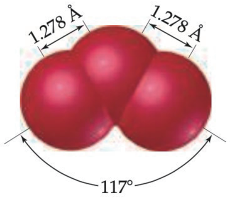


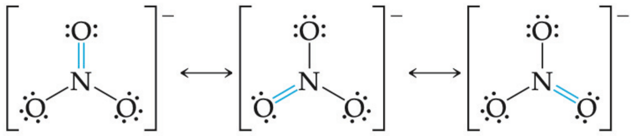
1.4.9

Resonance









1.4.10

Formal Charge

$$\text{Formal charge} = V - (L + \tfrac{1}{2}B)$$

V is the number of valence electrons in the free atom
L is the number of electrons present on the bonded atom as lone pairs
B is the number of bonding electrons on the atom.

	Ö=C=Ö			:Ö—C≡O:		
Valence electrons:	6	4	6	6	4	6
−(Electrons assigned to atom):	6	4	6	7	4	5
Formal charge:	0	0	0	−1	0	+1

1.4.10

Formal Charge Practice

Three possible Lewis structures for the thiocyanate ion, NCS^-, are

[:N̤̈—C≡S:]$^-$ [N̤̈=C=S̤̈]$^-$ [:N≡C—S̤̈:]$^-$

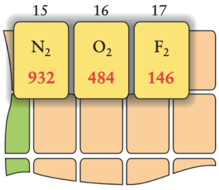
(**a**) Determine the formal charges in each structure.

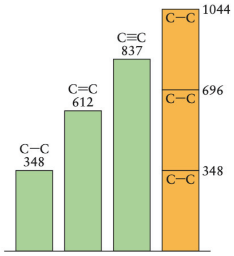
(**b**) Based on the formal charges, which Lewis structure is the dominant one?

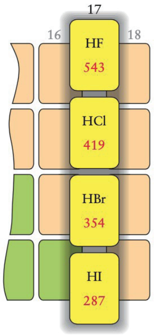
1.4.11

Bond Order, Strength, Length

The strength of a chemical bond is measured by its **dissociation energy**, *D*, the energy required to separate the bonded atoms.



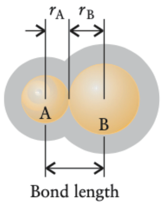


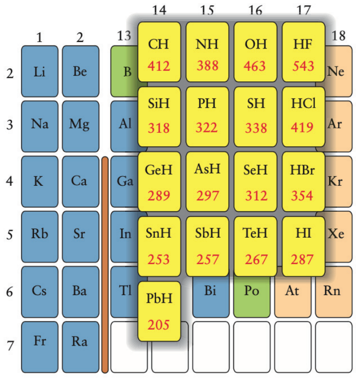


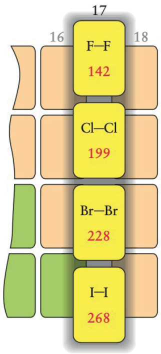
1.4.11

Bond Order, Strength, Length

Bond length is the distance between the centers of two atoms joined by a covalent bond.







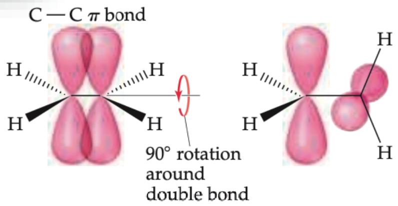
1.4

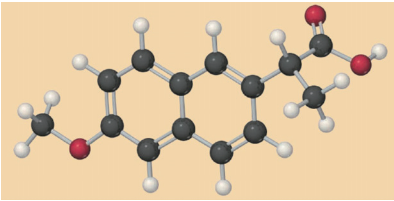
Summary & Practice

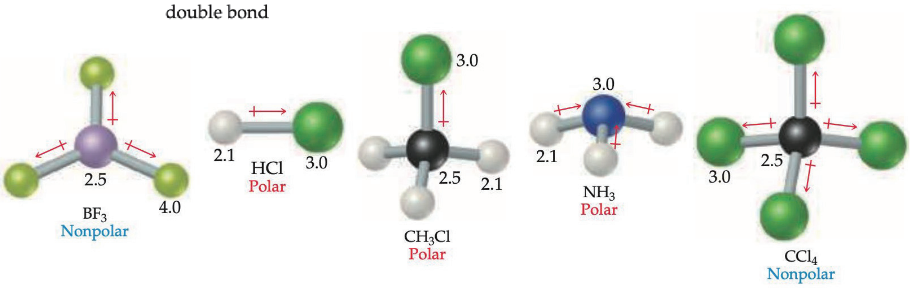
1. Concept

2. Example

1.5 Molecular Shape







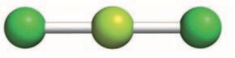
1.5.1 The VSEPR Model

valence-shell electron-pair repulsion model (VSEPR model) extends Lewis's theory of bonding to account for molecular shapes by adding rules that account for bond angles by noting the effect of repulsions between electrons:

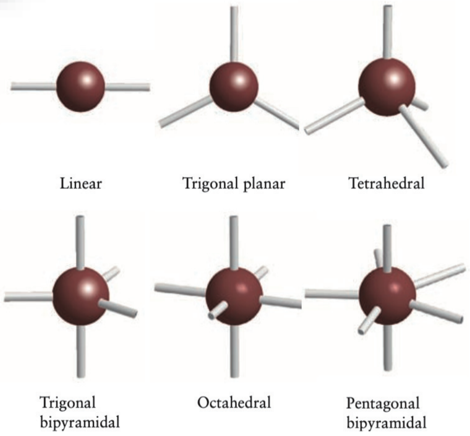
Rule 1 Regions of high electron concentration (bonds and lone pairs on the central atom) repel one another and, to minimize their repulsions, these regions move as far apart as possible while maintaining the same distance from the central atom.

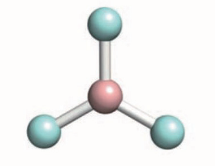
Rule 2 There is no distinction between single and multiple bonds: a multiple bond is treated as a single region of high electron concentration.

1.5.1 The VSEPR Model

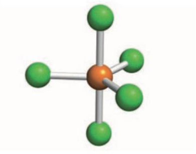


4 Beryllium chloride, $BeCl_2$





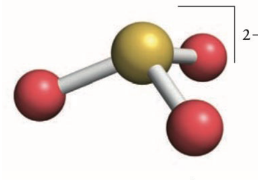
6 Boron trifluoride, BF_3



3 Phosphorus pentachloride, PCl_5

1.5.2 Molecules with Lone Pairs on the Central Atom

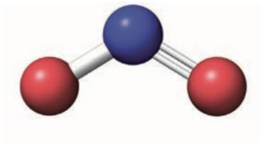
Rule 3 All regions of high electron density, lone pairs and bonds, are included in a description of the electronic arrangement, but only the positions of atoms are considered when identifying the shape of a molecule.



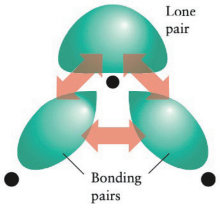
17 Sulfite ion, SO_3^{2-}

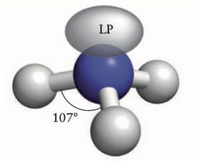
$:\ddot{O}-\dot{N}=\ddot{O}$

18 Nitrogen dioxide, NO_2



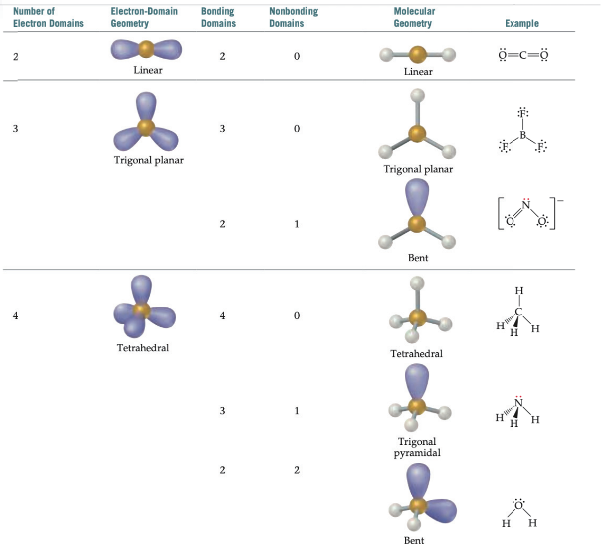
19 Nitrogen dioxide, NO_2





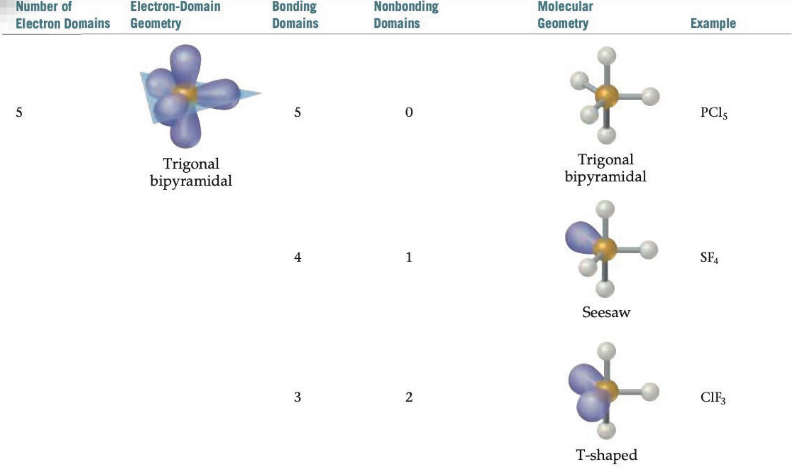
21 Ammonia, NH_3

1.5.3 Molecular Geometry Summary



Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
2	Linear	2	0	Linear	$\ddot{O}=C=\ddot{O}$
3	Trigonal planar	3	0	Trigonal planar	BF_3
		2	1	Bent	$[NO_2]^-$
4	Tetrahedral	4	0	Tetrahedral	CH_4
		3	1	Trigonal pyramidal	NH_3
		2	2	Bent	H_2O

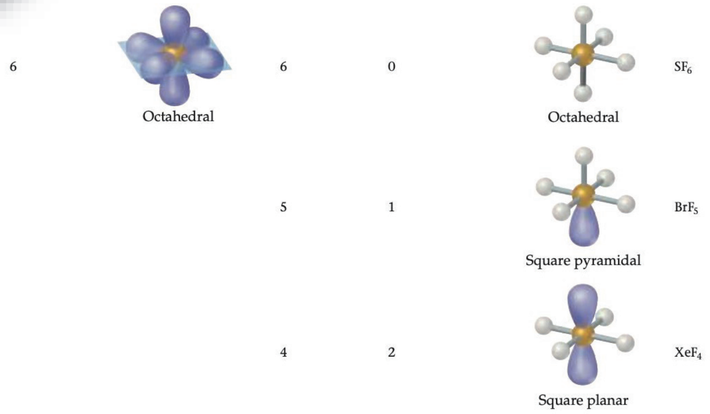
1.5.3 Molecular Geometry Summary



Number of Electron Domains	Electron-Domain Geometry	Bonding Domains	Nonbonding Domains	Molecular Geometry	Example
5	Trigonal bipyramidal	5	0	Trigonal bipyramidal	PCl_5
		4	1	Seesaw	SF_4
		3	2	T-shaped	ClF_3

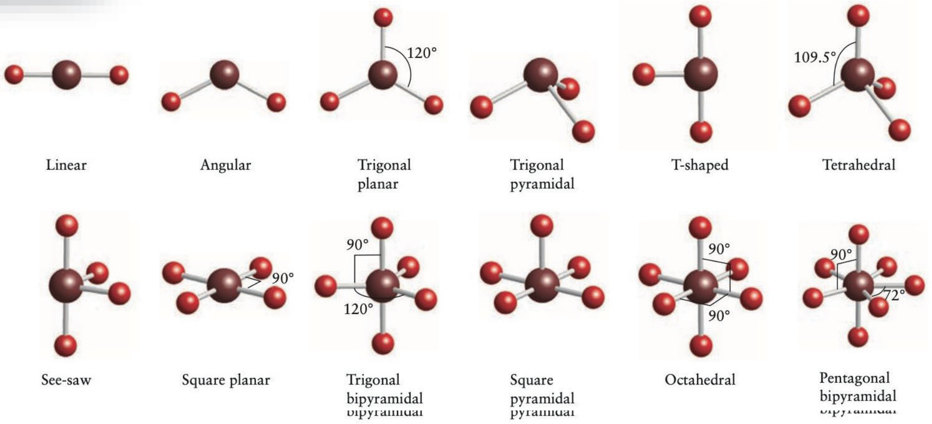
1.5.3

Molecular Geometry Summary



1.5.3

Molecular Geometry Summary

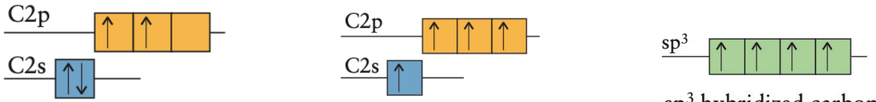


1.5.4

Hybridization

We often assume that the atomic orbitals on an atom (usually the central atom) mix to form new orbitals called **hybrid orbitals**.

The shape of any hybrid orbital is different from the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a mathematical operation called **hybridization.**



Carbon, [He]$2s^2 2p_x^{\ 1} 2p_y^{\ 1}$

Carbon, [He]$2s^1 2p_x^{\ 1} 2p_y^{\ 1} 2p_z^{\ 1}$

sp^3 hybridized carbon

1.5.4

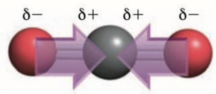
Hybridization

Electron arrangement	Number of atomic orbitals	Hybridization of the central atom	Number of hybrid orbitals
linear	2	sp	2
trigonal planar	3	sp^2	3
tetrahedral	4	sp^3	4
trigonal bipyramidal	5	sp^3d	5
octahedral	6	sp^3d^2	6

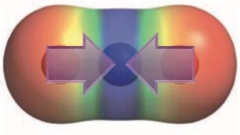
1.5.5

Polar Molecules

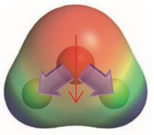
Polar molecule is a molecule with a nonzero dipole moment



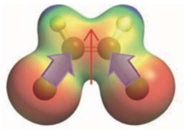
25 Carbon dioxide, CO_2



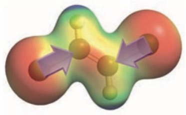
26 Carbon dioxide, CO_2



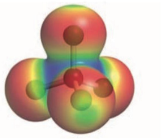
27 Water, H_2O



28 *cis*-Dichloroethene, $C_2H_2Cl_2$



29 *trans*-Dichloroethene, $C_2H_2Cl_2$



30 Tetrachloromethane, CCl_4

1.5.6

Practice: Predicting a Molecular Shape

4.19 Predict the shapes and estimate the bond angles of (a) the thiosulfate ion, $S_2O_3^{2-}$; (b) $(CH_3)_2Be$; (c) BH_2^-; (d) $SnCl_2$.

4.20 For each of the following molecules or ions, write the Lewis structure, list the number of lone pairs on the central atom, identify the shape, and estimate the bond angles: (a) PBr_5; (b) $XeOF_2$; (c) SF_5^+; (d) IF_3; (e) BrO_3^-.

4.21 Write the Lewis structure and give the approximate bond angles of (a) C_2H_4; (b) ClCN; (c) $OPCl_3$; (d) N_2H_4.

4.22 Write the Lewis structure and predict the shape of (a) ClF_5; (b) SbF_5; (c) IO_5^{3-}; (d) IO_6^{5-}.

4.23 Write the Lewis structure and predict the shape of (a) $O\mathbf{Sb}Cl_3$; (b) $\mathbf{S}O_2Cl_2$; (c) $\mathbf{I}O_2F_2^-$. The atom in boldface type is the central atom.

1.5.7 Practice: Lewis Structure and Shape

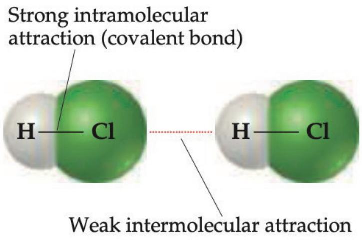
(a) CH_3Cl
(b) CS_2
(c) PH_3
(d) SiF_4
(e) H_2S
(f) NO_3^-
(g) CO_3^{2-}
(h) PO_4^{3-}
(i) SO_3^{2-}
(j) ClO_4^-
(k) SO_2
(l) NO_2^-

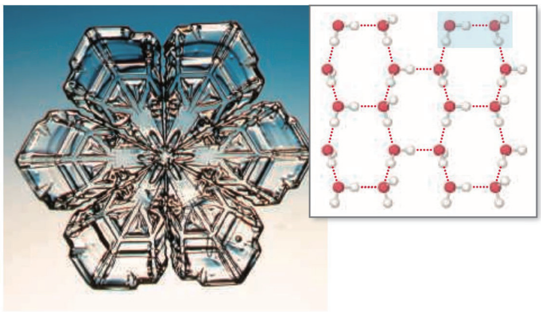
1.5 Summary & Practice

1. Concept

2. Example

1.6 State of Matter

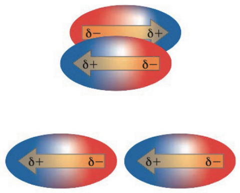


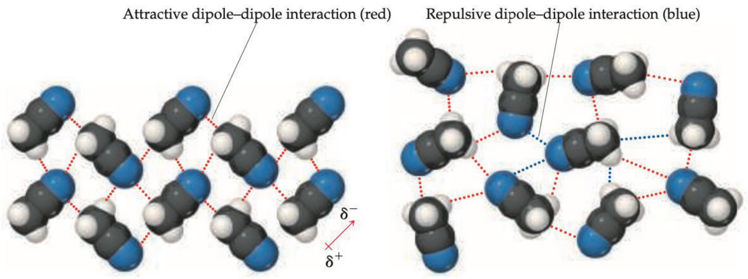


1.6.1

Intermolecular Forces Dipole-Dipole Force

The presence of a permanent dipole moment in polar molecules gives rise to **dipole– dipole interactions**



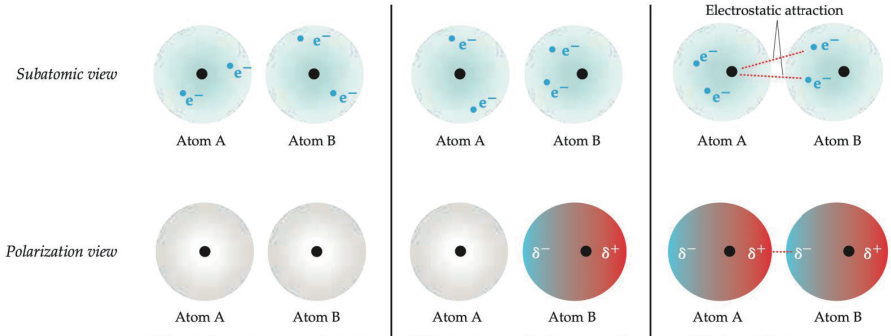


(a) Solid CH_3CN **(b)** Liquid CH_3CN

1.6.1

Intermolecular Forces London Dispersion Force

The motions of electrons in one atom influence the motions of electrons in its neighbors. The instantaneous dipole on one atom can induce an instantaneous dipole on an adjacent atom, causing the atoms to be attracted to each other. This attractive interaction is called the **London dispersion force.** It is significant only when molecules are very close together.

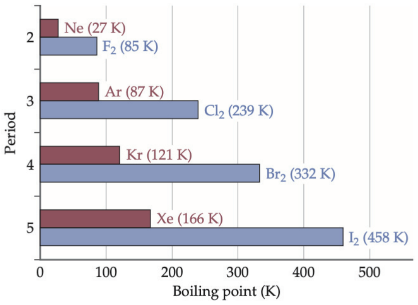


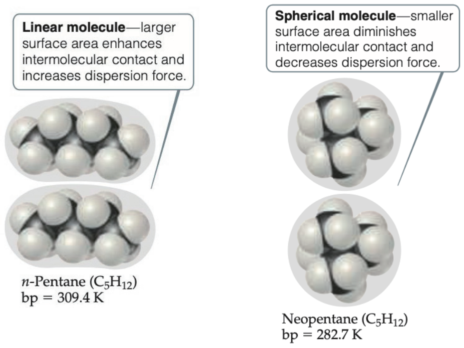
(a) Two helium atoms, no polarization **(b)** Instantaneous dipole on atom B **(c)** Induced dipole on atom A

1.6.1

Intermolecular Forces London Dispersion Force

The ease with which the charge distribution is distorted is called the molecule's **polarizability**.





Linear molecule—larger surface area enhances intermolecular contact and increases dispersion force.

Spherical molecule—smaller surface area diminishes intermolecular contact and decreases dispersion force.

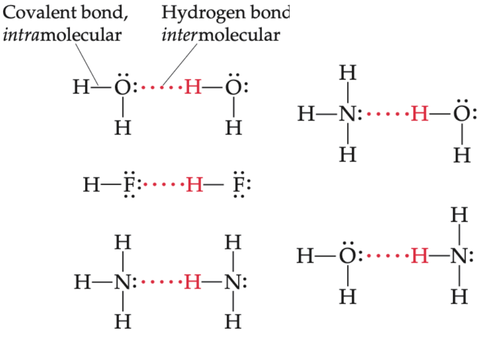
n-Pentane (C_5H_{12})
bp = 309.4 K

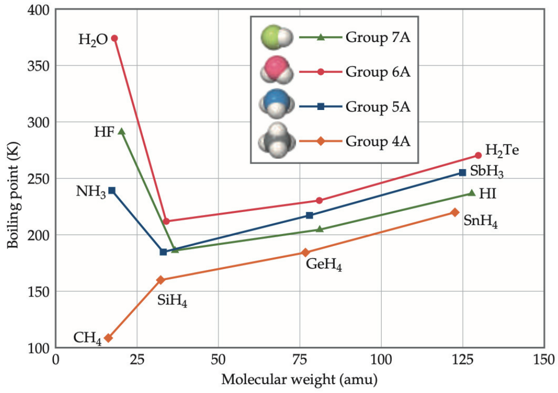
Neopentane (C_5H_{12})
bp = 282.7 K

1.6.1

Intermolecular Forces Hydrogen Bonding

hydrogen bond is an attraction between a hydrogen atom attached to a highly electronegative atom (usually F, O, or N) and a nearby small electronegative atom in another molecule or chemical group.

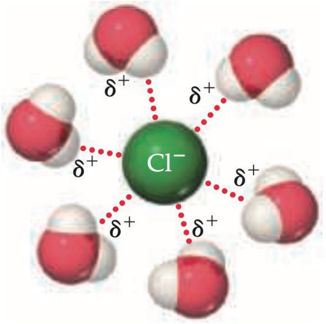




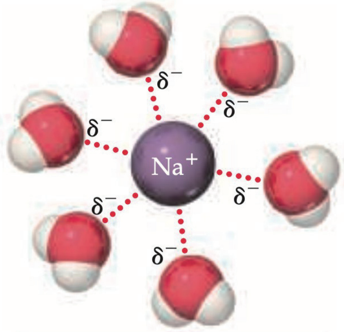
1.6.1

Intermolecular Forces Ion–Dipole Forces

An **ion–dipole force** exists between an ion and a polar molecule



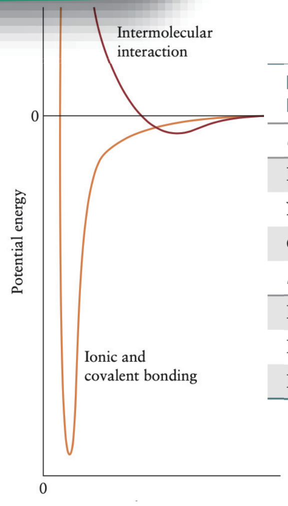
Positive ends of polar molecules are oriented toward negatively charged anion.



Negative ends of polar molecules are oriented toward positively charged cation.

1.6.1

Comparing Intermolecular Forces



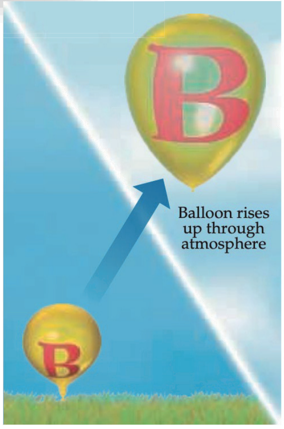
Force Holding Particles Together	Substance	Melting Point (K)	Boiling Point (K)
Chemical bonds			
Ionic bonds	Lithium fluoride (LiF)	1118	1949
Metallic bonds	Beryllium (Be)	1560	2742
Covalent bonds	Diamond (C)	3800	4300
Intermolecular forces			
Dispersion forces	Nitrogen (N_2)	63	77
Dipole–dipole interactions	Hydrogen chloride (HCl)	158	188
Hydrogen bonding	Hydrogen fluoride (HF)	190	293

1.6.1 Comparing Intermolecular Forces

1.When the molecules of two substances have comparable molecular weights and shapes, dispersion forces are approximately equal in the two substances.
2.When the molecules of two substances differ widely in molecular weights, and there is no hydrogen bonding, dispersion forces tend to determine which substance has the stronger intermolecular attractions.

Type of intermolecular interaction	**Atoms** Examples: Ne, Ar	**Nonpolar molecules** Examples: BF_3, CH_4	**Polar molecules without OH, NH, or HF groups** Examples: HCl, CH_3CN	**Polar molecules containing OH, NH, or HF groups** Examples: H_2O, NH_3	**Ionic solids dissolved in polar liquids** Examples: NaCl in H_2O
Dispersion forces (0.1–30 kJ/mol)	√	√	√	√	√
Dipole–dipole interactions (2–15 kJ/mol)			√	√	
Hydrogen bonding (10–40 kJ/mol)				√	
Ion–dipole interactions (>50 kJ/mol)					√

1.6.2 Gas



1.6.2.1 Pressure

The molecules of a gas move chaotically, colliding with each other and with the walls of their container. The impacts with the container walls exert a force—an outward push against the walls. The **pressure**, *P*, that a gas exerts is defined as the force, *F*, divided by the area, *A*, of the surface on.

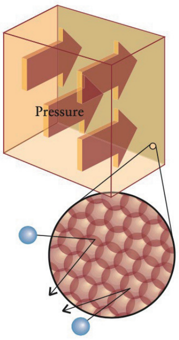
$$P = \frac{F}{A}$$

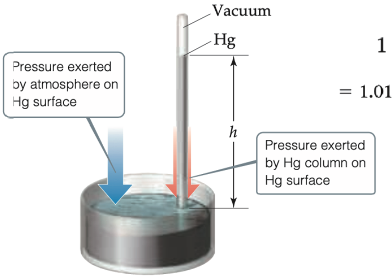
The SI unit of pressure is the **pascal,** Pa

$$1\ \text{Pa} = 1\ \text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}$$

$$1\ \text{atm} = 760.\ \text{mm Hg} = 760.\ \text{torr}$$

$$= 1.01325 \times 10^5\ \text{Pa} = 101.325\ \text{kPa} = 1.01325\ \text{bar}$$



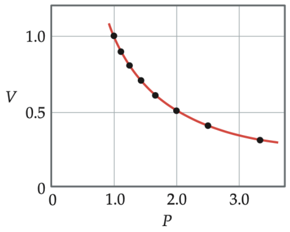


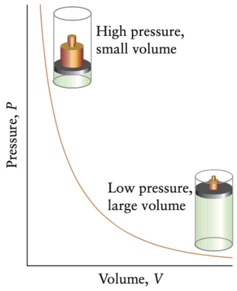
1.6.2.2

The Gas Laws 1:Boyle's law

The volume of a fixed quantity of gas maintained at constant temperature is inversely proportional to the pressure.

$$V = \text{constant} \times \frac{1}{P} \quad \text{or} \quad PV = \text{constant}$$



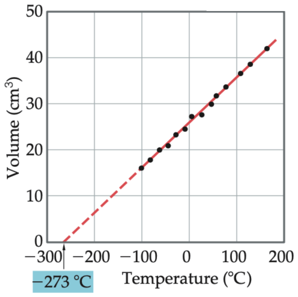


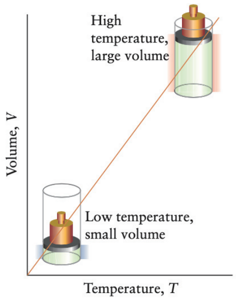
1.6.2.3

The Gas Laws 2:Charles's Law

The volume of a fixed amount of gas maintained at constant pressure is directly proportional to its absolute temperature.

$$V = \text{constant} \times T \quad \text{or} \quad \frac{V}{T} = \text{constant}$$





1.6.2.4

The Gas Laws 3:Avogadro's Law

Avogadro's hypothesis: Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

Avogadro's law: The volume of a gas maintained at constant temperature and pressure is directly proportional to the number of moles of the gas.

$$V = \text{constant} \times n \quad \text{or} \quad \frac{V}{n} = \text{constant}$$

	He	N_2	CH_4
Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0 °C	0 °C	0 °C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}

1.6.2.5 The Ideal Gas Equation

$$PV = nRT$$

Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m^3-Pa/mol-K*	8.314
L-torr/mol-K	62.36

The conditions 0 °C and 1 atm are referred to as **standard temperature and pressure (STP)**

1.6.2.6 Gas Mixtures and Partial Pressure

The total pressure of a mixture of gases is the sum of the partial pressures of its components.

$$P = P_A + P_B + \cdots$$

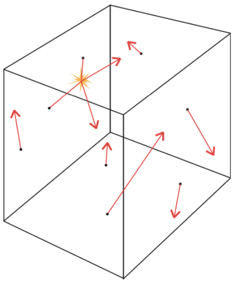
The mole fraction is defined as the number of moles of each component of the gas mixture expressed as a fraction of the total number of moles of molecules in the sample.

$$x_A = \frac{n_A}{n} = \frac{n_A}{n_A + n_B + \cdots}$$

$$\boxed{P_A = x_A P}$$

1.6.2.7 The Kinetic-Molecular Theory of Gases

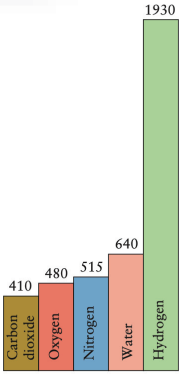
The **kinetic model** of a gas, which is also known as the "kinetic molecular theory" (KMT), is based on four assumptions



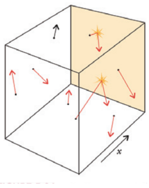
1. A gas consists of a collection of molecules in continuous random motion.
2. Gas molecules are infinitesimally small points.
3. The molecules move in straight lines until they collide.
4. The molecules do not influence one another except during collisions.

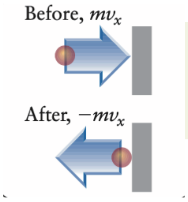
1.6.2.8

The Kinetic-Molecular Theory of Gases



The root mean square speeds of five gases at 25 °C, in meters per second.





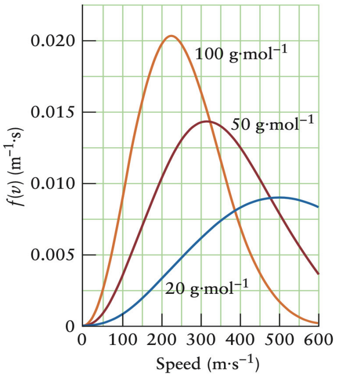
$$\Delta mv_x = \overbrace{mv_x}^{\text{initial}} - \overbrace{(-mv_x)}^{\text{final}} = 2mv_x$$

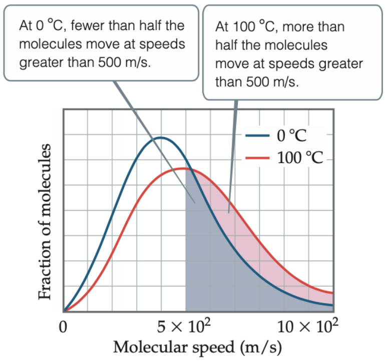
$$T = \frac{Mv_{\text{rms}}^2}{3R}$$

1.6.2.9

The Maxwell Distribution of Speeds

The molecules of all gases have a wide range of speeds. As the temperature increases, the root mean square speed and the range of speeds both increase.
The range of speeds is described by the Maxwell distribution

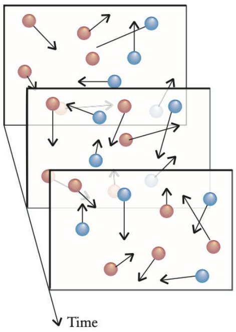




1.6.2.10

Molecular Effusion and Diffusion

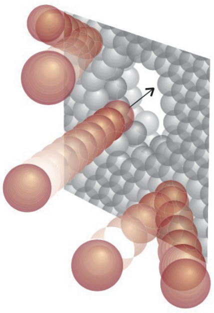
Diffusion is the gradual dispersal of one substance through another substance, such as krypton dispersing through a neon atmosphere.
Effusion is the escape of a gas through a small hole into a vacuum or very- low-pressure region



$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\text{molar mass}}}$$

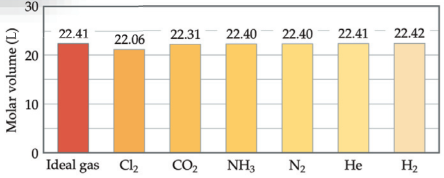
$$\text{Average speed} \propto \sqrt{T}$$

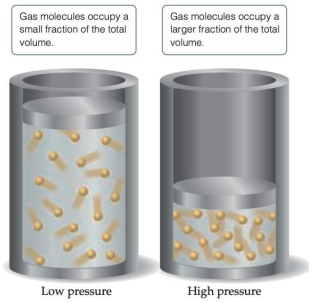
$$\text{Average speed} \propto \sqrt{\frac{T}{M}}$$



1.6.2.11

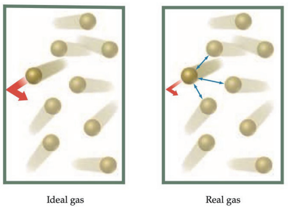
Real Gas: Deviations from Ideal Behavior





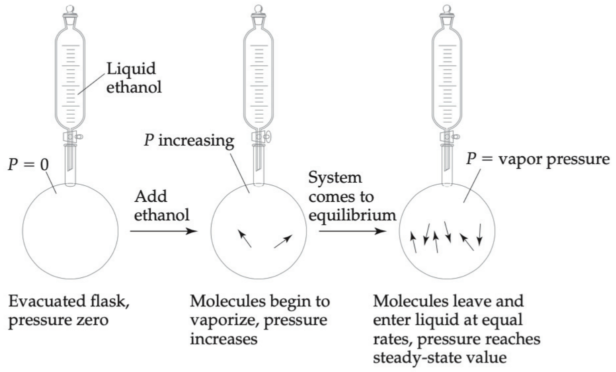
van der Waals equation:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$



1.6.2.12

Vapor Pressure



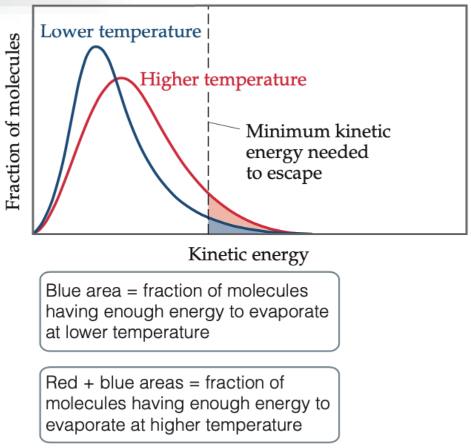
Molecules can escape from the surface of a liquid into the gas phase by evaporation.

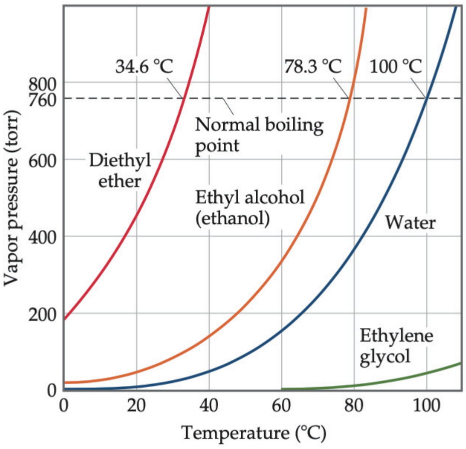
The ethanol quickly begins to evaporate. As a result, the pressure exerted by the vapor in the space above the liquid increases. After a short time, the pressure of the vapor attains a constant value, which we call the **vapor pressure**.

1.6.2.13

Volatility

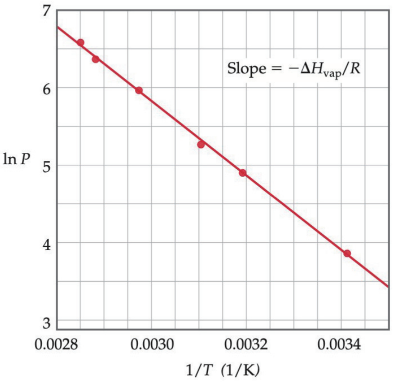
Liquids that evaporate readily are said to be **volatile**.





1.6.3 Clausius–Clapeyron Equation:

$$\ln P = \frac{-\Delta H_{\text{vap}}}{RT} + C$$

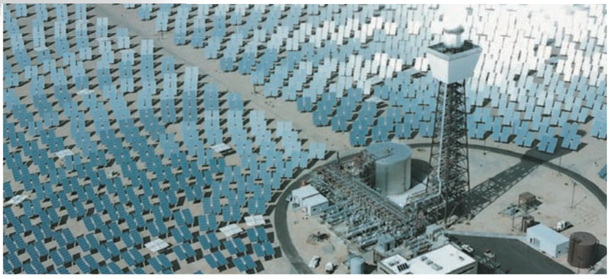


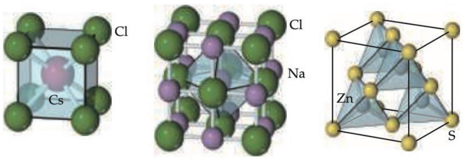
1.6 Summary & Practice

1. Concept

2. Example

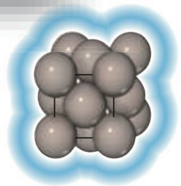
1.7 Crystal





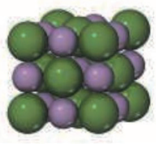
1.7.1

Classification of Solids



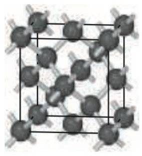
Metallic solids

Extended networks of atoms held together by metallic bonding (Cu, Fe)



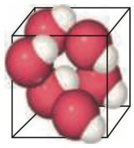
Ionic solids

Extended networks of ions held together by cation–anion interactions (NaCl, MgO)



Covalent-network solids

Extended networks of atoms held together by covalent bonds (C, Si)



Molecular solids

Discrete molecules held together by intermolecular forces (HBr, H_2O)

Polymers contain long chains of atoms (usually carbon), where the atoms within a given chain are connected by covalent bonds and adjacent chains are held to one another largely by weaker intermolecular forces.

Nanomaterials are solids in which the dimensions of individual crystals have been reduced to the order of 1–100 nm.

1.7.1

Classification of Solids

Molecular solids are assemblies of discrete molecules held in place by intermolecular forces.

Network solids consist of atoms covalently bonded to their neighbors throughout the extent of the solid.

Metallic solids, also called simply *metals,* consist of cations held together by a sea of electrons.

Ionic solids are built from the mutual attractions of cations and anions.

Class	Examples	Characteristics
metallic	s- and d-block elements	malleable, ductile, lustrous, electrically and thermally conducting
ionic	NaCl, KNO_3, $CuSO_4{\cdot}5H_2O$	hard, rigid, brittle; high melting and boiling points; those soluble in water give conducting solutions
network	B, C, black P, BN, SiO_2	hard, rigid, brittle; very high melting points; insoluble in water
molecular	$BeCl_2$, S_8, P_4, I_2, ice, glucose, naphthalene	relatively low melting and boiling points; brittle if pure

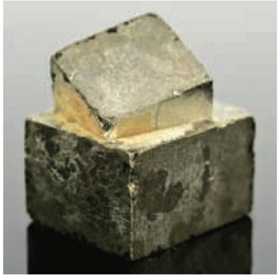
---

1.7.2

Structures of Solids & Unit Cells

Solids in which atoms are arranged in an orderly repeating pattern are called **crystalline solids**. **Amorphous solids** (from the Greek words for “without form”) lack the order found in crystalline solids.

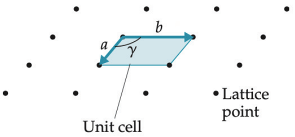
In a crystalline solid, there is a relatively small repeating unit, called a unit cell, that is made up of a unique arrangement of atoms and embodies the structure of the solid.

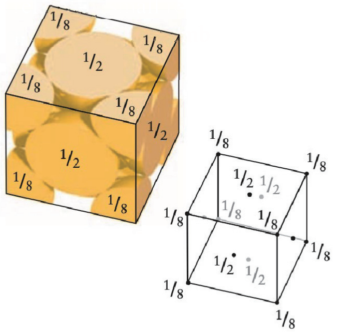


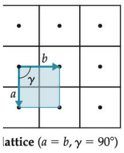
Iron pyrite (FeS_2), a crystalline solid

1.7.2 Structures of Solids & Unit Cells

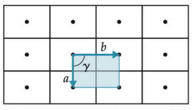
In a crystalline solid, there i … made up of a unique arrang … d a unit cell, that is … ure of the solid.



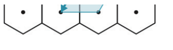


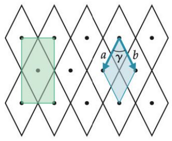


lattice (a = b, γ = 90°)



Rectangular lattice (a ≠ b, γ = 90°)

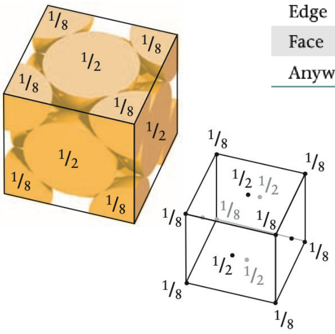

Hexagonal lattice (a = b, γ = 120°)

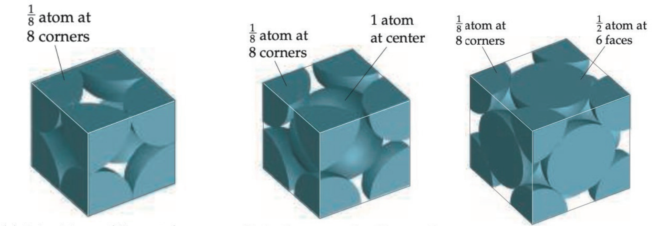


Rhombic lattice (a = b, γ = arbitrary)
Centered rectangular lattice

1.7.2 Structures of Solids & Unit Cells

Atom Location	Number of Unit Cells Sharing Atom	Fraction of Atom within Unit Cell
Corner	8	1/8 or 12.5%
Edge	4	1/4 or 25%
Face	2	1/2 or 50%
Anywhere else	1	1 or 100%





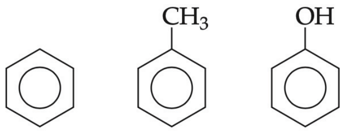
(a) Primitive cubic metal
1 atom per unit cell

(b) Body-centered cubic metal
2 atoms per unit cell

(c) Face-centered cubic metal
4 atoms per unit cell

1.7.3 Molecular Solids

Molecular solids consist of atoms or neutral molecules held together by dipole–dipole forces, dispersion forces, and/or hydrogen bonds. Because these intermolecular forces are weak, molecular solids are soft and have relatively low melting points.



	Benzene	Toluene	Phenol
Melting point (°C)	5	–95	43
Boiling point (°C)	80	111	182

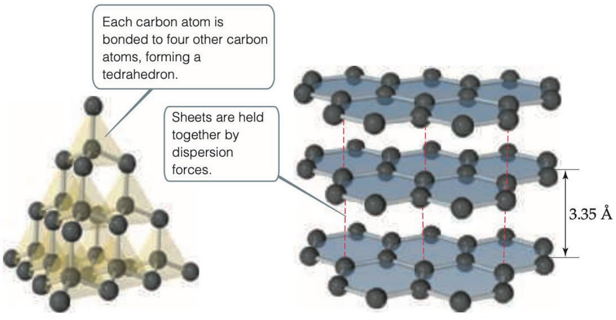
1.7.3 A Molecular Comparison of Gases, Liquids, and Solids

Characteristic Properties of the States of Matter

Gas	Liquid	Solid
Assumes both volume and shape of its container	Assumes shape of portion of container it occupies	Retains own shape and volume
Expands to fill its container	Does not expand to fill its container	Does not expand to fill its container
Is compressible	Is virtually incompressible	Is virtually incompressible
Flows readily	Flows readily	Does not flow
Diffusion within a gas occurs rapidly	Diffusion within a liquid occurs slowly	Diffusion within a solid occurs extremely slowly

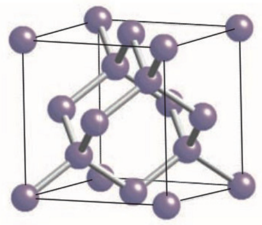
1.7.4 Network Solids

Covalent-network solids consist of atoms held together in large networks by covalent bonds. Because covalent bonds are much stronger than intermolecular forces, these solids are much harder and have higher melting points than molecular solids. Diamond and graphite, two allotropes of carbon, are two of the most familiar covalent-network solids.

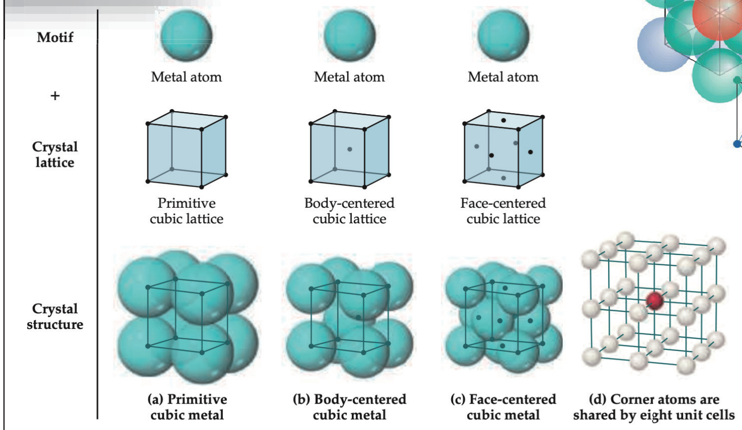


(a) Diamond

(b) Graphite



1.7.5 Metallic Solids

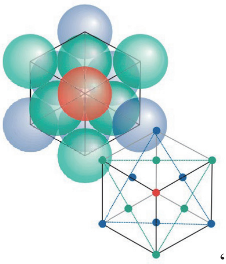


(a) Primitive cubic metal

(b) Body-centered cubic metal

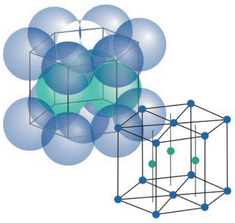
(c) Face-centered cubic metal

(d) Corner atoms are shared by eight unit cells



“cubic close- packed” or “face-centered cubic”

“hexagonal close-packed.”

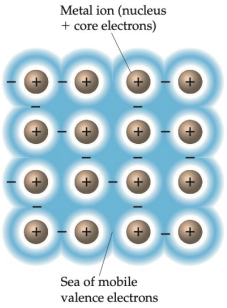


1.7.5 Metallic Solids

An **alloy** is a material that contains more than one element and has the characteristic properties of a metal.

When atoms of the solute in a solid solution occupy positions normally occupied by a solvent atom, we have a **substitutional alloy**.

When the solute atoms occupy interstitial positions in the “holes” between solvent atoms, we have an **interstitial alloy.**



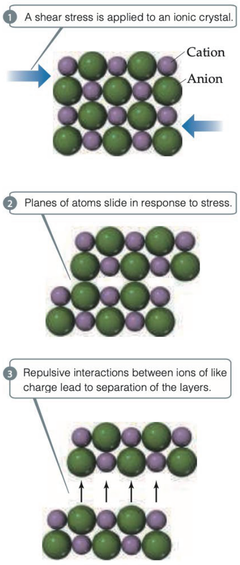
Some Common Alloys

Name	Primary Element	Typical Composition (by Mass)	Properties	Uses
Wood’s metal	Bismuth	50% Bi, 25% Pb, 12.5% Sn, 12.5% Cd	Low melting point (70 °C)	Fuse plugs, automatic sprinklers
Yellow brass	Copper	67% Cu, 33% Zn	Ductile, takes polish	Hardware items
Bronze	Copper	88% Cu, 12% Sn	Tough and chemically stable in dry air	Important alloy for early civilizations
Stainless steel	Iron	80.6% Fe, 0.4% C, 18% Cr, 1% Ni	Resists corrosion	Cookware, surgical instruments
Plumber’s solder	Lead	67% Pb, 33% Sn	Low melting point (275 °C)	Soldering joints
Sterling silver	Silver	92.5% Ag, 7.5% Cu	Bright surface	Tableware
Dental amalgam	Silver	70% Ag, 18% Sn, 10% Cu, 2% Hg	Easily worked	Dental fillings
Pewter	Tin	92% Sn, 6% Sb, 2% Cu	Low melting point (230 °C)	Dishes, jewelry

1.7.6 Ionic Structures

Properties of the Alkali Metal Halides

Compound	Cation–Anion Distance (Å)	Lattice Enthalpy (kJ/mol)	Melting Point (°C)
LiF	2.01	1030	845
NaCl	2.83	788	801
KBr	3.30	671	734
RbI	3.67	632	674



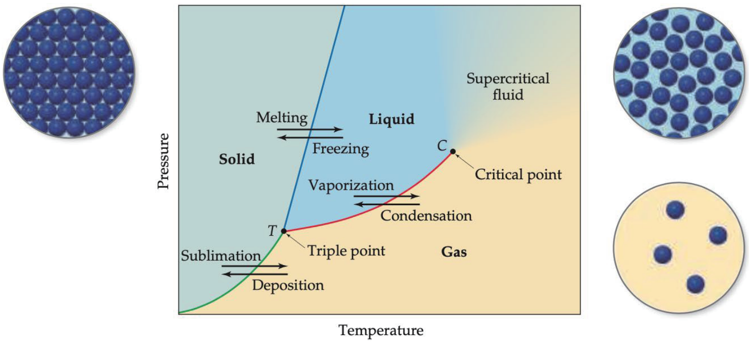
1.7 Summary & Practice

1. Concept

2. Example

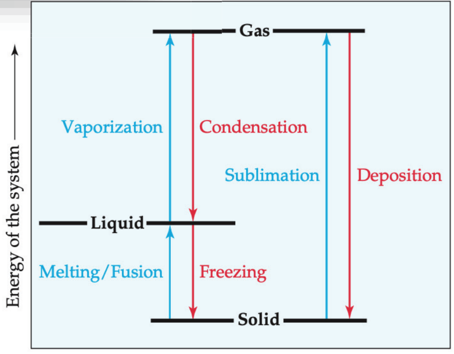
1.8

Phase Change

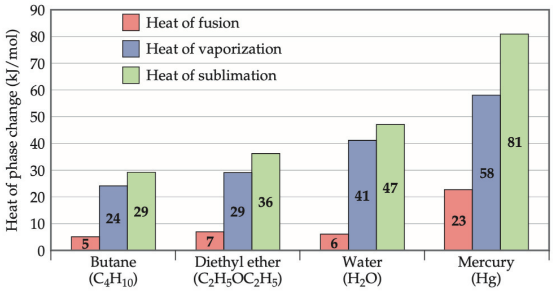


1.8.1

Phase Change



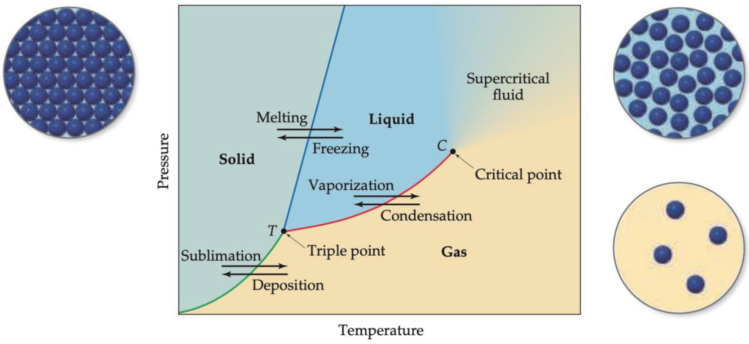
— Endothermic process (energy added to substance)
— Exothermic process (energy released from substance)



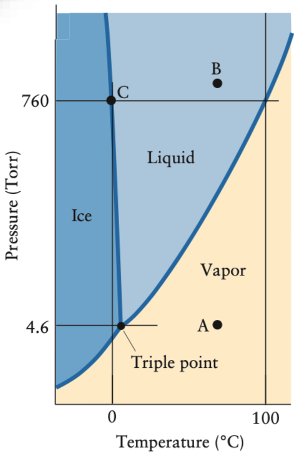
1.8.2

Phase Diagrams

A **phase diagram** is a graphic way to summarize the conditions under which equilibria exist between the different states of matter.



1.8.2 Phase Diagrams



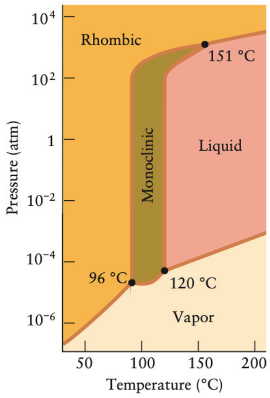
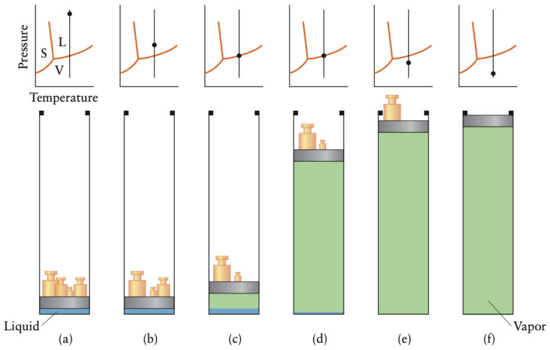


FIGURE 10.9 The phase diagram for sulfur. Notice that there are two solid phases and three triple points. The pressure scale, which is logarithmic, covers a very wide range of values.

1.8.2 Phase Diagrams

A **triple point** is a point where three phase boundaries meet on a phase diagram.



1.8 Summary & Practice

1. Concept

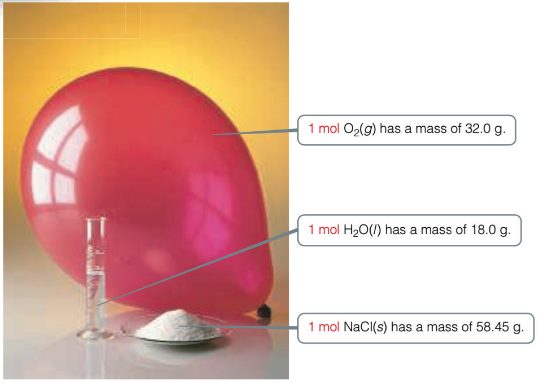
2. Example

UKChO

英国化学奥林匹克竞赛

Unit 2

Reaction & Stoichiometry



Unit 2

Reaction & Stoichiometry

2.1 Chemical equation

2.2 Calculation

2.3 Solution stoichiometry

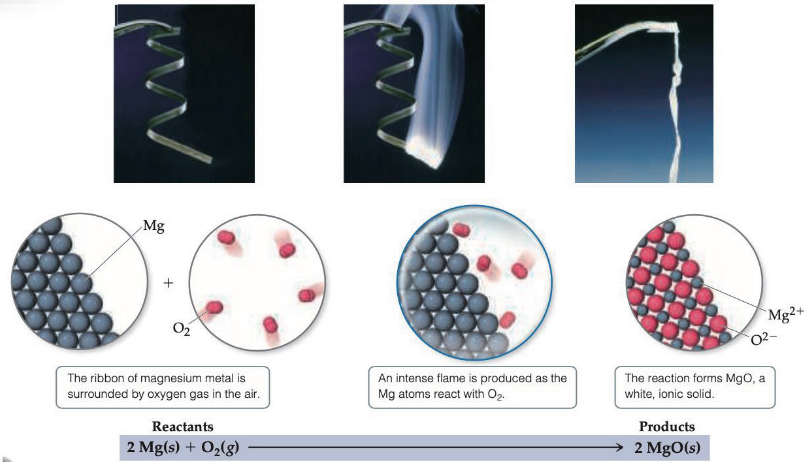
2.4 Acid & base

2.5 Weak Acid & Base

2.6 Aqueous Equilibrium

2.1

Chemical Equation



The ribbon of magnesium metal is surrounded by oxygen gas in the air.

An intense flame is produced as the Mg atoms react with O_2.

The reaction forms MgO, a white, ionic solid.

Reactants **Products**

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$$

2.1.1

Balancing Equations & Coefficient

Antoine Lavoisier (1734– 1794).

1.Interpreting and Balancing Chemical Equations

2. Indicating the States of Reactants and Products
(g), (l), (s) and (aq)

$$NaN_3 \longrightarrow Na + N_2$$

2.1.2

Combination Reactions

combination reactions, two or more substances react to form one product

Combination Reactions

$A + B \longrightarrow C$	Two or more reactants combine to form a single product. Many elements react with one another in this fashion to form compounds.
$C(s) + O_2(g) \longrightarrow CO_2(g)$	
$N_2(g) + 3\,H_2(g) \longrightarrow 2\,NH_3(g)$	
$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$	

2.1.3 Decomposition Reactions

Decomposition reaction one substance undergoes a reaction to produce two or more other substances

Decomposition Reactions

$C \longrightarrow A + B$	A single reactant breaks apart to form two or more substances. Many compounds react this way when heated.
$2\,KClO_3(s) \longrightarrow 2\,KCl(s) + 3\,O_2(g)$	
$PbCO_3(s) \longrightarrow PbO(s) + CO_2(g)$	
$Cu(OH)_2(s) \longrightarrow CuO(s) + H_2O(g)$	

$2\,NaN_3(s) \longrightarrow 2\,Na(s) + 3\,N_2(g)$

2.1.4 Combustion Reactions

Combustion reactions are rapid reactions that produce a flame. Most combustion reactions we observe involve O_2 from air as a reactant.

$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(g)$

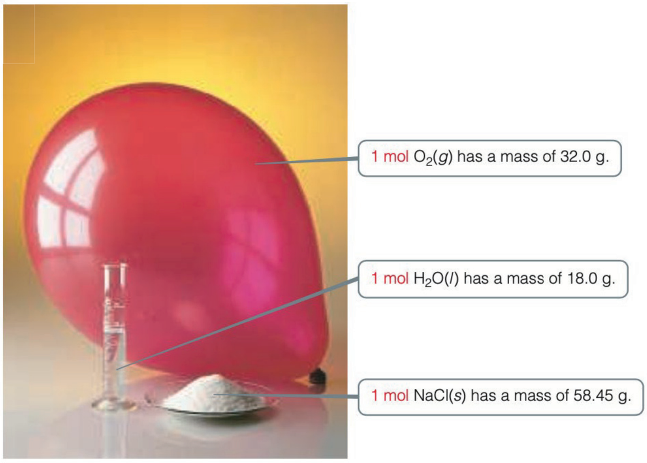
The state of the water in this reaction, $H_2O(g)$or $H_2O(l)$, depends on the reaction conditions.

2.1 Summary & Practice

1. Concept

2. Example

2.2 Calculation



2.2.1 Formula and Molecular Weights

The **formula weight** (FW) of a substance is the sum of the atomic weights (AW) of the atoms in the chemical formula of the substance.

$$\begin{aligned}\text{FW of } H_2SO_4 &= 2(\text{AW of H}) + (\text{AW of S}) + 4(\text{AW of O})\\ &= 2(1.0\text{ amu}) + 32.1\text{ amu} + 4(16.0\text{ amu})\\ &= 98.1\text{ amu}\end{aligned}$$

2.2.2 Percentage Composition from Chemical Formulas

The percentage composition of any element in a substance (sometimes called the **elemental composition** of a substance) is straightforward if the chemical formula is known.

$$\begin{matrix}\text{\% mass composition}\\ \text{of element}\end{matrix} = \frac{\begin{pmatrix}\text{number of atoms}\\ \text{of element}\end{pmatrix}\begin{pmatrix}\text{atomic weight}\\ \text{of element}\end{pmatrix}}{\text{formula weight of substance}} \times 100\%$$

2.2.3 Avogadro's Number and the Mole

One **mole** is the amount of matter that contains as many objects (atoms, molecules, or whatever other objects we are considering) as the number of atoms in exactly 12 g of isotopically pure ^{12}C

From experiments, scientists have determined this number to be $6.0221415 * 10^{23}$ （$6.02 * 10^{23}$），which is **Avogadro's Number**

$$1 \text{ mol } {}^{12}\text{C atoms} = 6.02 \times 10^{23}\ {}^{12}\text{C atoms}$$

$$1 \text{ mol } H_2O \text{ molecules} = 6.02 \times 10^{23}\ H_2O \text{ molecules}$$

$$1 \text{ mol } NO_3^- \text{ ions} = 6.02 \times 10^{23}\ NO_3^- \text{ ions}$$

2.2.4 Molar Mass

The atomic weight of an element in atomic mass units is numerically equal to the mass in grams of 1mol of that element.

Cl has an atomic weight of 35.5 amu ⇒ 1 mol Cl has a mass of 35.5 g.

Au has an atomic weight of 197 amu ⇒ 1 mol Au has a mass of 197 g.

*The mass in grams of one mole, often abbreviated as 1 mol, of a substance (that is, the mass in grams per mole) is called the **molar mass** of the substance.*

2.2.4 Mole Relationships n=m/M

Name of Substance	Formula	Formula Weight (amu)	Molar Mass (g/mol)	Number and Kind of Particles in One Mole
Atomic nitrogen	N	14.0	14.0	6.02×10^{23} N atoms
Molecular nitrogen or "dinitrogen"	N_2	28.0	28.0	6.02×10^{23} N_2 molecules $2(6.02 \times 10^{23})$ N atoms
Silver	Ag	107.9	107.9	6.02×10^{23} Ag atoms
Silver ions	Ag^+	107.9[a]	107.9	6.02×10^{23} Ag^+ ions
Barium chloride	$BaCl_2$	208.2	208.2	6.02×10^{23} $BaCl_2$ formula units 6.02×10^{23} Ba^{2+} ions $2(6.02 \times 10^{23})$ Cl^- ions


Grams ← Use molar mass → Moles ← Use Avogadro's number → Formula units

2.2.4 Mole Relationships n=m/M

(USNCO -2020-2)

How many hydrogen atoms are in 2.50 g of pharmacolite, $CaHAsO_4 \cdot 2H_2O$ ($M = 216.0$)?

(A) 6.97×10^{21} **(B)** 2.09×10^{22}

(C) 2.79×10^{22} **(D)** 3.48×10^{22}

2.2.4 Mole Relationships n=m/M

(USNCO -2020-6)

A 5.00 g mixture of potassium sulfide and potassium chloride contains 2.80 g potassium. What percentage by mass of the mixture is potassium sulfide?

(A) 13.8% **(B)** 19.2% **(C)** 44.0% **(D)** 96.1%

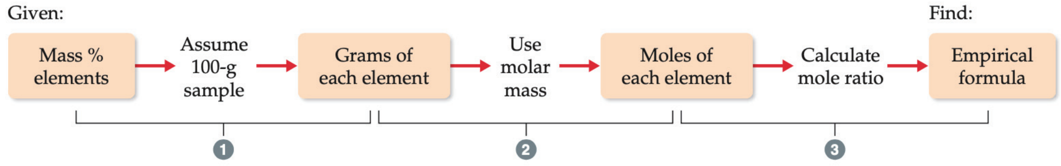
2.2.5 Empirical Formulas from Analyses

Mercury and chlorine, for example, combine to form a compound that is measured to be 74.0% mercury and 26.0% chlorine by mass.

$$(74.0\,\text{g}\,\cancel{\text{Hg}})\left(\frac{1\text{ mol Hg}}{200.6\,\text{g}\,\cancel{\text{Hg}}}\right) = 0.369\text{ mol Hg}$$

$$(26.0\,\text{g}\,\cancel{\text{Cl}})\left(\frac{1\text{ mol Cl}}{35.5\,\text{g}\,\cancel{\text{Cl}}}\right) = 0.732\text{ mol Cl}$$

$HgCl_2$



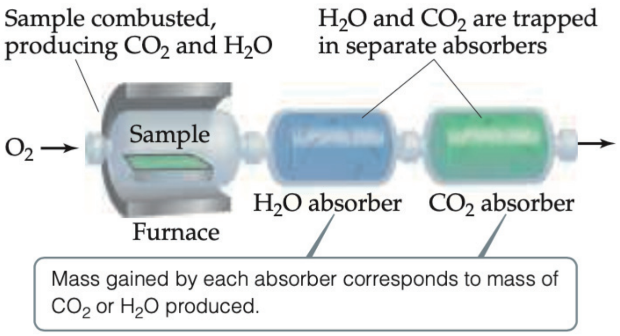
Given:

Mass % elements → Assume 100-g sample → Grams of each element → Use molar mass → Moles of each element → Calculate mole ratio → Empirical formula

Find:

① ② ③

2.2.6 Combustion Analysis



2.2.6 Combustion Analysis

(USNCO -2020-1)

A 2.50 L sample of butane gas (C_4H_{10}), measured at 22.0 °C and 1.20 atm pressure, is combusted completely and the carbon dioxide gas collected at the same pressure and temperature. What volume of CO_2 is produced?

(A) 2.50 L **(B)** 9.00 L

(C) 10.0 L **(D)** 22.5 L

2.2.7 Limiting Reagent

The reactant that is completely consumed in a reaction is called the **limiting reactant** because it determines, or limits, the amount of product formed. The other reactants are sometimes called **excess reactants**.

	$2\,H_2(g)$	+	$O_2(g)$	$\longrightarrow$	$2\,H_2O(g)$
Before reaction:	10 mol		7 mol		0 mol
Change (reaction):	−10 mol		−5 mol		+10 mol
After reaction:	0 mol		2 mol		10 mol

2.2.7 Limiting Reagent

The reactant that is completely consumed in a reaction is called the **limiting reactant** because it determines, or limits, the amount of product formed. The other reactants are sometimes called **excess reactants**.

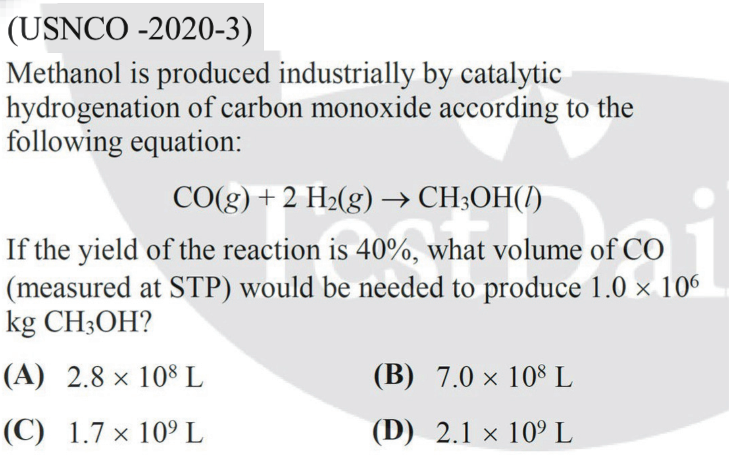
	$2\,H_2(g)$	$+\;O_2(g)$	$\longrightarrow\;2\,H_2O(g)$
Before reaction:	10 mol	7 mol	0 mol
Change (reaction):	−10 mol	−5 mol	+10 mol
After reaction:	0 mol	2 mol	10 mol

2.2.8 Theoretical and Percent Yields

The quantity of product calculated to form when all of a limiting reactant is consumed is called the **theoretical yield.**
The amount of product actually obtained, called the **actual yield**, is almost always less than (and can never be greater than) the theoretical yield.

$$\text{Percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

2.2.8 Theoretical and Percent Yields



(USNCO -2020-3)
Methanol is produced industrially by catalytic hydrogenation of carbon monoxide according to the following equation:

$$CO(g) + 2\,H_2(g) \rightarrow CH_3OH(l)$$

If the yield of the reaction is 40%, what volume of CO (measured at STP) would be needed to produce 1.0×10^6 kg CH_3OH?

(A) 2.8×10^8 L **(B)** 7.0×10^8 L

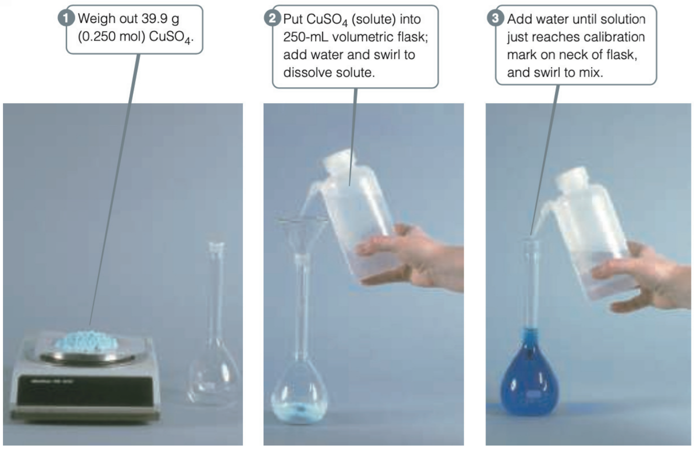
(C) 1.7×10^9 L **(D)** 2.1×10^9 L

2.2 Summary & Practice

1. Concept

2. Example

2.3 Solution Stoichiometry



① Weigh out 39.9 g (0.250 mol) $CuSO_4$.

② Put $CuSO_4$ (solute) into 250-mL volumetric flask; add water and swirl to dissolve solute.

③ Add water until solution just reaches calibration mark on neck of flask, and swirl to mix.

2.3.1 Concentrations of Solutions

Scientists use the term **concentration** to designate the amount of solute dissolved in a given quantity of solvent or quantity of solution. The greater the amount of solute dissolved in a certain amount of solvent, the more concentrated the resulting solution.

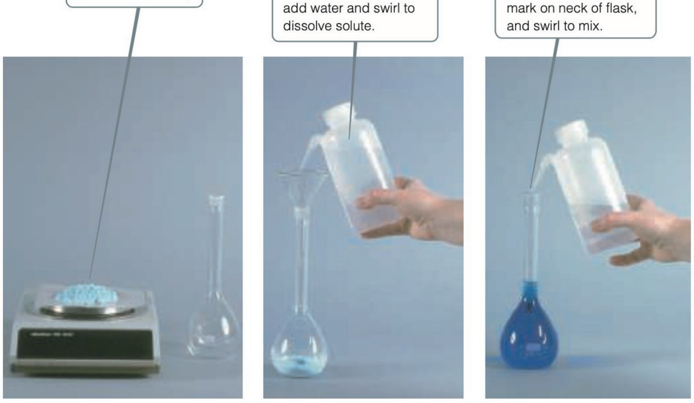
Molarity (symbol *M*) expresses the concentration of a solution as the number of moles of solute in a liter of solution

$$\text{Molarity} = \frac{\text{moles solute}}{\text{volume of solution in liters}}$$

2.3.1

Concentrations of Solutions

A 1.00 molar solution (written 1.00 *M*) contains 1.00 mol of solute in every liter of solution



① Weigh out 39.9 g (0.250 mol) $CuSO_4$.

② Put $CuSO_4$ (solute) into 250-mL volumetric flask; add water and swirl to dissolve solute.

③ Add water until solution just reaches calibration mark on neck of flask, and swirl to mix.

2.3.2

Interconverting Molarity, Moles, and Volume

$$\text{Liters} = \text{mol} \times 1/M = \cancel{\text{mol}} \times \text{liters}/\cancel{\text{mol}}$$

(USNCO -2020-5)

What is the concentration of H_2O_2 in a solution that is 30.0% by mass hydrogen peroxide and has a density of 1.11 g cm^{-3}?

(A) 9.79 M	**(B)** 12.6 M
(C) 18.5 M	**(D)** 32.6 M

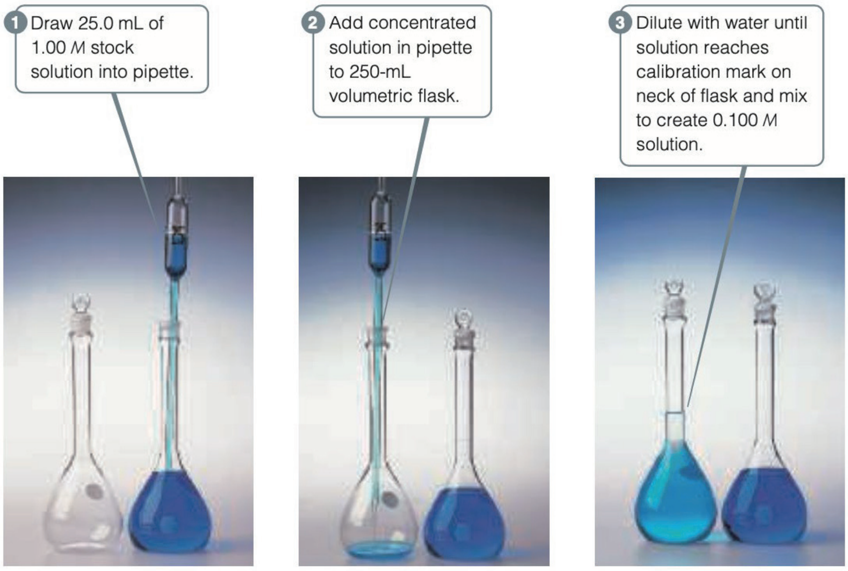
2.3.3

Dilution

Aqueous solutions of lower concentrations can then be obtained by adding water, a process called **dilution.**

$$\text{Moles solute before dilution} = \text{moles solute after dilution}$$

$$\text{Moles solute in conc soln} = \text{moles solute in dilute soln}$$
$$M_{\text{conc}} \times V_{\text{conc}} = M_{\text{dil}} \times V_{\text{dil}}$$



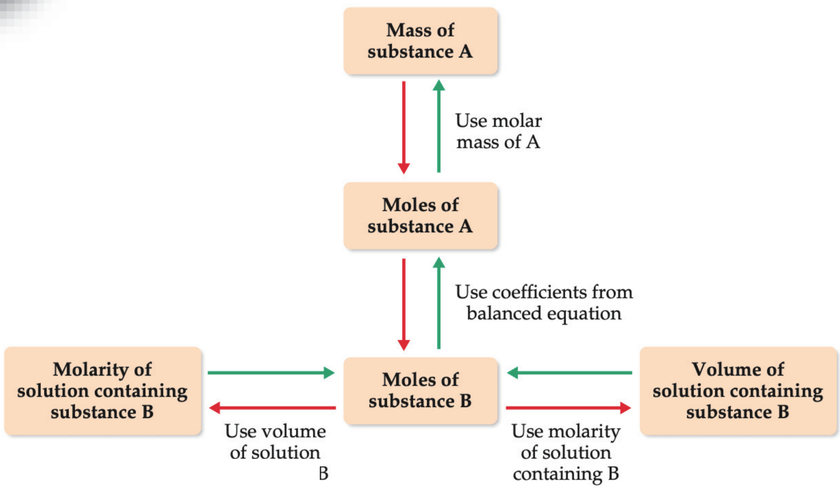
1 Draw 25.0 mL of 1.00 *M* stock solution into pipette.

2 Add concentrated solution in pipette to 250-mL volumetric flask.

3 Dilute with water until solution reaches calibration mark on neck of flask and mix to create 0.100 *M* solution.

Preparing 250.0 mL of 0.100 *M* $CuSO_4$ by dilution of 1.00 *M* $CuSO_4$.

2.3.4 Solution Stoichiometry and Chemical Analysis



Mass of substance A

Use molar mass of A

Moles of substance A

Use coefficients from balanced equation

Molarity of solution containing substance B

Use volume of solution B

Moles of substance B

Use molarity of solution containing B

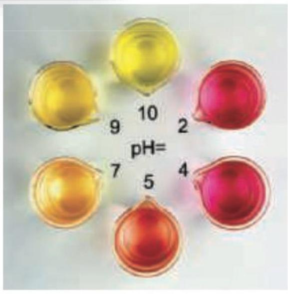
Volume of solution containing substance B

2.3 Summary & Practice

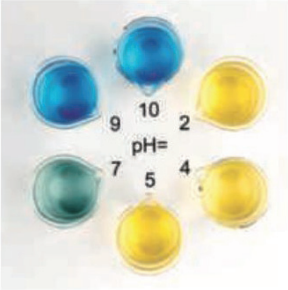
1. Concept

2. Example

2.4 Acid & Base



Methyl red



Bromthymol blue

Phenolphthalein

2.4.1 Arrhenius Acids and Bases

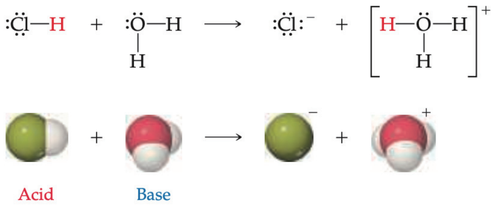
- An *acid* is a substance that, when dissolved in water, increases the concentration of H^+ ions.
- A *base* is a substance that, when dissolved in water, increases the concentration of OH^- ions.

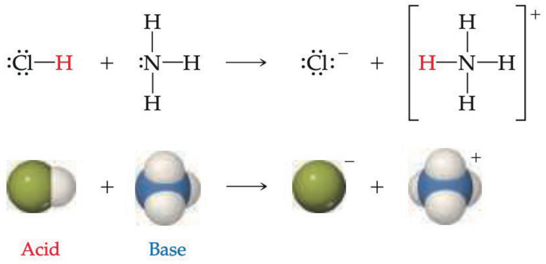
$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq)$$

2.4.2 Brønsted–Lowry Acids and Bases

- **Brønsted–Lowry acid** An *acid* is a substance (molecule or ion) that *donates* a proton to another substance.
- **Brønsted–Lowry base** A *base* is a substance that *accepts* a proton.

$$HCl(g) + H_2O(l) \longrightarrow Cl^-(aq) + H_3O^+(aq)$$





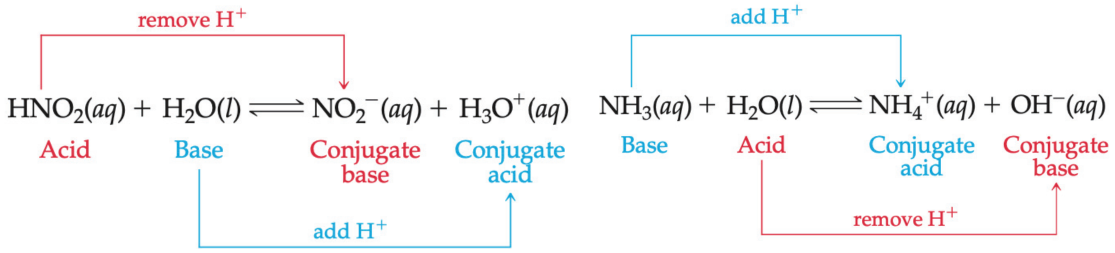
The transfer of a proton always involves both an acid (donor) and a base (acceptor).

2.4.2

Brønsted–Lowry Acids and Bases

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

An acid and a base such as HA and A⁻ that differ only in the presence or absence of a proton are called a **conjugate acid–base pair**



remove H^+

$HNO_2(aq) + H_2O(l) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$

Acid Base Conjugate base Conjugate acid

add H^+

add H^+

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

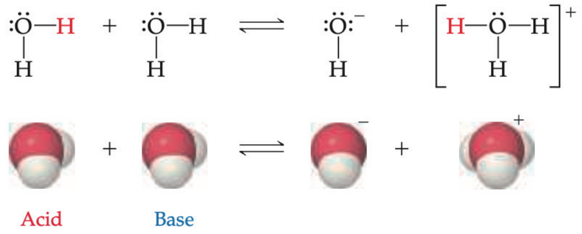
Base Acid Conjugate acid Conjugate base

remove H^+

2.4.3

The Autoionization of Water

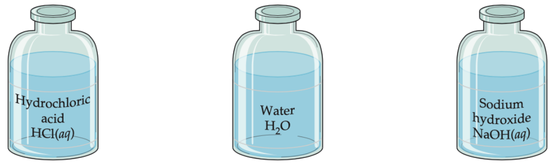
$$H_2O(l) + H_2O(l) \rightleftharpoons OH^-(aq) + H_3O^+(aq)$$



$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \quad \text{(at 25 °C)}$$

2.4.4

Acidic or Basic



Acidic solution
$[H^+] > [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

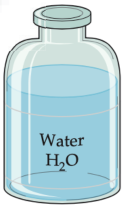
Neutral solution
$[H^+] = [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

Basic solution
$[H^+] < [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

A substance capable of acting as either an acid or a base is called **amphiprotic**

2.4.5

The pH Scale



Neutral solution
$[H^+] = [OH^-]$
$[H^+][OH^-] = 1.0 \times 10^{-14}$

$$pH = -\log[H^+]$$

$$pH = -\log(1.0 \times 10^{-7}) = -(-7.00) = 7.00$$

	Acidic	Neutral	Basic
pH	<7.00	7.00	>7.00
$[H^+](M)$	$>1.0 \times 10^{-7}$	1.0×10^{-7}	$<1.0 \times 10^{-7}$
$[OH^-](M)$	$<1.0 \times 10^{-7}$	1.0×10^{-7}	$>1.0 \times 10^{-7}$

2.4.6

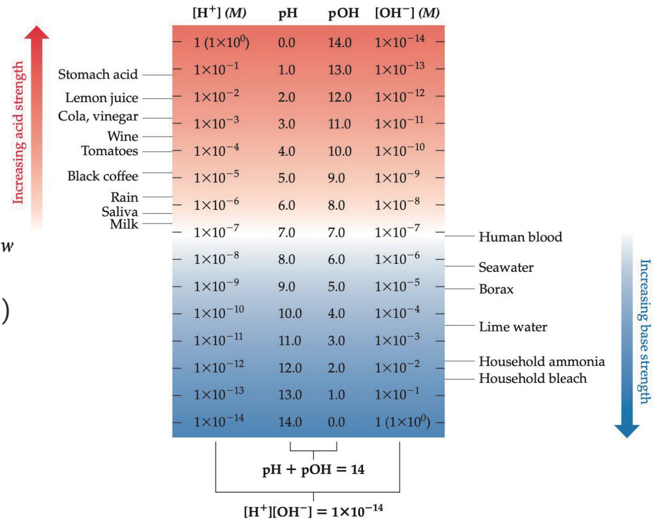
pOH and Other "p" Scales

$$pOH = -\log[OH^-]$$

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

$$-\log[H^+] + (-\log[OH^-]) = -\log K_w$$

$$pH + pOH = 14.00 \quad (\text{at } 25\,°C)$$



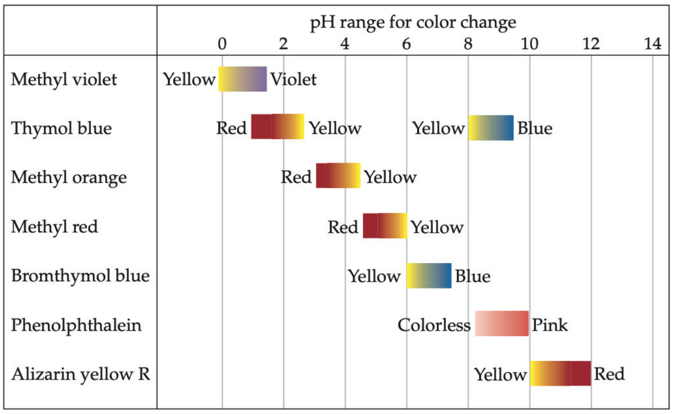
$[H^+]$ (*M*)	pH	pOH	$[OH^-]$ (*M*)
$1\ (1\times10^{0})$	0.0	14.0	1×10^{-14}
1×10^{-1}	1.0	13.0	1×10^{-13}
1×10^{-2}	2.0	12.0	1×10^{-12}
1×10^{-3}	3.0	11.0	1×10^{-11}
1×10^{-4}	4.0	10.0	1×10^{-10}
1×10^{-5}	5.0	9.0	1×10^{-9}
1×10^{-6}	6.0	8.0	1×10^{-8}
1×10^{-7}	7.0	7.0	1×10^{-7}
1×10^{-8}	8.0	6.0	1×10^{-6}
1×10^{-9}	9.0	5.0	1×10^{-5}
1×10^{-10}	10.0	4.0	1×10^{-4}
1×10^{-11}	11.0	3.0	1×10^{-3}
1×10^{-12}	12.0	2.0	1×10^{-2}
1×10^{-13}	13.0	1.0	1×10^{-1}
1×10^{-14}	14.0	0.0	$1\ (1\times10^{0})$

2.4.7

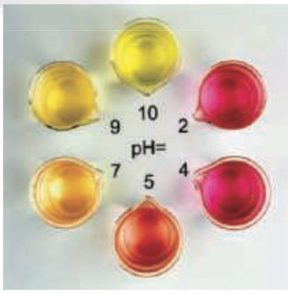
Measuring pH

A digital pH meter

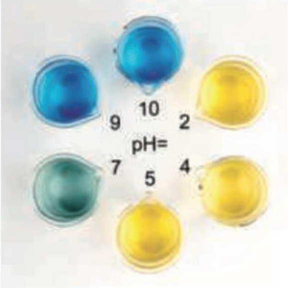
pH ranges for common acid–base indicators



2.4.7 Measuring pH



Methyl red



Bromthymol blue

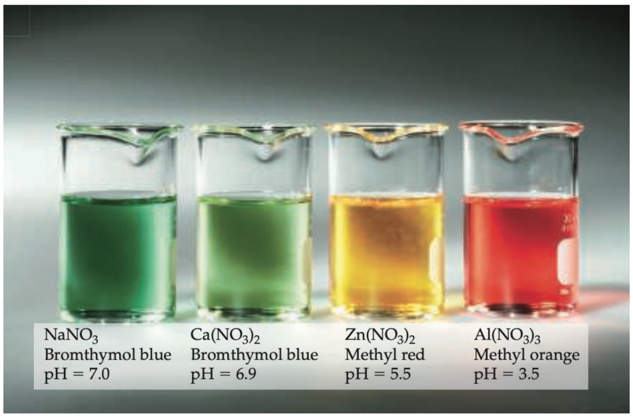
Phenolphthalein

2.4 Summary & Practice

1. Concept

2. Example

2.5 Weak Acid & Base



$NaNO_3$
Bromthymol blue
pH = 7.0

$Ca(NO_3)_2$
Bromthymol blue
pH = 6.9

$Zn(NO_3)_2$
Methyl red
pH = 5.5

$Al(NO_3)_3$
Methyl orange
pH = 3.5

2.5.1

Strong Acids and Bases

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq) \quad \text{(complete ionization)}$$

The seven most common strong acids include six monoprotic acids HCl, HBr, HI, HNO_3, $HClO_3$, and $HClO_4$, and one diprotic acid (H_2SO_4). Nitric acid (HNO_3) exemplifies the behavior of the monoprotic strong acids

Strong base:The most common soluble strong bases are the ionic hydroxides of the alkali metals, such as NaOH, KOH, and the ionic hydroxides of heavier alkaline earth metals, such as $Sr(OH)_2$.

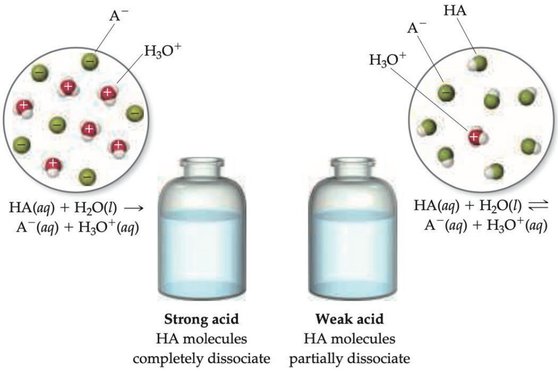
2.5.2

Weak Acids

Most acidic substances are weak acids and therefore only partially ionized in aqueous solution.

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

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



2.5.2

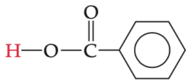
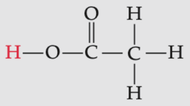
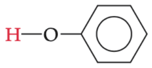
Weak Acids

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

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

Ka is called the **acid-dissociation constant** for acid HA

Some Weak Acids in Water at 25 °C

Acid	Structural Formula*	Conjugate Base	K_a
Chlorous ($HClO_2$)	H—O—Cl—O	ClO_2^-	1.0×10^{-2}
Hydrofluoric (HF)	H—F	F^-	6.8×10^{-4}
Nitrous (HNO_2)	H—O—N=O	NO_2^-	4.5×10^{-4}
Benzoic (C_6H_5COOH)		$C_6H_5COO^-$	6.3×10^{-5}
Acetic (CH_3COOH)		CH_3COO^-	1.8×10^{-5}
Hypochlorous (HOCl)	H—O—Cl	OCl^-	3.0×10^{-8}
Hydrocyanic (HCN)	H—C≡N	CN^-	4.9×10^{-10}
Phenol (HOC_6H_5)		$C_6H_5O^-$	1.3×10^{-10}

Conjugate Acid–Base Pairs Arranged by Strength

pK_a	Acid name	Acid formula	Base formula	Base name	pK_b
	Strong acid			*Very weak base*	
	hydroiodic acid	HI	I^-	iodide ion	
	perchloric acid	$HClO_4$	ClO_4^-	perchlorate ion	
	hydrobromic acid	HBr	Br^-	bromide ion	
	hydrochloric acid	HCl	Cl^-	chloride ion	
	sulfuric acid	H_2SO_4	HSO_4^-	hydrogen sulfate ion	
	chloric acid	$HClO_3$	ClO_3^-	chlorate ion	
	nitric acid	HNO_3	NO_3^-	nitrate ion	
	hydronium ion	H_3O^+	H_2O	*water*	
1.92	hydrogen sulfate ion	HSO_4^-	SO_4^{2-}	sulfate ion	12.08
3.37	nitrous acid	HNO_2	NO_2^-	nitrite ion	10.63
3.45	hydrofluoric acid	HF	F^-	fluoride ion	10.55
4.75	acetic acid	CH_3COOH	$CH_3CO_2^-$	acetate ion	9.25
6.37	carbonic acid	H_2CO_3	HCO_3^-	hydrogen carbonate ion	7.63
6.89	hydrosulfuric acid	H_2S	HS^-	hydrogen sulfide ion	7.11
9.25	ammonium ion	NH_4^+	NH_3	ammonia	4.75
9.31	hydrocyanic acid	HCN	CN^-	cyanide ion	4.69
10.25	hydrogen carbonate ion	HCO_3^-	CO_3^{2-}	carbonate ion	3.75
	methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	methylamine	3.44
	water	H_2O	OH^-	*hydroxide ion*	
	ammonia	NH_3	NH_2^-	amide ion	
	hydrogen	H_2	H^-	hydride ion	
	methane	CH_4	CH_3^-	methide ion	
	hydroxide ion	OH^-	O^{2-}	oxide ion	
	Very weak acid			*Strong base*	

2.5.3 Calculating Ka from pH

$$HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

$$pH = -\log[H^+] = 2.38$$
$$\log[H^+] = -2.38$$
$$[H^+] = 10^{-2.38} = 4.2 \times 10^{-3}\,M$$

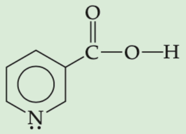
$$(0.10 - 4.2 \times 10^{-3})\,M \simeq 0.10\,M$$

$$K_a = \frac{(4.2 \times 10^{-3})(4.2 \times 10^{-3})}{0.10} = 1.8 \times 10^{-4}$$

	$HCOOH(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$HCOO^-(aq)$
Initial concentration (M)	0.10	0	0
Change in concentration (M)	-4.2×10^{-3}	$+4.2 \times 10^{-3}$	$+4.2 \times 10^{-3}$
Equilibrium concentration (M)	$(0.10 - 4.2 \times 10^{-3})$	4.2×10^{-3}	4.2×10^{-3}

Practice

Niacin, one of the B vitamins, has the molecular structure shown at the right. A 0.020 M solution of niacin has a pH of 3.26. What is the acid-dissociation constant for niacin?



2.5.4 Calculating from pH from Ka

calculate the pH at 25 °C of a 0.30 M solution of acetic acid

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq) \qquad K_a = 1.8 \times 10^{-5}$$

	$CH_3COOH(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$CH_3COO^-(aq)$
Initial concentration (M)	0.30	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$(0.30 - x)$	x	x

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5}$$

$$K_a = \frac{x^2}{0.30} = 1.8 \times 10^{-5}$$

$$x^2 = (0.30)(1.8 \times 10^{-5}) = 5.4 \times 10^{-6}$$
$$x = \sqrt{5.4 \times 10^{-6}} = 2.3 \times 10^{-3}$$
$$[H^+] = x = 2.3 \times 10^{-3}\,M$$
$$pH = -\log(2.3 \times 10^{-3}) = 2.64$$

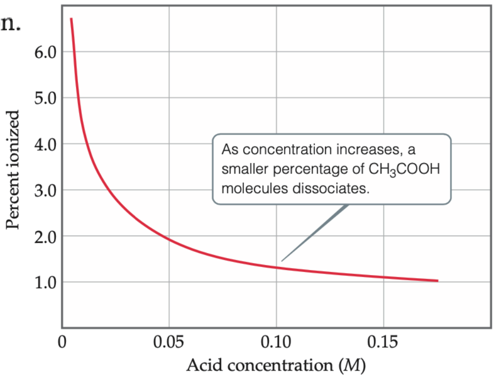
2.5.5

Percent Ionization

$$\text{Percent ionization} = \frac{\text{concentration of ionized HA}}{\text{original concentration of HA}} \times 100\%$$

The stronger the acid, the greater the percent ionization.

$$\text{Percent ionization} = \frac{[H^+]_{\text{equilibrium}}}{[HA]_{\text{initial}}} \times 100\%$$



As concentration increases, a smaller percentage of CH_3COOH molecules dissociates.

2.5.6

Weak Bases

$$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$$

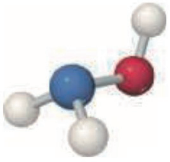
$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

K_b, the **base-dissociation constant**, *always refers to the equilibrium in which a base reacts with H_2O to form the corresponding conjugate acid and OH^-.*

Ammonia
NH_3

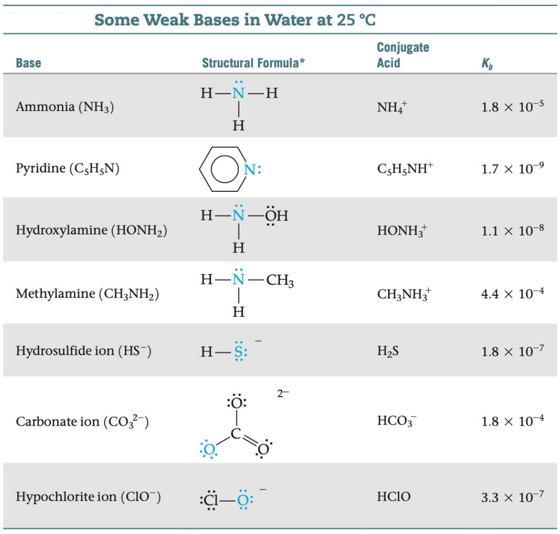
Methylamine
CH_3NH_2



Hydroxylamine
NH_2OH

2.5.6

Weak Bases



Some Weak Bases in Water at 25 °C

Base	Structural Formula*	Conjugate Acid	K_b
Ammonia (NH_3)	$\begin{array}{c}\mathrm{H-\ddot{N}-H}\\ \vert\\ \mathrm{H}\end{array}$	NH_4^+	1.8×10^{-5}
Pyridine (C_5H_5N)	N:	$C_5H_5NH^+$	1.7×10^{-9}
Hydroxylamine ($HONH_2$)	$\begin{array}{c}\mathrm{H-\ddot{N}-\ddot{\underset{..}{O}}H}\\ \vert\\ \mathrm{H}\end{array}$	$HONH_3^+$	1.1×10^{-8}
Methylamine (CH_3NH_2)	$\begin{array}{c}\mathrm{H-\ddot{N}-CH_3}\\ \vert\\ \mathrm{H}\end{array}$	$CH_3NH_3^+$	4.4×10^{-4}
Hydrosulfide ion (HS^-)	$\mathrm{H-\ddot{\underset{..}{S}}:}^{-}$	H_2S	1.8×10^{-7}
Carbonate ion (CO_3^{2-})	:Ö: C O O $^{2-}$	HCO_3^-	1.8×10^{-4}
Hypochlorite ion (ClO^-)	$\mathrm{:\ddot{\underset{..}{Cl}}-\ddot{\underset{..}{O}}:}^{-}$	HClO	3.3×10^{-7}

2.5.7

Relationship Between K_a and K_b

$$\begin{array}{rcl} NH_4^+(aq) & \rightleftharpoons & NH_3(aq) + H^+(aq) \\ NH_3(aq) + H_2O(l) & \rightleftharpoons & NH_4^+(aq) + OH^-(aq) \\ \hline H_2O(l) & \rightleftharpoons & H^+(aq) + OH^-(aq) \end{array}$$

$$K_a = \frac{[NH_3][H^+]}{[NH_4^+]} \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_a \times K_b = \left(\frac{[\cancel{NH_3}][H^+]}{[\cancel{NH_4^+}]}\right)\left(\frac{[\cancel{NH_4^+}][OH^-]}{[\cancel{NH_3}]}\right)$$

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

$$K_a \times K_b = K_w \quad \text{(for a conjugate acid–base pair)}$$

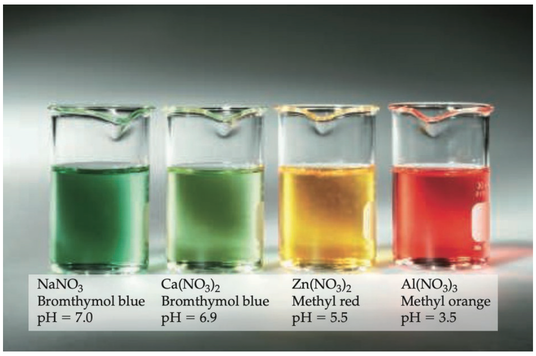
Acid	K_a	**Base**	K_b
HNO_3	(Strong acid)	NO_3^-	(Negligible basicity)
HF	6.8×10^{-4}	F^-	1.5×10^{-11}
CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
H_2CO_3	4.3×10^{-7}	HCO_3^-	2.3×10^{-8}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCO_3^-	5.6×10^{-11}	CO_3^{2-}	1.8×10^{-4}

2.5.8

Hydrolysis of Salts

Many ions react with water to generate $H^+(aq)$ or $OH^-(aq)$ ions. This type of reaction is often called **hydrolysis**. The pH of an aqueous salt solution can be predicted qualitatively by considering the salt's cations and anions.

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$



2.5.9

Structure and Acid Strength

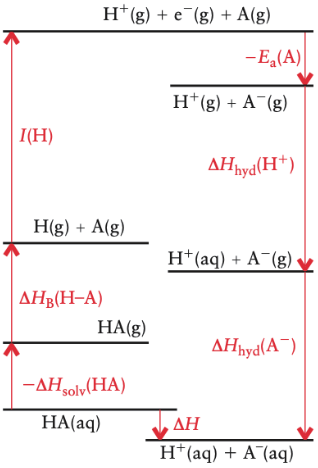
Step	**Reaction**	**Enthalpy change**
Removal of HA from solution:	$HA(aq) \rightarrow HA(g)$	$-\Delta H_{solv}(HA)$
Dissociation of gaseous HA:	$HA(g) \rightarrow H(g) + A(g)$	$\Delta H_B(H{-}A)$
Ionization of H:	$H(g) \rightarrow H^+(g) + e^-(g)$	$I(H)$
Electron attachment to A:	$A(g) + e^-(g) \rightarrow A^-(g)$	$-E_a(A)$
Hydration of H^+:	$H^+(g) + H_2O(l) \rightarrow H_3O^+(aq)$	$\Delta H_{hyd}(H^+)$
Hydration of A^-:	$A^-(g) \rightarrow A^-(aq)$	$\Delta H_{hyd}(A^-)$

The enthalpy change for the overall process $HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)$ is therefore

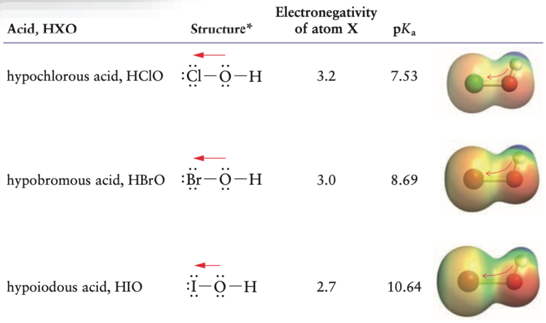
$$\Delta H = -\Delta H_{solv}(HA) + \Delta H_B(H{-}A) + I(H) - E_a(A) + \Delta H_{hyd}(H^+) + \Delta H_{hyd}(A^-)$$

	HF	HCl	HBr	HI
ΔH (kJ·mol^{-1})	−15	−41	−51	−43

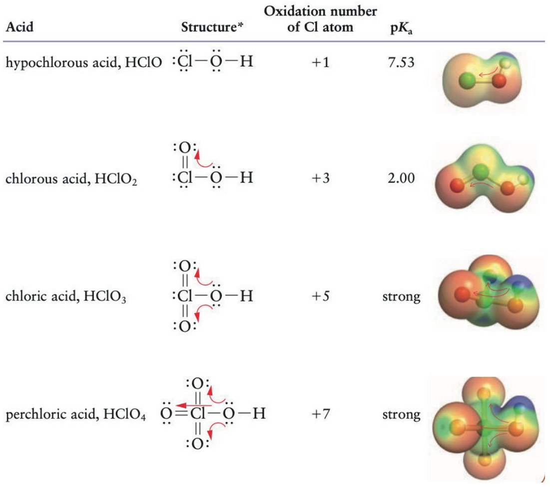
Acid strengths of binary acids across a period correlate with electron affinities; acid strengths down a group correlate with bond strength.



2.5.10 Strengths of Oxoacids and Carboxylic Acids

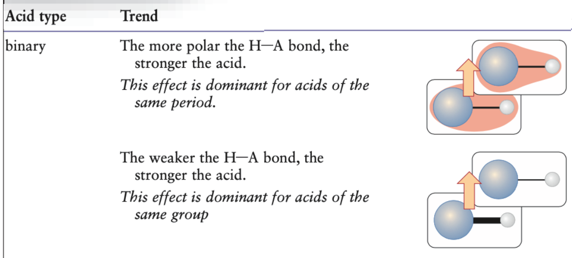


Acid, HXO	Structure*	Electronegativity of atom X	pK_a
hypochlorous acid, HClO	:Cl—O—H	3.2	7.53
hypobromous acid, HBrO	:Br—O—H	3.0	8.69
hypoiodous acid, HIO	:I—O—H	2.7	10.64

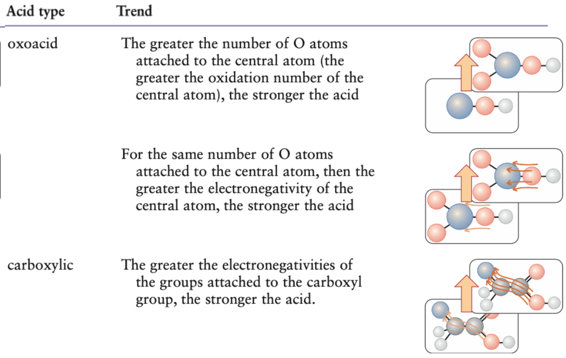


Acid	Structure*	Oxidation number of Cl atom	pK_a
hypochlorous acid, HClO	:Cl—O—H	+1	7.53
chlorous acid, $HClO_2$	:O: ‖ :Cl—O—H	+3	2.00
chloric acid, $HClO_3$	:O: ‖ :Cl—O—H ‖ :O:	+5	strong
perchloric acid, $HClO_4$	:O: ‖ O=Cl—O—H ‖ :O:	+7	strong

2.5.10 Strengths of Oxoacids and Carboxylic Acids



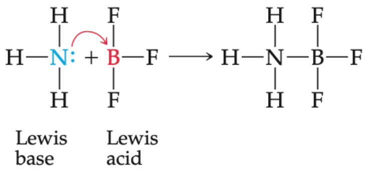
Acid type	Trend
binary	The more polar the H—A bond, the stronger the acid. *This effect is dominant for acids of the same period.*
	The weaker the H—A bond, the stronger the acid. *This effect is dominant for acids of the same group*



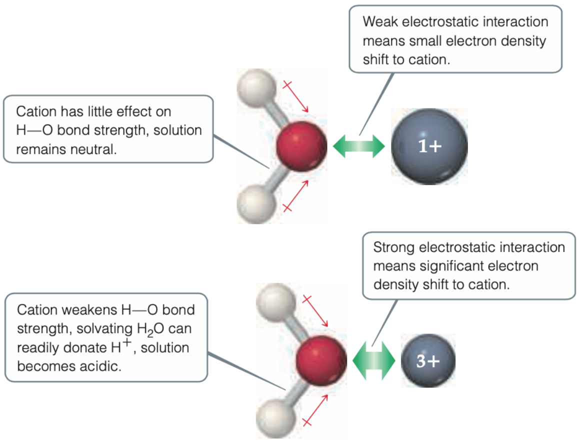
Acid type	Trend
oxoacid	The greater the number of O atoms attached to the central atom (the greater the oxidation number of the central atom), the stronger the acid
	For the same number of O atoms attached to the central atom, then the greater the electronegativity of the central atom, the stronger the acid
carboxylic	The greater the electronegativities of the groups attached to the carboxyl group, the stronger the acid.

2.5.11 Lewis Acids and Bases

- A **Lewis acid** is an electron-pair acceptor.
- A **Lewis base** is an electron-pair donor.



$$H_3N: + BF_3 \longrightarrow H_3N\text{—}BF_3$$



Weak electrostatic interaction means small electron density shift to cation.

Cation has little effect on H—O bond strength, solution remains neutral.

Strong electrostatic interaction means significant electron density shift to cation.

Cation weakens H—O bond strength, solvating H_2O can readily donate H^+, solution becomes acidic.

2.5

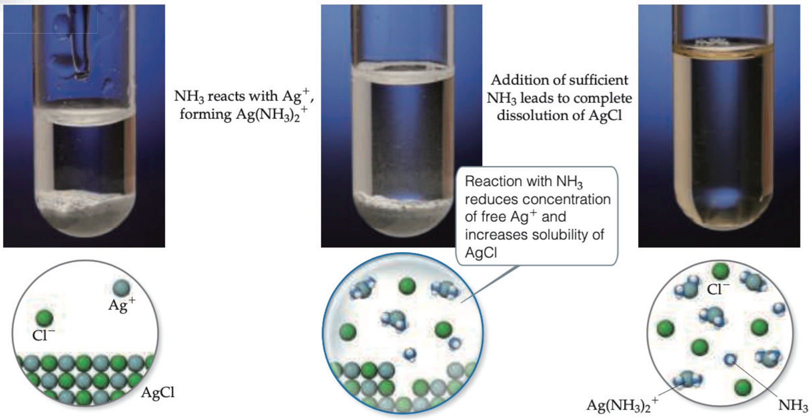
Summary & Practice

1. Concept

2. Example

2.6

Aqueous Equilibria



2.6.1

The Common-Ion Effect

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

Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[H^+]$

Common-Ion Effect:

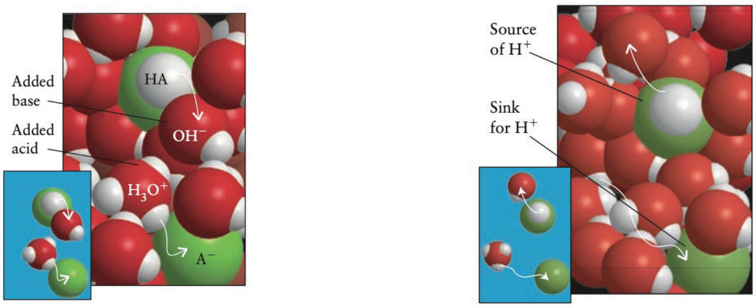
Whenever a weak electrolyte and a strong electrolyte containing a common ion are together in solution, the weak electrolyte ionizes less than it would if it were alone in solution.

2.6.2

Buffers

Buffer, a solution in which the pH resists change when small amounts of strong acids or bases are added

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$



A buffer is a mixture of a weak conjugate acid–base pair that stabilizes the pH of a solution by providing both a source and a sink for protons

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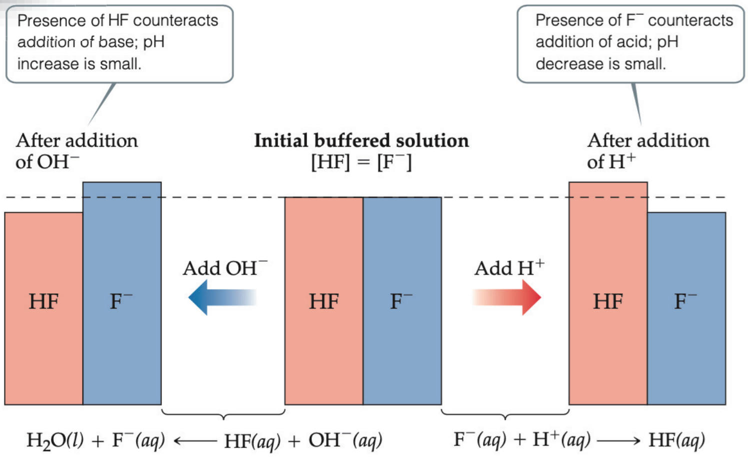
2.6.2

Buffers



Presence of HF counteracts addition of base; pH increase is small.

Presence of F^- counteracts addition of acid; pH decrease is small.

After addition of OH^-

Initial buffered solution
$[HF] = [F^-]$

After addition of H^+

$$H_2O(l) + F^-(aq) \longleftarrow HF(aq) + OH^-(aq)$$

$$F^-(aq) + H^+(aq) \longrightarrow HF(aq)$$

2.6.2

Composition and Action of Buffers

- Mix a weak acid or a weak base with a salt of that acid or base. For example, the CH_3COOH/CH_3COO^- buffer can be prepared by adding CH_3COONa to a solution of CH_3COOH. Similarly, the NH_4^+/NH_3 buffer can be prepared by adding NH_4Cl to a solution of NH_3.
- Make the conjugate acid or base from a solution of weak base or acid by the addition of a strong acid or base. For example, to make the CH_3COOH/CH_3COO^- buffer, you could start with a solution of CH_3COOH and add some NaOH to the solution—enough to neutralize about half of CH_3COOH according to the reaction

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

2.6.3 Calculating the pH of a Buffer

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

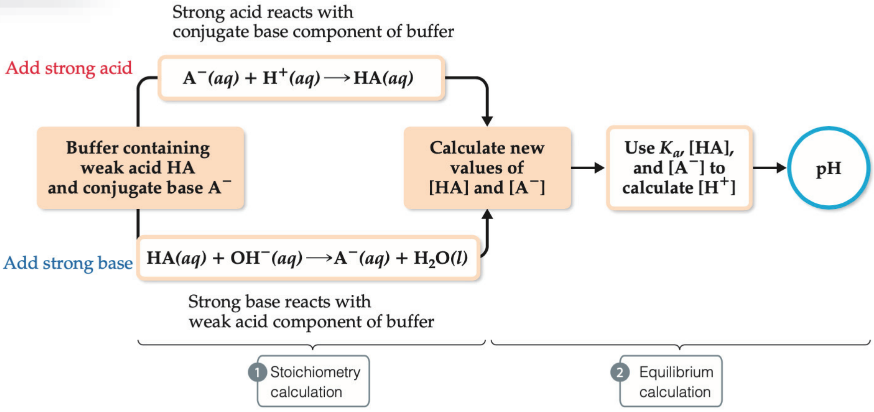
$$[H^+] = K_a\frac{[HA]}{[A^-]}$$

$$pH = pK_a - \log\frac{[HA]}{[A^-]} = pK_a + \log\frac{[A^-]}{[HA]}$$

when [base] = [acid]

$$pH = pK_a$$

2.6.4 Addition of Strong Acids or Bases to Buffers



Strong acid reacts with conjugate base component of buffer

Add strong acid

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

Buffer containing weak acid HA and conjugate base A^-

Calculate new values of [HA] and [A^-]

Use K_a, [HA], and [A^-] to calculate [H^+]

pH

Add strong base

$HA(aq) + OH^-(aq) \longrightarrow A^-(aq) + H_2O(l)$

Strong base reacts with weak acid component of buffer

① Stoichiometry calculation

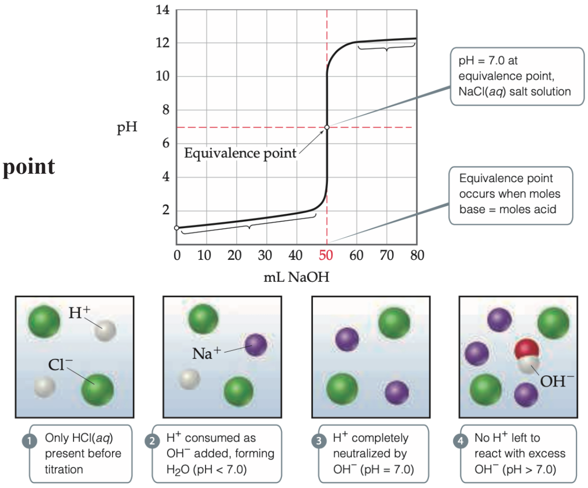
② Equilibrium calculation

2.6.5 Acid-Base Titrations

- to determine the concentration of one of the reactants
- to determine the equilibrium constant for the reaction

Strong Acid–Strong Base Titrations

1. Initial pH
2. Between initial pH and equivalence point
3. Equivalence point
4. After equivalence point



pH = 7.0 at equivalence point, NaCl(*aq*) salt solution

Equivalence point occurs when moles base = moles acid

① Only HCl(*aq*) present before titration

② H^+ consumed as OH^- added, forming H_2O (pH < 7.0)

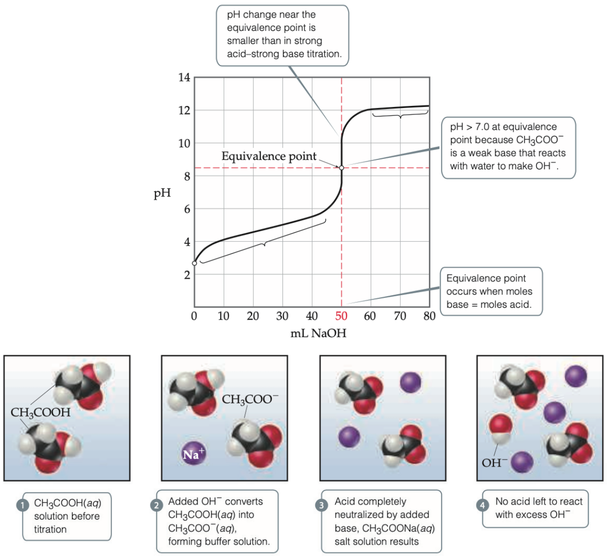
③ H^+ completely neutralized by OH^- (pH = 7.0)

④ No H^+ left to react with excess OH^- (pH > 7.0)

2.6.5 Acid-Base Titrations

Weak Acid–Strong Base Titrations

1. Initial pH
2. Between initial pH and equivalence point
3. Equivalence point
4. After equivalence point



pH change near the equivalence point is smaller than in strong acid–strong base titration.

pH > 7.0 at equivalence point because CH_3COO^- is a weak base that reacts with water to make OH^-.

Equivalence point occurs when moles base = moles acid.

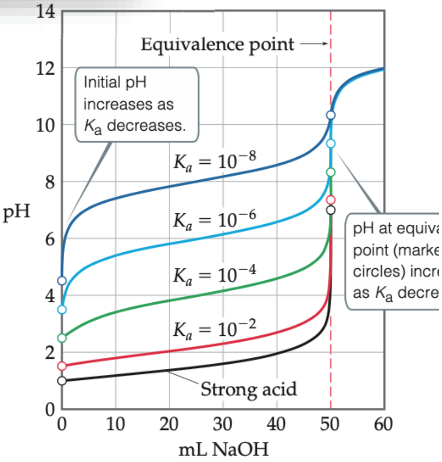
① $CH_3COOH(aq)$ solution before titration

② Added OH^- converts $CH_3COOH(aq)$ into $CH_3COO^-(aq)$, forming buffer solution.

③ Acid completely neutralized by added base, $CH_3COONa(aq)$ salt solution results

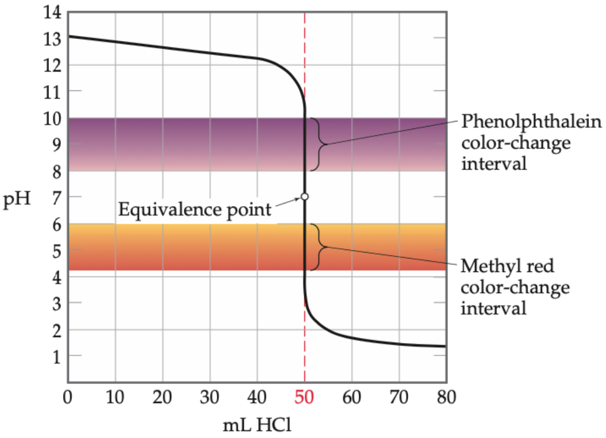
④ No acid left to react with excess OH^-

2.6.6 Acid–Base Indicator

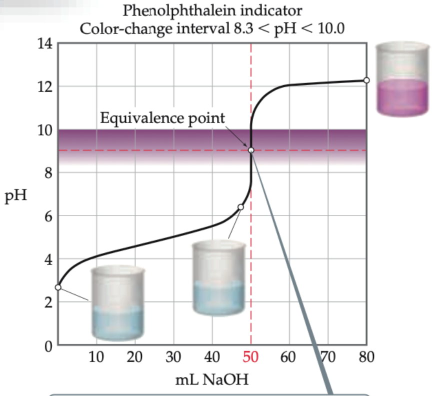


Initial pH increases as K_a decreases.

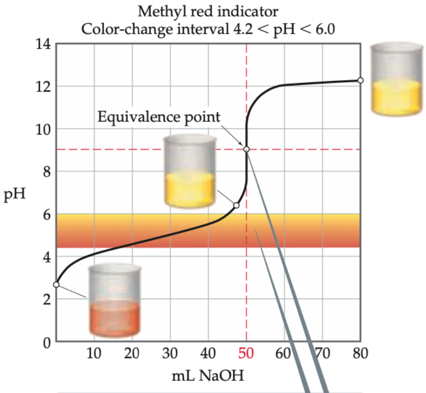
pH at equiva
point (marke
circles) incr
as K_a decre



2.6.6 Acid–Base Indicator



Good choice. Suitable indicator for titration of a weak acid with a strong base because equivalence point falls within the color-change interval



Poor choice. Unsatisfactory indicator for titration of a weak acid with a strong base because color changes before reaching equivalence point

2.6

Summary & Practice

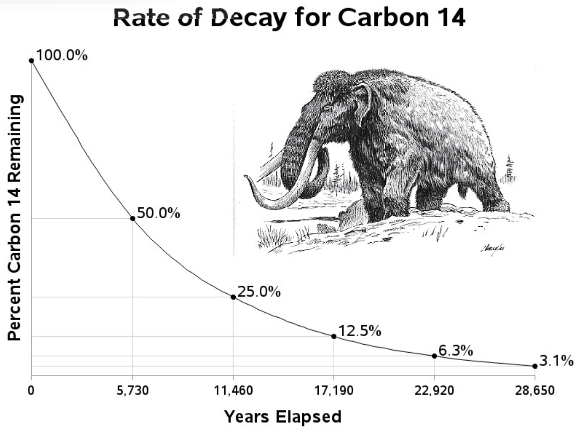
1. Concept

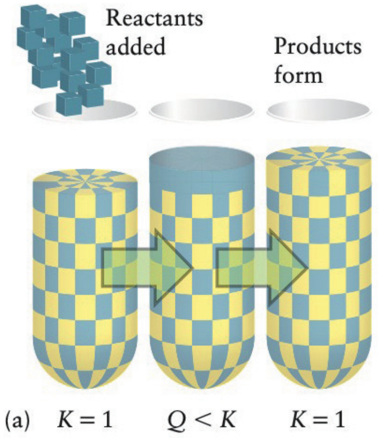
2. Example

UKChO

英国化学奥林匹克竞赛

Unit 3 Rate and Equilibrium





Unit 3 Rate and Equilibrium

1.Reaction Rates

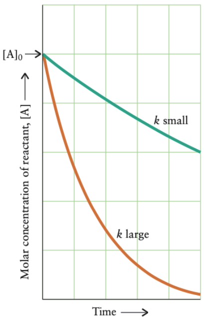
2.Reaction Mechanism

3.Factors That Affect Reaction Rates

4.Equilibrium

5.Equilibrium shift

3.1 Reaction Rates



3.1.1 Reaction Rate

Reaction rate is defined as the change in concentration of one of the reactants or products divided by the time interval over which the change takes place.

$$\text{Average rate of consumption of R} = -\frac{\Delta[\mathrm{R}]}{\Delta t}$$

$$\text{Average rate of formation of P} = \frac{\Delta[\mathrm{P}]}{\Delta t}$$

Because the rate may change as time passes, we denote the **average reaction rate** in a particular interval as the change in molar concentration of a reactant R, $\Delta[R]=[R]t_2—[R]t_1$, divided by the time interval $\Delta t=t_2—t_1$

3.1.2 Unique Average Reaction Rate

$$a\,\mathrm{A} + b\,\mathrm{B} \rightarrow c\,\mathrm{C} + d\,\mathrm{D}$$

$$\text{Unique average reaction rate} = -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t}$$

3.1.3 Change of Rate with Time

$$C_4H_9Cl(aq) + H_2O(l) \longrightarrow C_4H_9OH(aq) + HCl(aq)$$

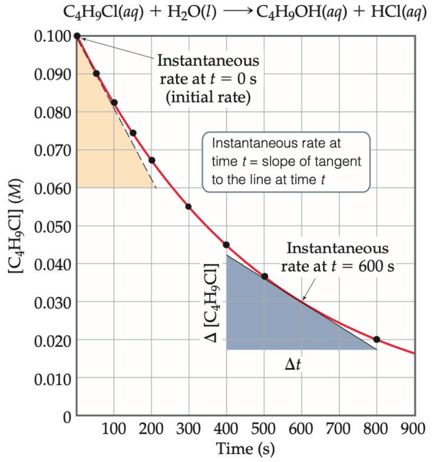
TABLE 14.1 Rate Data for Reaction of C_4H_9Cl with Water

Time, t (s)	$[C_4H_9Cl]$ (M)	Average Rate (M/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

3.1.4 Instantaneous Rate

The rate at a particular instant during the reaction. The instantaneous rate is determined from the slope of the curve at a particular point in time.

Does the instantaneous rate increase, decrease, or remain the same as the reaction proceeds?



3.1.5 Rate Law

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2\,H_2O(l)$$

Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C

Experiment Number	Initial NH_4^+ Concentration (M)	Initial NO_2^- Concentration (M)	Observed Initial Rate (M/s)
1	0.0100	0.200	5.4×10^{-7}
2	0.0200	0.200	10.8×10^{-7}
3	0.0400	0.200	21.5×10^{-7}
4	0.200	0.0202	10.8×10^{-7}
5	0.200	0.0404	21.6×10^{-7}
6	0.200	0.0808	43.3×10^{-7}

3.1.5 Rate Law

$$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$$

$$\text{Rate} = k[NH_4^+][NO_2^-]$$

An equation such as Equation, which shows how the rate depends on reactant concentrations, is called a **rate law**

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = k[A]^m[B]^n$$

The constant k is called the **rate constant.**

3.1.6 Reaction Order

The rate law for most reactions has the form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \ldots$$

The exponents m and n are called **reaction orders**.

The **overall reaction order** is the sum of the orders with respect to each reactant represented in the rate law.

For any reaction, the rate law must be determined experimentally.

3.1.7 Using Initial Rates to Determine Rate Laws

The initial rate of a reaction A + B $\longrightarrow$ C was measured for three different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A](*M*)	[B](*M*)	Initial Rate (*M*/s)
1	0.100	0.100	4.0×10^{-5}
2	0.100	0.200	4.0×10^{-5}
3	0.200	0.100	16.0×10^{-5}

Using these data, determine (**a**) the rate law for the reaction, (**b**) the rate constant, (**c**) the rate of the reaction when $[A] = 0.050\,M$ and $[B] = 0.100\,M$.

3.1.8

Magnitudes and Units of Rate Constants

The units of the rate constant depend on the overall reaction order of the rate law. In a reaction that is second order overall, for example, the units of the rate constant must satisfy the equation:

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})^2$$

Hence, in our usual units of molarity for concentration and seconds for time, we have

$$\text{Units of rate constant} = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{\cancel{M}/\text{s}}{M^{\cancel{2}}} = M^{-1}\,\text{s}^{-1}$$

What are the units of the rate constant for the following rate law

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g) \qquad \text{Rate} = k[N_2O_5]$$

$$H_2(g) + I_2(g) \longrightarrow 2\,HI(g) \qquad \text{Rate} = k[H_2][I_2]$$

$$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g) \qquad \text{Rate} = k[CHCl_3][Cl_2]^{1/2}$$

3.1.9

First-Order Reaction

A **first-order reaction** is one whose rate depends on the concentration of a single reactant raised to the first power. If a reaction of the type A ⟶ products is first order, the rate law is:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$$

$$\ln[A]_t - \ln[A]_0 = -kt \quad \text{or} \quad \ln\frac{[A]_t}{[A]_0} = -kt$$

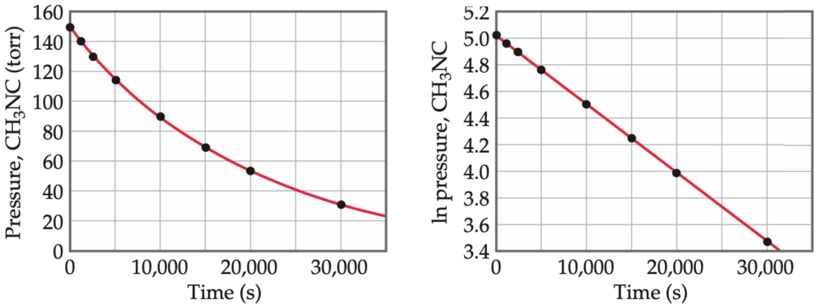
$$\ln[A]_t = -kt + \ln[A]_0$$

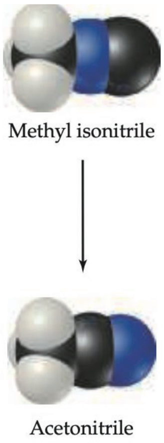
3.1.9

First-Order Reaction

$$\begin{tikzcd} \ln[A]_t = \arrow[d, leftrightarrow] & -kt \arrow[d, leftrightarrow] & + \ln[A]_0 \arrow[d, leftrightarrow] \\ y = & mx & + b \end{tikzcd}$$

$$\ln[CH_3NC]_t = -kt + \ln[CH_3NC]_0$$





3.1.10

Second-Order Reaction

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

$$\frac{1}{[\text{A}]_t} = kt + \frac{1}{[\text{A}]_0}$$

The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300 °C, $NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$. Is the reaction first or second order in NO_2?

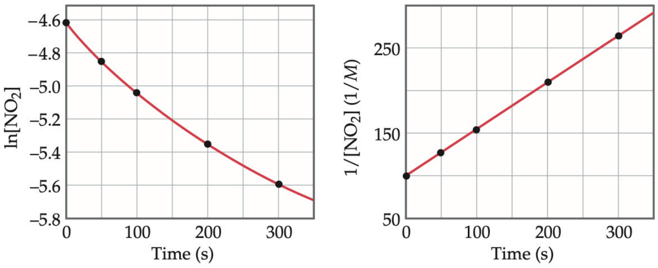
Time (s)	$[NO_2]$ (*M*)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

3.1.10

Second-Order Reaction

$NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$

Time (s)	$[NO_2]$ (*M*)	$\ln[NO_2]$	$1/[NO_2]$ (1/*M*)
0.0	0.01000	−4.605	100
50.0	0.00787	−4.845	127
100.0	0.00649	−5.037	154
200.0	0.00481	−5.337	208
300.0	0.00380	−5.573	263

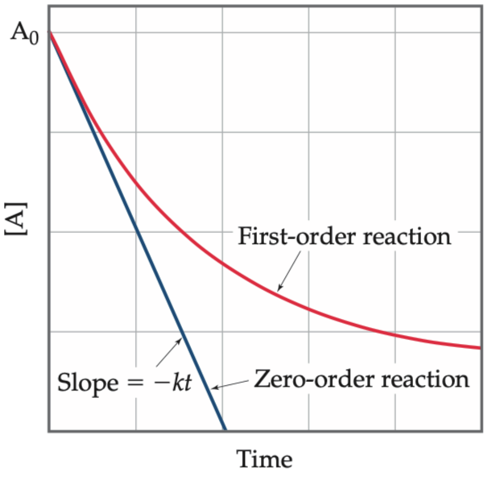


3.1.11

Zero-Order Reaction

$$\text{Rate} = \frac{-\Delta[\text{A}]}{\Delta t} = k$$

$$[\text{A}]_t = -kt + [\text{A}]_0$$



3.1.12 Half-Life

The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to reach half its initial value, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$. Half-life is a convenient way to describe how fast a reaction occurs, especially if it is a first-order process. A fast reaction has a short half-life.

3.1.12 Half-Life

When $[A]_t = \frac{[A]_0}{2}$ ↓

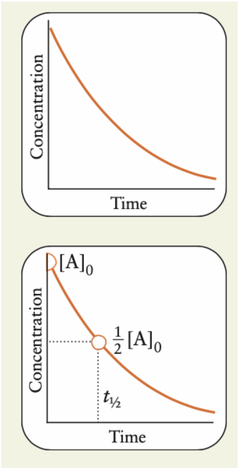
$$\ln [A]_t = \ln [A]_0 - kt$$

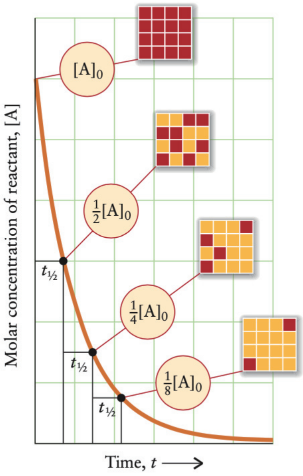
$$\ln \frac{[A]_0}{2} = \ln [A]_0 - kt_{1/2}$$

$$\ln [A]_0 - \ln 2 = \ln [A]_0 - kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

3.1.12 Half-Life



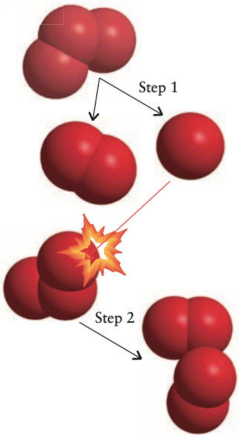


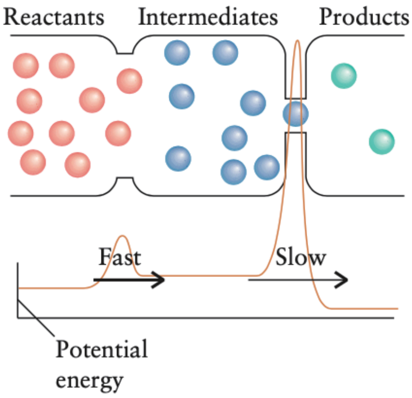
3.1 Summary & Practice

1. Concept

2. Example

3.2 Reaction Mechanism





3.2.1 Elementary Reaction

The reason is that all but the simplest reactions are the outcome of several, and sometimes many, steps called **elementary reactions.** Each elementary reaction describes a distinct event, often a collision of particles.
To describe how a reaction takes place, chemists propose a **reaction mechanism,** a sequence of elementary reactions or steps.

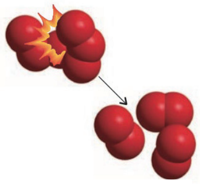
One-step mechanism: Two O_3 molecules collide and rearrange into three O_2 molecules (**FIG. 15.16**):

$$+ O_3 \longrightarrow O_2 + O_2 + O_2$$

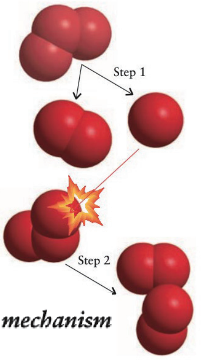
Two-step mechanism: In the first step, an O_3 molecule is energized by solar radiation and dissociates into an O atom and an O_2 molecule. In the second step, the O atom attacks another O_3 molecule to produce two more O_2 molecules (FIG. 15.17):

Step 1 $O_3 \longrightarrow O_2 + O$

Step 2 $O + O_3 \longrightarrow O_2 + O_2$



One-step mechanism



Two-step mechanism

3.2.2 The Rate Laws of Elementary Reactions

Rate Laws of Elementary Reactions

Molecularity	Elementary reaction	Rate law
1	$\mathrm{A} \longrightarrow$ products	rate = $k[\mathrm{A}]$
2	$\mathrm{A} + \mathrm{B} \longrightarrow$ products	rate = $k[\mathrm{A}][\mathrm{B}]$
	$\mathrm{A} + \mathrm{A} \longrightarrow$ products	rate = $k[\mathrm{A}]^2$
3	$\mathrm{A} + \mathrm{B} + \mathrm{C} \longrightarrow$ products	rate = $k[\mathrm{A}][\mathrm{B}][\mathrm{C}]$
	$\mathrm{A} + \mathrm{A} + \mathrm{B} \longrightarrow$ products	rate = $k[\mathrm{A}]^2[\mathrm{B}]$
	$\mathrm{A} + \mathrm{A} + \mathrm{A} \longrightarrow$ products	rate = $k[\mathrm{A}]^3$

3.2.3 The Rate Laws of Overall Reactions

$2\,\mathrm{NO(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{NO_2(g)}$ Rate of formation of $\mathrm{NO_2} = k[\mathrm{NO}]^2[\mathrm{O_2}]$

Step 1 A fast bimolecular dimerization and its reverse:

$\mathrm{NO} + \mathrm{NO} \longrightarrow \mathrm{N_2O_2}$ Rate of formation of $\mathrm{N_2O_2} = k_1[\mathrm{NO}]^2$

$\mathrm{N_2O_2} \longrightarrow \mathrm{NO} + \mathrm{NO}$ Rate of consumption of $\mathrm{N_2O_2} = k_1'[\mathrm{N_2O_2}]$

Step 2 A slow bimolecular reaction in which an $\mathrm{O_2}$ molecule collides with the dimer:

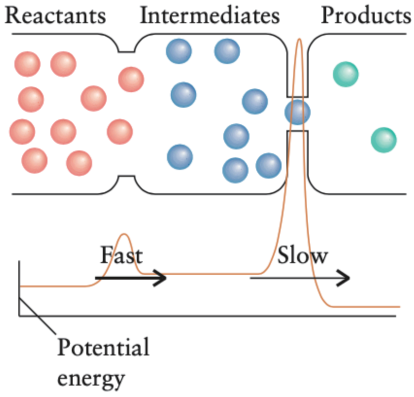
$\mathrm{O_2} + \mathrm{N_2O_2} \longrightarrow \mathrm{NO_2} + \mathrm{NO_2}$ Rate of consumption of $\mathrm{N_2O_2} = k_2[\mathrm{N_2O_2}][\mathrm{O_2}]$

Rate-determining step： the slowest step

3.2.3 The Rate Laws of Overall Reactions

Rate-determining step： the slowest step

The slowest elementary step in a sequence of reactions that governs the overall rate of formation of products



$$\mathrm{NO} + \mathrm{NO} \rightleftharpoons \mathrm{N_2O_2} \qquad K = \frac{[\mathrm{N_2O_2}]}{[\mathrm{NO}]^2}$$

Rate of formation of $\mathrm{NO_2} = 2k_2[\mathrm{N_2O_2}][\mathrm{O_2}] = 2k_2K[\mathrm{NO}]^2[\mathrm{O_2}]$

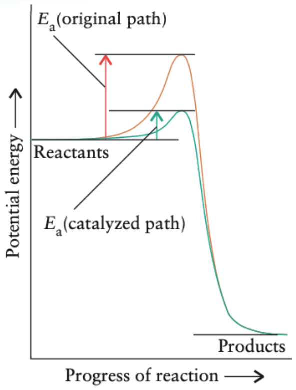
Think： equilibrium step

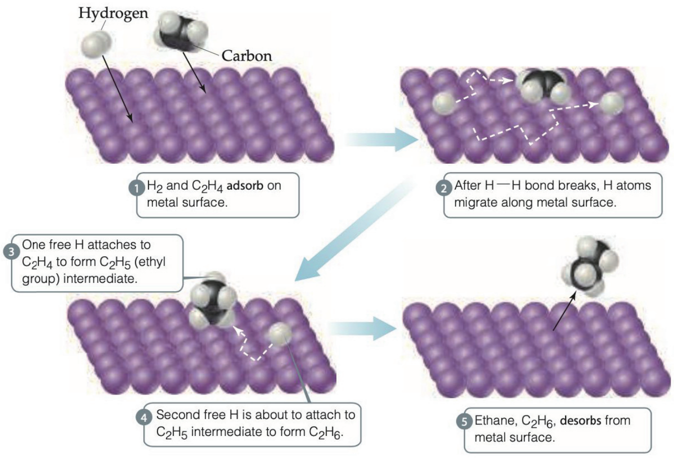
3.2 Summary & Practice

1. Concept

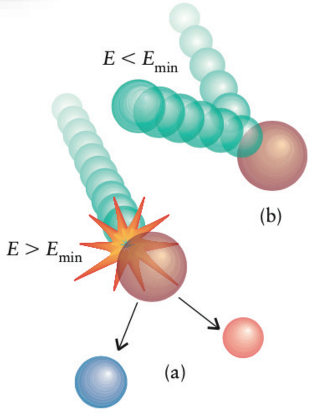
2. Example

3.3 Factors That Affect Reaction Rates





3.3.1 Collision Theory

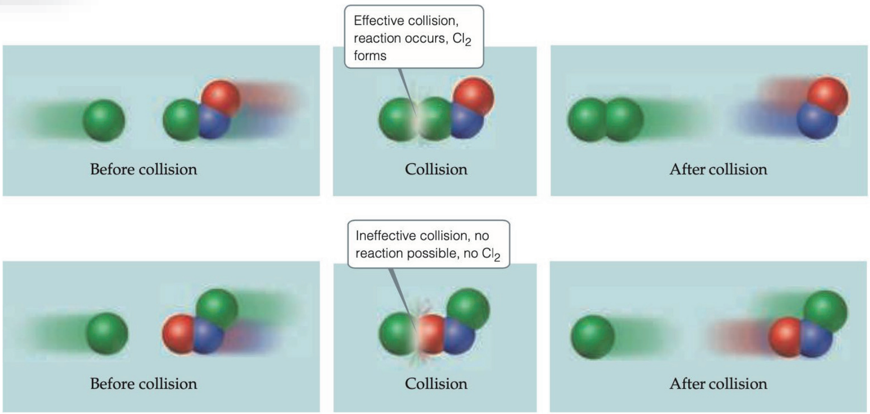


We assume that a reaction can take place only if reactants meet. In a gas, that meeting is a collision, and so the model that we are building is called the **collision theory** of reactions.

In this model, we suppose that molecules behave like defective billiard balls: they bounce apart if they collide at low speed, but they might smash into pieces when the impact is more energetic. If two molecules collide with less than a certain kinetic energy, they simply bounce apart. If they meet with more than that kinetic energy, reactant bonds can break and new bonds can form, resulting in products

3.3.1

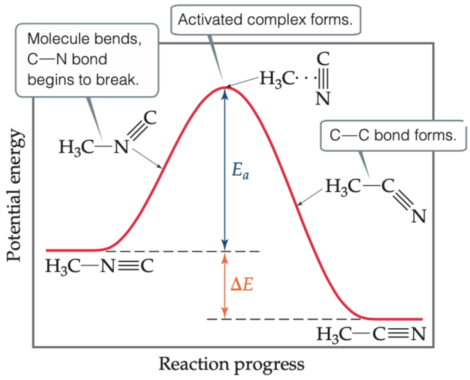
Collision Theory

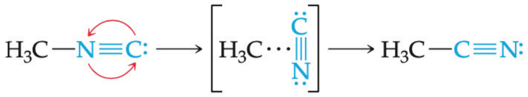


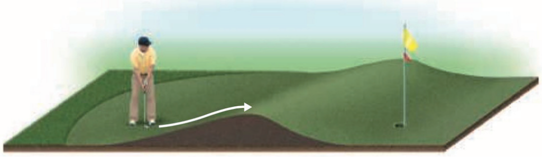
3.3.2

Activation Energy

The minimum energy required to initiate a chemical reaction is called the **activation energy**, *Ea*, and its value varies from reaction to reaction.

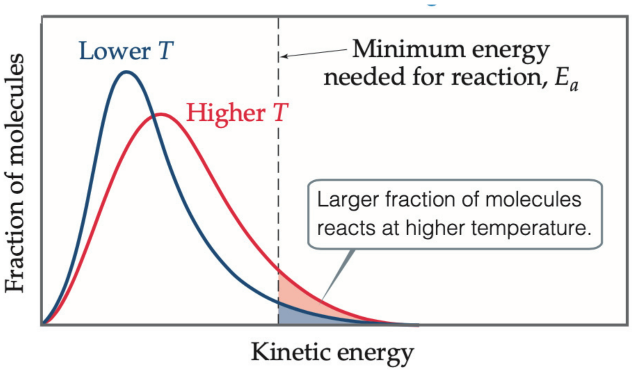






3.3.3

How Temperature Affect Rate



3.3.4

Arrhenius Equation

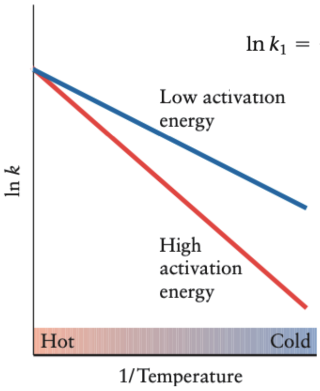
$$k = Ae^{-E_a/RT}$$

frequency factor, *A*, is constant, or nearly so, as temperature is varied.

$$\ln k = \ln Ae^{-E_a/RT}$$

$$\ln k = \ln e^{-E_a/RT} + \ln A$$

$$\begin{array}{ccccc} \ln k & = & -\dfrac{E_a}{RT} & + & \ln A \\ \updownarrow & & \updownarrow & & \updownarrow \\ y & = & mx & + & b \end{array}$$



$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{and} \quad \ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

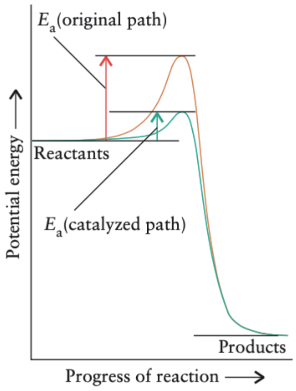
$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

3.3.5

Catalysis

A **catalyst** is a substance that changes the speed of a chemical reaction without undergoing a permanent chemical change itself.

A catalyst speeds up a reaction by providing an alternative pathway—a different reaction mechanism—between reactants and products. This new pathway has a lower activation energy than the original pathway



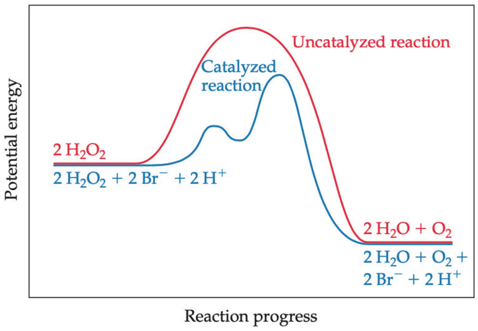
3.3.6

Homogeneous Catalysis

$$2\,H_2O_2(aq) \longrightarrow 2\,H_2O(l) + O_2(g)$$

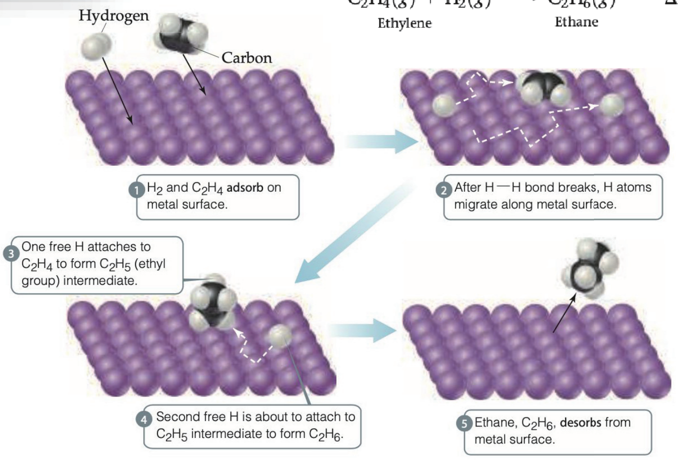
$$2\,Br^-(aq) + H_2O_2(aq) + 2\,H^+(aq) \longrightarrow Br_2(aq) + 2\,H_2O(l)$$

$$Br_2(aq) + H_2O_2(aq) \longrightarrow 2\,Br^-(aq) + 2\,H^+(aq) + O_2(g)$$



3.3.7 Heterogeneous Catalysis

$$\underset{\text{Ethylene}}{C_2H_4(g)} + H_2(g) \longrightarrow \underset{\text{Ethane}}{C_2H_6(g)} \qquad \Delta H^\circ = -137\ \text{kJ/mol}$$



3.3.8 Factors That Affect Reaction Rates

Reactant concentrations
Pressure

Reaction temperature
Catalyst

Physical state of the reactants (surface area)

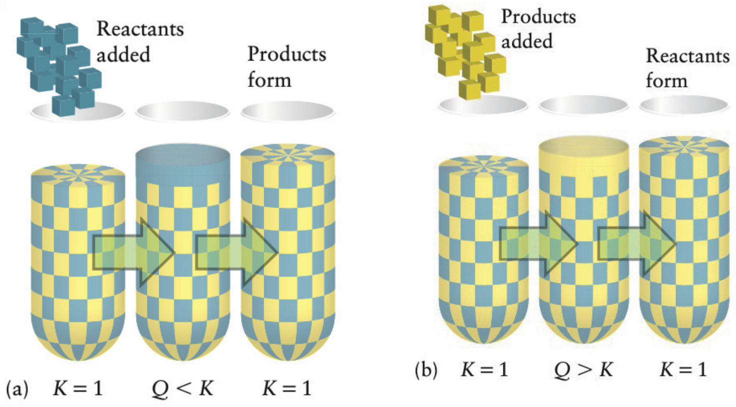
3.3 Summary & Practice

1. Concept

2. Example

3.4

Equilibrium



3.4.1

The Concept of Equilibrium

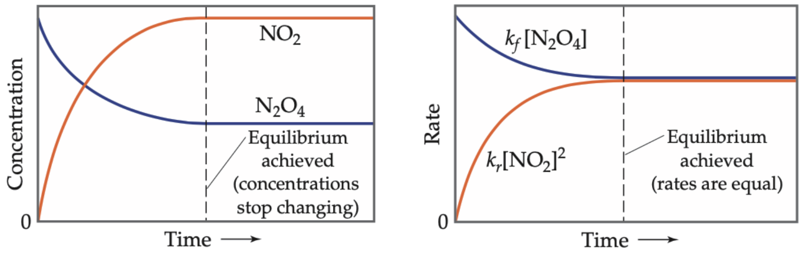
Chemical equilibrium *occurs when the forward and reverse reactions proceed at equal rates.*

$$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$$

Colorless Brown

Forward reaction: $N_2O_4(g) \longrightarrow 2\ NO_2(g)$ $\quad \text{Rate}_f = k_f[N_2O_4]$

Reverse reaction: $2\ NO_2(g) \longrightarrow N_2O_4(g)$ $\quad \text{Rate}_r = k_r[NO_2]^2$



3.4.2

The Equilibrium Constant

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$$

Haber process

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$a\text{A} + b\text{B} \rightleftharpoons d\text{D} + e\text{E}$$

$$K_c = \frac{[\text{D}]^d[\text{E}]^e}{[\text{A}]^a[\text{B}]^b} \begin{array}{l} \longleftarrow \text{products} \\ \longleftarrow \text{reactants} \end{array}$$

The equilibrium-constant expression depends only on the stoichiometry of the reaction, not on its mechanism.

3.4.3 Equilibrium Constants in Terms of Pressure, Kp

$$K_p = \frac{(P_D)^d(P_E)^e}{(P_A)^a(P_B)^b} \qquad PV = nRT, \text{ so } P = \frac{n}{V}RT$$

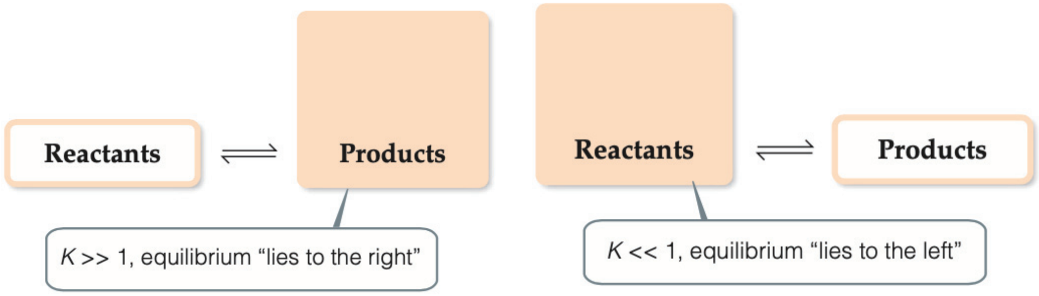
$$K_p = \frac{([D]RT)^d([E]RT)^e}{([A]RT)^a([B]RT)^b} = \left(\frac{[D]^d[E]^e}{[A]^a[B]^b}\right)\frac{(RT)^{d+e}}{(RT)^{a+b}}$$

$$K_p = K_c(RT)^{(d+e)-(a+b)} = K_c(RT)^{\Delta n}$$

3.4.4 Applications of Equilibrium Constants

If $K \gg 1$ *(large K):* Equilibrium lies to right, products predominate

If $K \ll 1$ *(small K):* Equilibrium lies to left, reactants predominate



Reactants ⇌ **Products**

$K >> 1$, equilibrium "lies to the right"

Reactants ⇌ **Products**

$K << 1$, equilibrium "lies to the left"

3.4.5 Stoichiometry and Equilibrium Constants

1. The equilibrium constant of a reaction in the *reverse* direction is the *inverse* (or *reciprocal*) of the equilibrium constant of the reaction in the forward direction:

$$A + B \rightleftharpoons C + D \quad K_1$$
$$C + D \rightleftharpoons A + B \quad K = 1/K_1$$

2. The equilibrium constant of a reaction that has been *multiplied* by a number is equal to the original equilibrium constant raised to a *power* equal to that number.

$$A + B \rightleftharpoons C + D \quad K_1$$
$$nA + nB \rightleftharpoons nC + nD \quad K = K_1^n$$

3. The equilibrium constant for a net reaction made up by adding *two or more reactions* is the *product* of the equilibrium constants for the individual reactions:

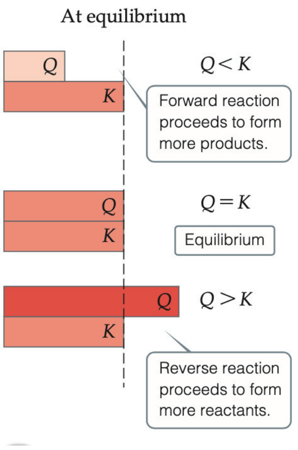
$$\begin{array}{ll} A + B \rightleftharpoons C + D & K_1 \\ C + F \rightleftharpoons G + A & K_2 \\ \hline B + F \rightleftharpoons D + G & K_3 = (K_1)(K_2) \end{array}$$

3.4.6

Predicting the Direction of Reaction

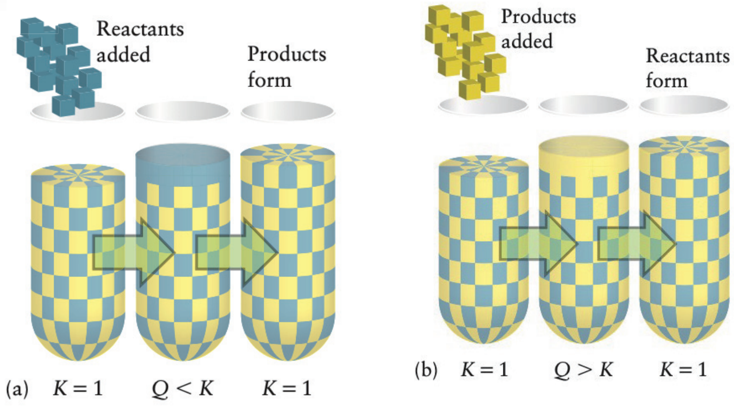
The ***reaction quotient****, Q, is a number obtained by substituting reactant and product concentrations or partial pressures at any point during a reaction into an equilibrium-constant expression.*

- $Q < K$: The concentration of products is too small and that of reactants too large. The reaction achieves equilibrium by forming more products; it proceeds from left to right.
- $Q = K$: The reaction quotient equals the equilibrium constant only if the system is at equilibrium.
- $Q > K$: The concentration of products is too large and that of reactants too small. The reaction achieves equilibrium by forming more reactants; it proceeds from right to left.



3.5

Equilibrium Shift

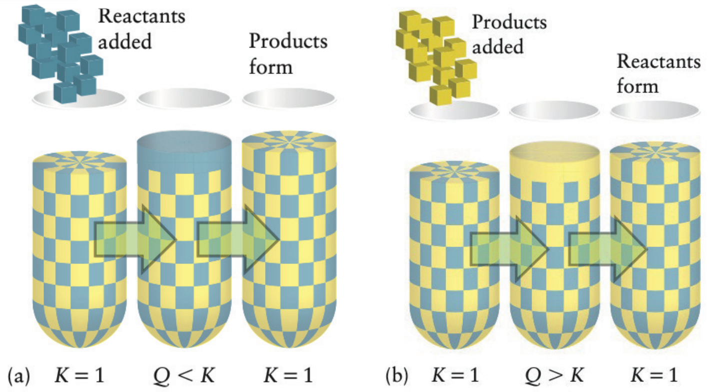


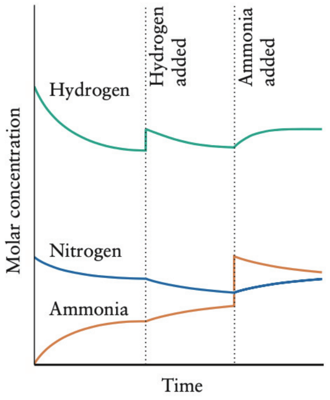
3.5.1

Le Châtelier’s Principle

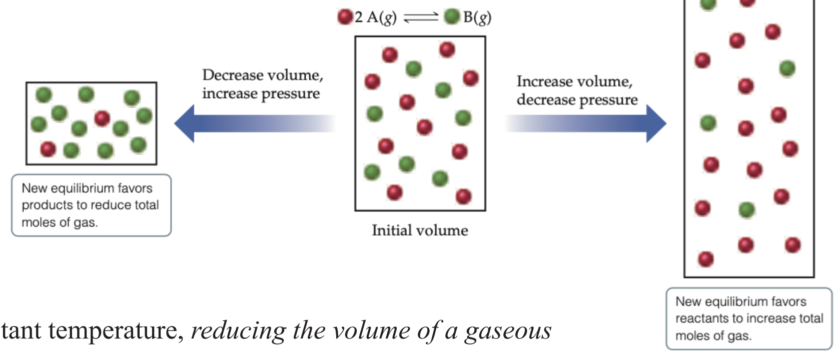
If a system at equilibrium is disturbed by a change in temperature, pressure, or a component concentration, the system will shift its equilibrium position so as to counteract the effect of the disturbance.

3.5.2 Adding and Removing Reagents





3.5.3 Effects of Volume and Pressure Changes



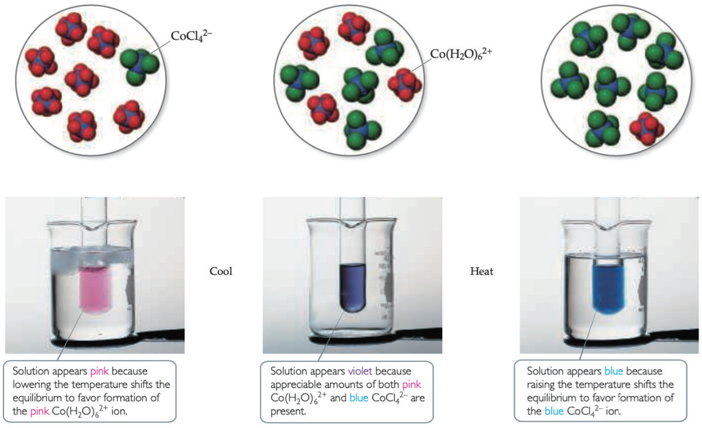
At constant temperature, *reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.*

3.5.4 Effect of Temperature Changes

$\Delta H > 0$, endothermic reaction

$$\text{Heat} + Co(H_2O)_6^{2+}(aq) + 4\,Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6\,H_2O(l)$$

Pink Blue



Solution appears pink because lowering the temperature shifts the equilibrium to favor formation of the pink $Co(H_2O)_6^{2+}$ ion.

Solution appears violet because appreciable amounts of both pink $Co(H_2O)_6^{2+}$ and blue $CoCl_4^{2-}$ are present.

Solution appears blue because raising the temperature shifts the equilibrium to favor formation of the blue $CoCl_4^{2-}$ ion.

When the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the excess reactant (or product), namely heat.

3.5.5

Effect of Temperature Changes

To find the quantitative relation between the equilibrium constants for the same reaction at two temperatures T_1 and T_2, we note that Eq. 8 allows us to write the relation between standard Gibbs free energies of reaction and the equilibrium constants K_1 and K_2 at the two temperatures:

$$\Delta G_{\mathrm{r},1}^\circ = -RT_1 \ln K_1 \qquad \Delta G_{\mathrm{r},2}^\circ = -RT_2 \ln K_2$$

$$\ln K_1 - \ln K_2 = -\frac{1}{R}\left\{\frac{\Delta G_{\mathrm{r},1}^\circ}{T_1} - \frac{\Delta G_{\mathrm{r},2}^\circ}{T_2}\right\}$$

At this point, we introduce the definition of $\Delta G_\mathrm{r}^\circ$ in terms of $\Delta H_\mathrm{r}^\circ$ and $\Delta S_\mathrm{r}^\circ$:

$$\Delta G_{\mathrm{r},1}^\circ = \Delta H_{\mathrm{r},1}^\circ - T_1\Delta S_{\mathrm{r},1} \qquad \Delta G_{\mathrm{r},2}^\circ = \Delta H_{\mathrm{r},2}^\circ - T_2\Delta S_{\mathrm{r},2}^\circ$$

which gives

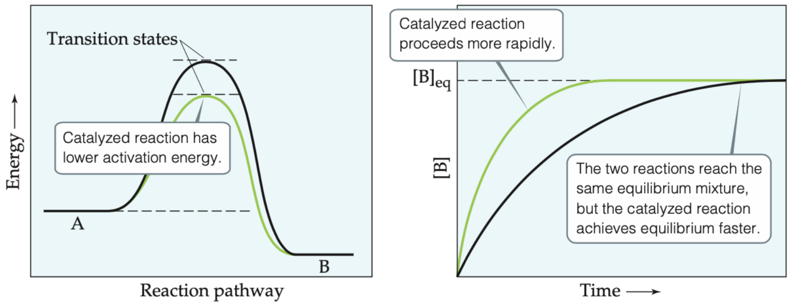
$$\begin{aligned}\ln K_1 - \ln K_2 &= -\frac{1}{R}\left\{\frac{\overbrace{\Delta H_{\mathrm{r},1}^\circ - T_1\Delta S_{\mathrm{r},1}^\circ}^{\Delta G_{\mathrm{r},1}^\circ}}{T_1} - \frac{\overbrace{\Delta H_{\mathrm{r},2}^\circ - T_2\Delta S_{\mathrm{r},2}^\circ}^{\Delta G_{\mathrm{r},2}^\circ}}{T_2}\right\}\\ &= -\frac{1}{R}\left\{\frac{\Delta H_{\mathrm{r},1}^\circ}{T_1} - \frac{\Delta H_{\mathrm{r},2}^\circ}{T_2} - \Delta S_{\mathrm{r},1}^\circ + \Delta S_{\mathrm{r},2}^\circ\right\}\end{aligned}$$

It is usually reasonable to assume that $\Delta H_\mathrm{r}^\circ$ and $\Delta S_\mathrm{r}^\circ$ are both approximately independent of temperature over the range of temperatures of interest. When we make that approximation, the reaction entropies cancel, and we are left with

$$\ln K_1 - \ln K_2 = -\frac{\Delta H_\mathrm{r}^\circ}{R}\left\{\frac{1}{T_1} - \frac{1}{T_2}\right\}$$

3.5.6

Catalyst

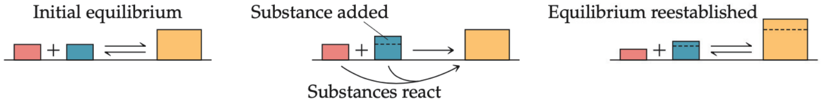


Le Châtelier's Principle

If a system at equilibrium is disturbed by a change in **concentration**, **pressure**, or **temperature**, the system will shift its equilibrium position so as to counter the effect of the disturbance.

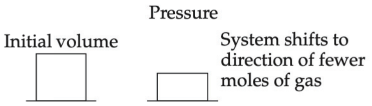
Concentration: adding or removing a reactant or product

If a substance is added to a system at equilibrium, the system reacts to consume some of the substance. If a substance is removed from a system, the system reacts to produce more of substance.



Pressure: changing the pressure by changing the volume

At constant temperature, reducing the volume of a gaseous equilibrium mixture causes the system to shift in the direction that reduces the number of moles of gas.



Temperature:

If the temperature of a system at equilibrium is increased, the system reacts as if we added a reactant to an endothermic reaction or a product to an exothermic reaction. The equilibrium shifts in the direction that consumes the "excess reagent," namely, heat.

Endothermic		Exothermic	
Increasing *T*	Reaction shifts right	Increasing *T*	Reaction shifts left
Decreasing *T*	Reaction shifts left	Decreasing *T*	Reaction shifts right

3.5

Summary & Practice

1. Concept

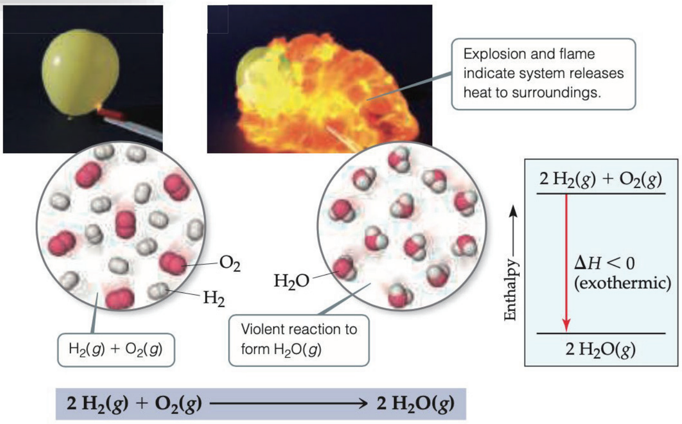
2. Example

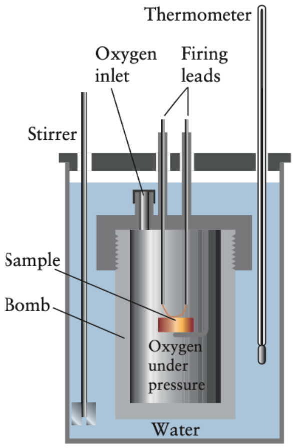
UKChO

英国化学奥林匹克竞赛

Unit 4

Thermodynamics





Unit 4

Thermodynamics

1.Temperature、Energy &The first law of thermodynamics

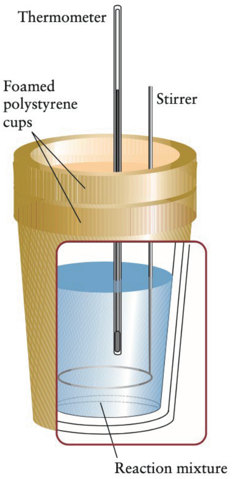
2.Enthalpy

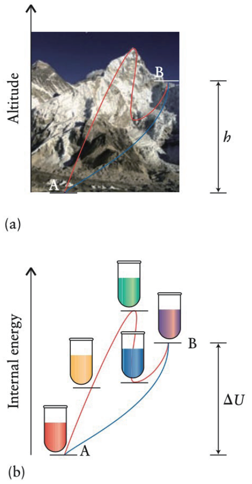
3.Hess’s law & Born-Haber cycle

4.Entropy and the second law of thermodynamics

5.Gibbs free energy

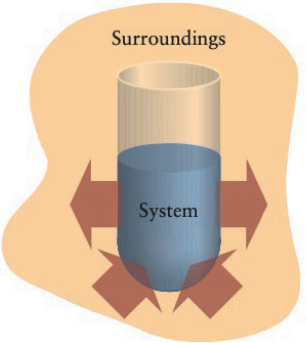
4.1 System, State, and Energy

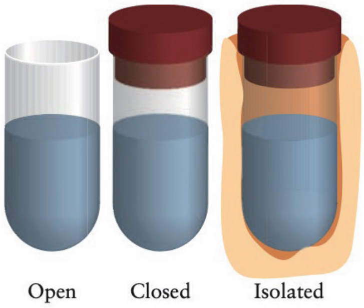




4.1.1 System and Surrounding

The region in which we are interested, such as a flask of gas, a beaker of acid, a reaction mixture, or a muscle fiber, is called a **system.**





In thermodynamics, the universe consists of a system and its surroundings.
An **open system** can exchange both matter and energy with the surroundings.
A **closed system** can exchange only energy; an isolated system can exchange nothing.
An **isolated system** has no contact with its surroundings. (sealed inside rigid, thermally insulating walls)

4.1.2 Internal Energy

In thermodynamics, the total store of energy in a system is called its **internal energy,** U.

Internal energy: a system is the sum of all the kinetic and potential energies of the components of the system.

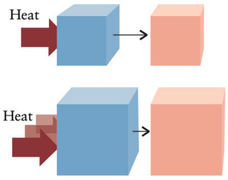
If the internal energy increases by 15 J during a change, we write U=+15 J

Heat is the transfer of energy as a result of a temperature difference. When energy is transferred as heat and no other processes occur, ΔU=q. When energy enters a system as heat, q is positive; when energy leaves a system as heat, q is negative.

4.1.3 Heat

Heat: In thermodynamics, **heat** is the energy transferred as a result of a temperature difference.
Heat transfer: Energy flows as heat from a high-temperature region to a low-temperature region.

$$\text{Heat capacity} = \frac{\text{heat supplied}}{\text{temperature rise produced}} \quad \text{that is,} \quad C = \frac{q}{\Delta T}$$



$q = C\Delta T = mC_s\Delta T$ C_s specific heat capacity

$q = nC_m\Delta T$ C_m molar heat capacity

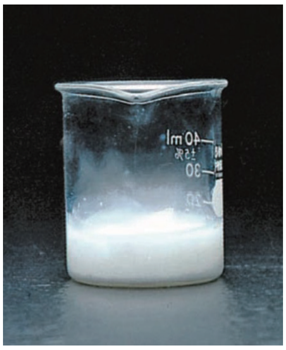
The heat capacity of an object determines the change in its temperature brought about by the quantity of energy transferred as heat: an object with a large heat capacity requires a lot of heat to bring about a given rise in temperature. Heat capacity is an extensive property, so a large object (bottom) has a larger heat capacity than a small object (top) made of the same material. Heat capacities also, in general, depend on temperature.

4.1.4 Exothermic & Endothermic

A process in which the system loses heat is called **exothermic** (*exo*-means "out of").

The thermite reaction is so exothermic that it melts the metal that it produces and can be used to weld railroad tracks together.
Aluminum metal is reacting with iron(III) oxide, Fe_2O_3, causing a shower of molten iron sparks.

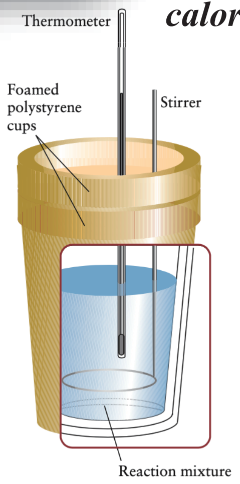
When a process occurs in which the system absorbs heat, the process is called **endothermic** (*endo*-means "into").

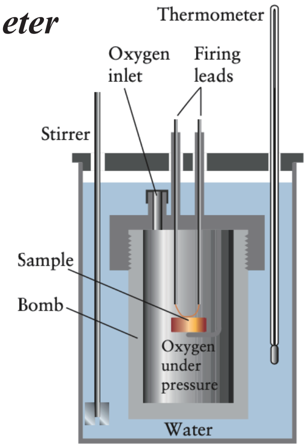


The endothermic reaction between ammonium thiocyanate, NH_4SCN, and barium hydroxide octahydrate, $Ba(OH)_2 \cdot 8H_2O$, absorbs a lot of heat and can cause water vapor in the air to freeze on the outside of the beaker.

4.1.5 The Measurement of Heat

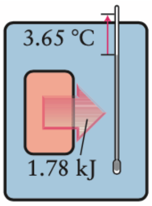
calorimeter

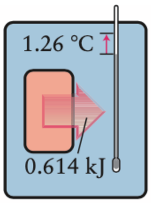




Practice：
calculate C

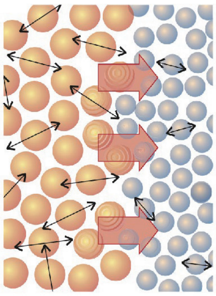
Think：
What should we assume





4.1.6 The First Law of Thermodynamics

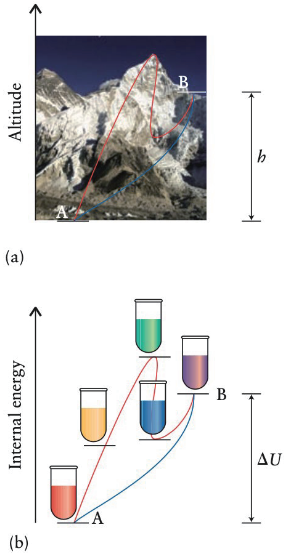
The internal energy of an isolated system is constant.



$$\Delta U = q + w$$

On an atomic scale, the transfer of energy as heat can be pictured as a process in which the vigorous thermal motion of atoms in the system jostle the less vigorously moving atoms of the surroundings and transfer some of their energy to them. The double-headed arrows represent the motion of the atoms; the large pink arrows represent the direction of heat transfer.

4.1.7 State Function



According to the first law, if an isolated system has a certain internal energy at one instant and we inspect it again later, then we shall find that it still has exactly the same internal energy, no matter how much time has passed.
We summarize these statements by saying that the internal energy is a ***state function***, a property that depends only on the current state of the system and is independent of how that state was prepared.

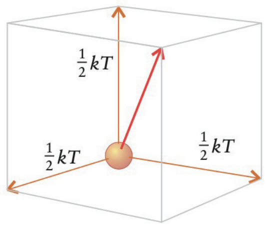
The ***pressure***, ***volume***, ***temperature***, and ***density*** of a system are also state functions.

State functions depend only on the current state of the system, any change in its value is independent of how the change in state was brought about

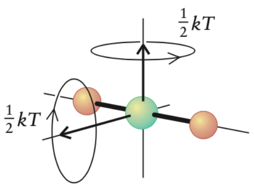
4.1.8 A Molecular Interlude: The Origin of Internal Energy

Internal energy is energy stored in a system as kinetic energy and potential energy. It includes all the energies of interaction of the fundamental particles that make up atoms:

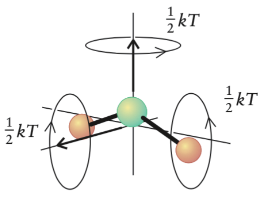
- the interactions between electrons and nuclei in the atoms that make up molecules
- the translational, rotational, and vibrational energies of the molecules
- the interactions between different molecules



translational energy



rotational energy



vibrational energy

4.1.8

A Molecular Interlude: The Origin of Internal Energy

A system at high temperature has a greater internal energy than the same system at a lower temperature.

The average value of each quadratic contribution to the energy of a molecule in a sample at a temperature T is equal to $\frac{1}{2}kT$.

A molecule can move through space along any of three dimensions, so it has *three* translational modes of motion, each one giving a quadratic contribution to the energy. It follows from the equipartition theorem that the average translational kinetic energy of a molecule in a sample at a temperature T is $3 \times \frac{1}{2}kT = \frac{3}{2}kT$. The contribution to the molar internal energy (the energy per mole of molecules, U_m) is therefore N_A times this value, or

$$U_m(\text{translation}) = \frac{3}{2}\overbrace{N_A k}^{R}T = \frac{3}{2}RT$$

We can conclude that if the gas is heated through ΔT, then the change in its molar internal energy, ΔU_m, is $\Delta U_m = \frac{3}{2}R\Delta T$. For instance, if the gas is heated from 20. °C to 100. °C (so $\Delta T = +80.\ \text{K}$), then its molar internal energy increases by $\frac{3}{2} \times (8.314\ \text{J·K}^{-1}\text{·mol}^{-1}) \times (80.\ \text{K})$, or $1.0\ \text{kJ·mol}^{-1}$.

4.1

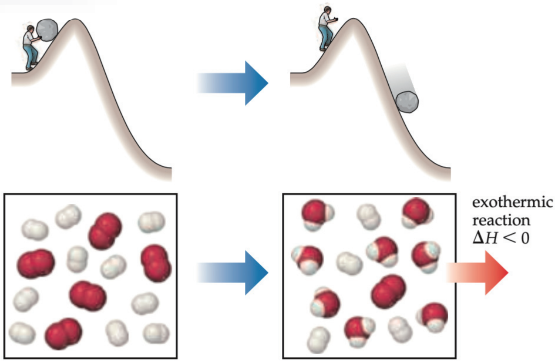
Summary & Practice

1. Concept

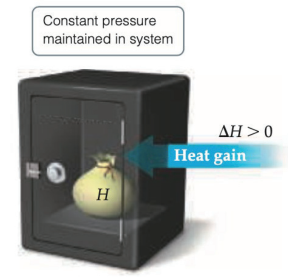
2. Example

4.2

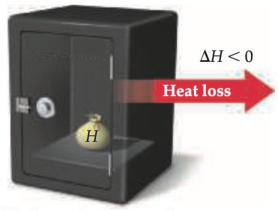
Enthalpy



Constant pressure maintained in system



(a) An endothermic reaction



(b) An exothermic reaction

4.2.1

Enthalpy Definition

The state function that allows us to keep track of energy changes at constant pressure is called the **enthalpy**, *H*

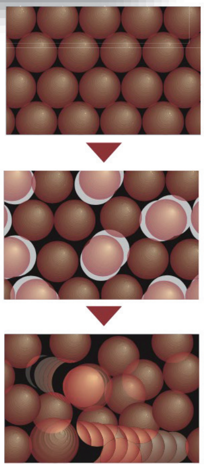
$$H = U + PV$$

A change in the enthalpy of a system is equal to the heat released or absorbed at constant pressure.

At constant pressure, and with no nonexpansion work: $\Delta H = q$

4.2.2

The Enthalpy of Physical Change



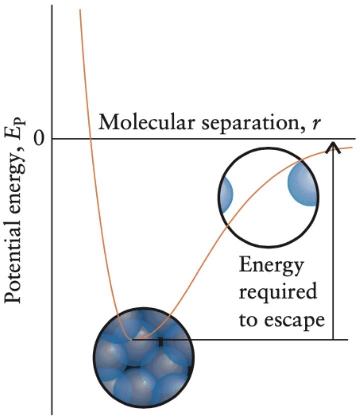
Enthalpy of vaporization □

$$\Delta H_{\text{vap}} = H_{\text{m}}(\text{vapor}) - H_{\text{m}}(\text{liquid})$$

$$2\,H_2O(l) \longrightarrow 2\,H_2O(g) \qquad \Delta H = +88\text{ kJ}$$

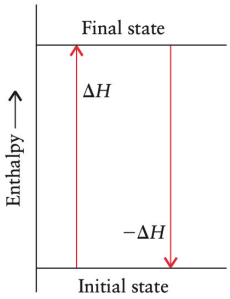
Enthalpy of fusion

$$\Delta H_{\text{fus}} = H_{\text{m}}(\text{liquid}) - H_{\text{m}}(\text{solid})$$



4.2.2

The Enthalpy of Physical Change



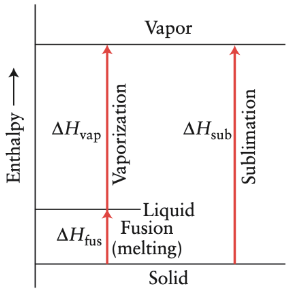
Enthalpy of freezing

$$\Delta H_{\text{reverse process}} = -\Delta H_{\text{forward process}}$$

Enthalpy of sublimation

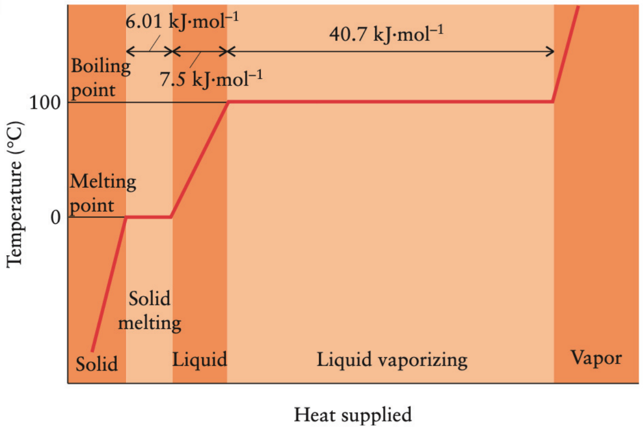
$$\Delta H_{\text{sub}} = H_{\text{m}}(\text{vapor}) - H_{\text{m}}(\text{solid})$$

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$



4.2.3

Heating Curve



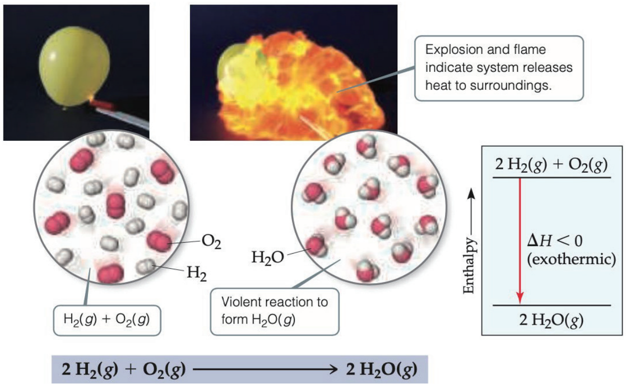
The temperature of a sample is constant at its melting and boiling points, even though heat is being supplied. The slope of a heating curve is steeper for a phase with a low heat capacity than for one with a high heat capacity.

4.2.4

Reaction Enthalpies

$\Delta H = H_{\text{final}} - H_{\text{initial}}$ $\Delta H = H_{\text{products}} - H_{\text{reactants}}$ ΔH_{rxn}

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(g) \qquad \Delta H = -483.6\,\text{kJ}$$

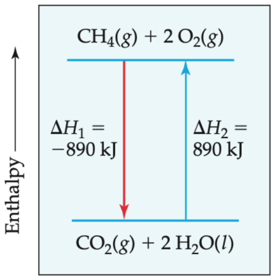


4.2.4

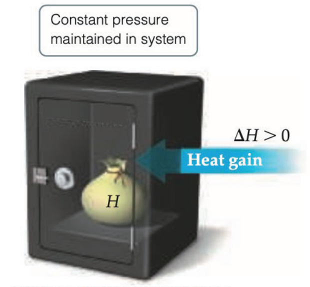
Reaction Enthalpies

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \qquad \Delta H = -890.\,\text{kJ}$$

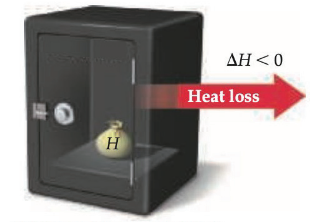
$$CO_2(g) + 2\,H_2O(l) \longrightarrow CH_4(g) + 2\,O_2(g) \qquad \Delta H = +890.\,\text{kJ}$$



$$2\,CH_4(g) + 4\,O_2(g) \longrightarrow 2\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H = -1780.\,\text{kJ}$$



(a) An endothermic reaction



(b) An exothermic reaction

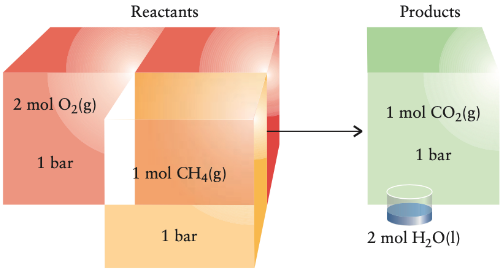
4.2.5

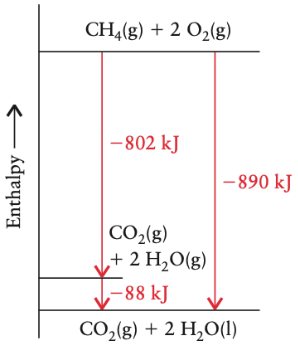
Standard Reaction Enthalpies

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(g) \qquad \Delta H = -802\ kJ$$

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2\ H_2O(l) \qquad \Delta H = -890.\ kJ$$

Standard reaction enthalpies refer to reactions in which the reactants and products are in their standard state, the pure form at 1 bar; they are usually reported for a temperature of 298.15 K.



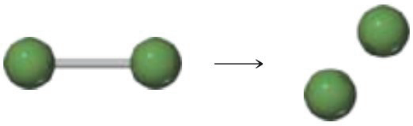


4.2.6

Bond Enthalpies

The **bond enthalpy** is the enthalpy change, Δ*H*, for the breaking of a particular bond in one mole of a gaseous substance.

$$Cl_2(g) \longrightarrow 2Cl(g)$$

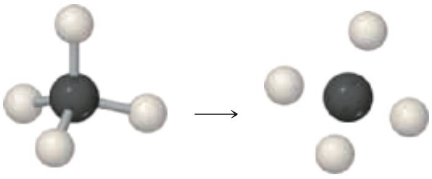


Which is more stable at room temperature, a Cl_2 molecule or two separate Cl atoms?
What is the energy difference between the Cl_2 molecule and the separated atoms?

4.2.6

Bond Enthalpies

$$CH_4(g) \longrightarrow C(g) + 4\ H(g) \qquad \Delta H = 1660\ kJ$$



Because there are four equivalent C—H bonds in methane, the enthalpy of this reaction is four times the enthalpy needed to break a single C—H bond. Therefore, the average C—H bond enthalpy in CH_4 is $D(C—H) = (1660/4)\ kJ/mol = 415\ kJ/mol$.

The bond enthalpy is always a positive quantity because energy is required to break chemical bonds. Conversely, energy is always released when a bond forms between two gaseous atoms or molecular fragments. The greater the bond enthalpy, the stronger the bond.

4.2.6

Bond Enthalpies

$$\Delta H_{\text{rxn}} = \sum (\text{bond enthalpies of bonds broken}) - \sum (\text{bond enthalpies of bonds formed})$$

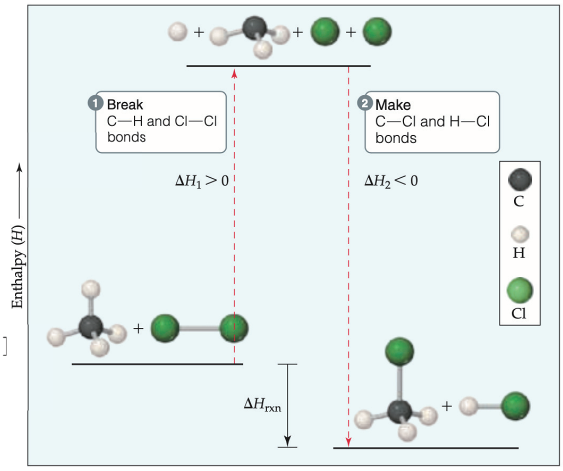
$$H{-}CH_3(g) + Cl{-}Cl(g) \longrightarrow Cl{-}CH_3(g) + H{-}Cl(g)$$

Bonds broken: 1 mol C—H, 1 mol Cl—Cl

Bonds formed: 1 mole C—Cl, 1 mol H—Cl

$$\Delta H_{\text{rxn}} = [D(C{-}H) + D(Cl{-}Cl)] - [D(C{-}Cl) + D(H{-}Cl)]$$

$$\Delta H_{\text{rxn}} = (413\text{ kJ} + 242\text{ kJ}) - (328\text{ kJ} + 431\text{ kJ}) = -104\text{ kJ}$$



4.2.7

Standard Enthalpies of Formation

The **standard enthalpy of formation,** $\Delta H_f°$, of a substance is the standard reaction enthalpy per mole of formula units for the formation of a substance from its elements in their *most stable form,* as in the reaction for the formation of ethanol:

$$2\,C(gr) + 3\,H_2(g) + \tfrac{1}{2}\,O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H° = -277.69\text{ kJ}$$

A Note on Good Practice: You should always be alert to the difference between a quantity *per* mole of molecules and the same quantity *for or of* a mole of molecules. Standard enthalpies of formation are expressed per mole of molecules, as in $-277.69\text{ kJ}\cdot\text{mol}^{-1}$; the standard enthalpy of forming 1 mol $C_2H_5OH(l) = -277.69$ kJ. The point might seem picky, but it will help you to keep units straight. ■

By definition, the standard enthalpy of formation of the most stable form of any element is zero because there is no formation reaction needed when the element is already in its standard state.

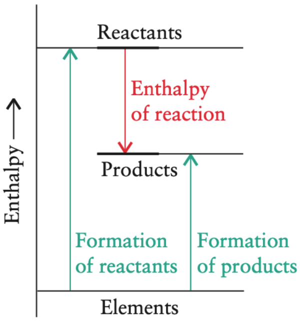
4.2.7

Standard Enthalpies of Formation

$$\Delta H° = \underbrace{\sum n\Delta H_f°(\text{products})}_{\text{sum over products}} - \underbrace{\sum n\Delta H_f°(\text{reactants})}_{\text{sum over reactants}}$$

Standard Enthalpies of Formation at 25 °C (kJ·mol⁻¹)*

Substance	Formula	$\Delta H_f°$	Substance	Formula	$\Delta H_f°$
Inorganic compounds			**Organic compounds**		
ammonia	$NH_3(g)$	−46.11	benzene	$C_6H_6(l)$	+49.0
carbon dioxide	$CO_2(g)$	−393.51	ethanol	$C_2H_5OH(l)$	−277.69
carbon monoxide	$CO(g)$	−110.53	ethyne (acetylene)	$C_2H_2(g)$	+226.73
dinitrogen tetroxide	$N_2O_4(g)$	+9.16			
hydrogen chloride	$HCl(g)$	−92.31	glucose	$C_6H_{12}O_6(s)$	−1268
hydrogen fluoride	$HF(g)$	−271.1	methane	$CH_4(g)$	−74.81
nitrogen dioxide	$NO_2(g)$	+33.18			
nitric oxide	$NO(g)$	+90.25			
sodium chloride	$NaCl(s)$	−411.15			
water	$H_2O(l)$	−285.83			
	$H_2O(g)$	−241.82			



4.2.7 Standard Enthalpies of Formation

$$\Delta H^\circ = \overbrace{\sum n\Delta H_f^\circ(\text{products})}^{\text{sum over products}} - \overbrace{\sum n\Delta H_f^\circ(\text{reactants})}^{\text{sum over reactants}}$$

Calculate a standard enthalpy of reaction

$$2\ NH_2CH_2COOH(s) + 3\ O_2(g) \longrightarrow H_2NCONH_2(s) + 3\ CO_2(g) + 3\ H_2O(l)$$

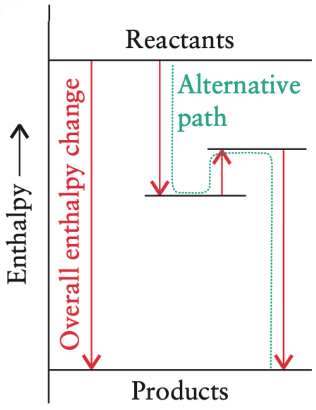
$\Delta H_f^\circ(H_2NCONH_2, s) = -333.51\ kJ{\cdot}mol^{-1}$
$\Delta H_f^\circ(CO_2, g) = -393.51\ kJ{\cdot}mol^{-1}$
$\Delta H_f^\circ(H_2O, l) = -285.83\ kJ{\cdot}mol^{-1}$
$\Delta H_f^\circ(NH_2CH_2COOH, s) = -532.9\ kJ{\cdot}mol^{-1}$
$\Delta H_f^\circ(O_2, g) = 0$

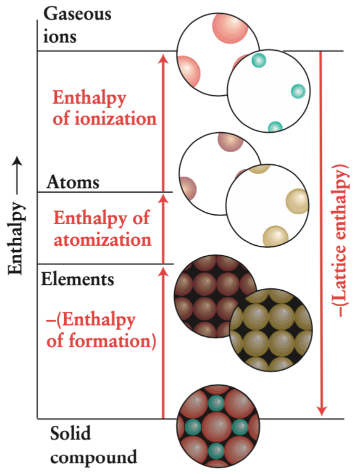
4.2 Summary & Practice

1. Concept

2. Example

4.3 Hess's Law & Born-Haber Cycle





4.3.1 Hess's Law

Hess's law states that *if a reaction is carried out in a series of steps, ΔH for the overall reaction equals the sum of the enthalpy changes for the individual steps.*

$$\begin{array}{llr} & CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g) & \Delta H = -802\text{ kJ} \\ \text{(Add)} & 2\,H_2O(g) \longrightarrow 2\,H_2O(l) & \Delta H = -88\text{ kJ} \\ \hline & CH_4(g) + 2\,O_2(g) + 2\,H_2O(g) \longrightarrow CO_2(g) + 2\,H_2O(l) + 2\,H_2O(g) & \Delta H = -890\text{ kJ} \end{array}$$

The net equation is

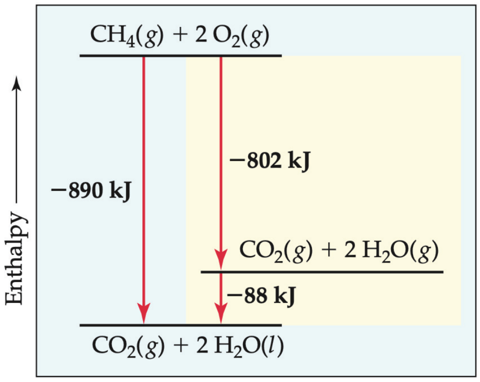
$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(l) \quad \Delta H = -890\text{ kJ}$$

4.3.1 Hess's Law

The overall enthalpy change for the process is independent of the number of steps and independent of the path by which the reaction is carried out.

This law is a consequence of the fact that enthalpy is a state function. We can therefore calculate ΔH for any process as long as we find a route for which ΔH is known for each step.

This means that a relatively small number of experimental measurements can be used to calculate ΔH for a vast number of reactions.



4.3.1 Hess's Law

Calculate the standard enthalpy of the reaction $3\,C(gr) + 4\,H_2(g) \rightarrow C_3H_8(g)$ from the following experimental data:

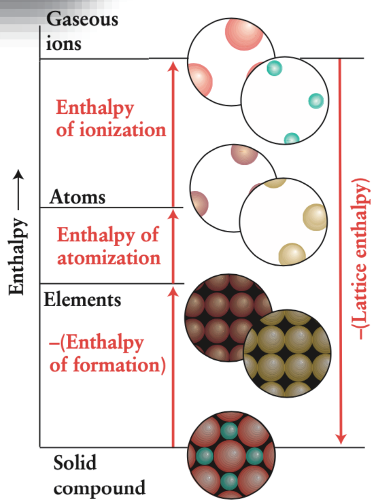
(a) $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l) \qquad \Delta H^\circ = -2220.\text{ kJ}$

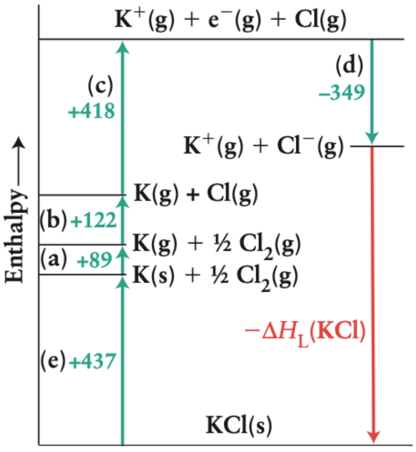
(b) $C(gr) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -394\text{ kJ}$

(c) $H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -286\text{ kJ}$

4.3.2

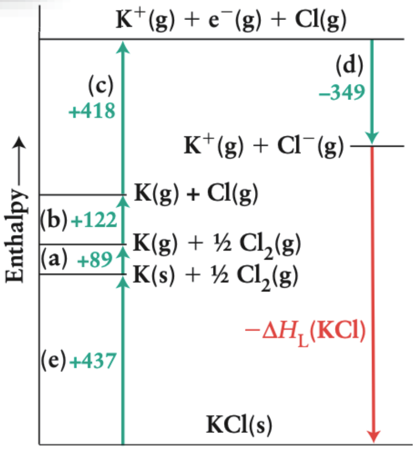
The Born-Haber Cycle





4.3.2

The Born-Haber Cycle



QUESTION:

1. Lattice energy
2. Meaning of a-d

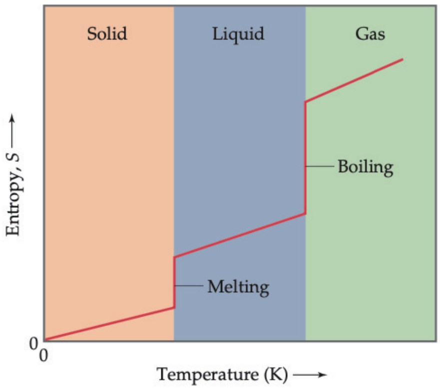
4.3

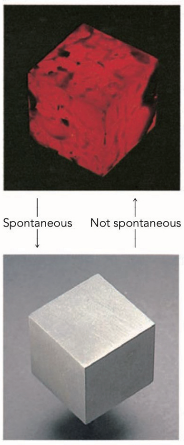
Summary & Practice

1. Concept

2. Example

4.4 Entropy and the Second Law of Thermodynamics



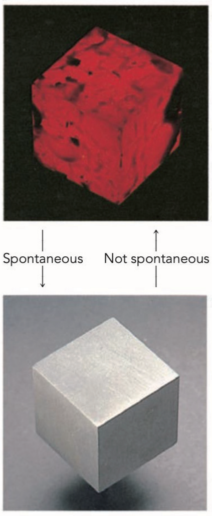


4.4.1 Spontaneous Change

A **spontaneous change** is a change that has a tendency to occur without needing to be driven by an external influence.

A nonspontaneous change can be brought about only by doing work.

A process is spontaneous if it has a tendency to occur without being driven by an external influence; spontaneous changes need not be fast.



A red-hot block of metal (top) cools spontaneously to the temperature of its surroundings, the cool air around it (bottom).

4.4.2 Entropy

Entropy, S , a measure of disorder. *Low entropy means little disorder; high entropy means great disorder* .

The entropy of an isolated system increases in the course of any spontaneous change.

ΔS, in a system depends only on the initial and final states of the system and not on the path taken from one state to the other:

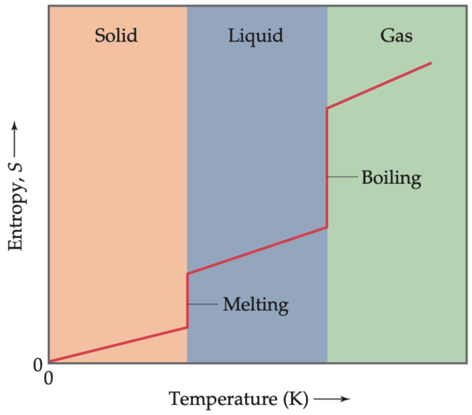
$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

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

4.4.3

ΔS for Phase Changes

The entropy of a substance increases when it melts and when it vaporizes.



4.4.4

ΔS in Reaction

$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

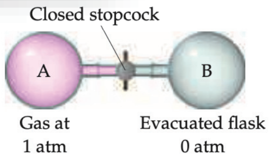
Standard Molar Entropies: Molar entropies for substances in their standard states are known as **standard molar entropies** and denoted S°.
The standard state for any substance is defined as the pure substance at 1 atm pressure

Substance	S° (J/mol-K)
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

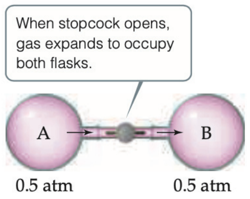
4.4.5

The Second Law of Thermodynamics

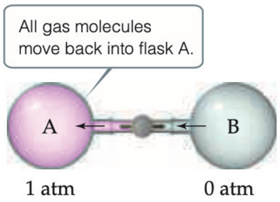
The entropy of the universe increases for any spontaneous process.



Reversible Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$
Irreversible Process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$



This process is spontaneous



This process is not spontaneous

4.4.6 The Third Law of Thermodynamics

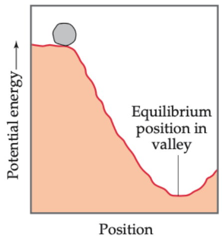
The entropy of a pure, perfect crystalline substance at absolute zero is zero: $S(0\,\mathrm{K}) = 0$.

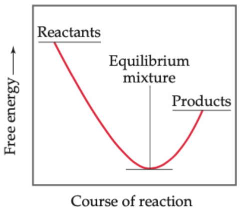
4.4 Summary & Practice

1. Concept

2. Example

4.5 Gibbs Free Energy





4.5.1 Gibbs Free Energy

Gibbs proposed a new state function, now called the **Gibbs free energy** (or just **free energy**), G, and defined as

$$G = H - TS$$

where T is the absolute temperature. For an isothermal process, the change in the free energy of the system, ΔG, is

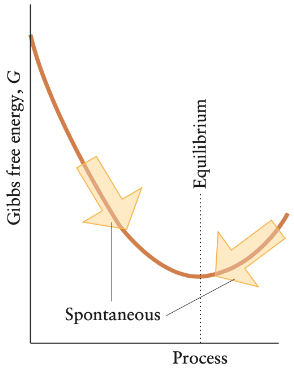
$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S_{\text{tot}} = \Delta S + \overbrace{\Delta S_{\text{surr}}}^{-\Delta H/T} = \Delta S - \frac{\Delta H}{T}$$

4.5.1 Gibbs Free Energy

At constant temperature and pressure, the direction of spontaneous change is the direction of decreasing Gibbs free energy.



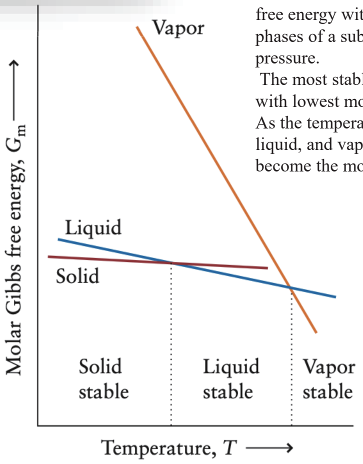
The great importance of the introduction of Gibbs free energy is that, *provided that the temperature and pressure are constant, we can predict the spontaneity of a process solely in terms of the thermodynamic properties of the system.*

4.5.2 The Effect of Temperature

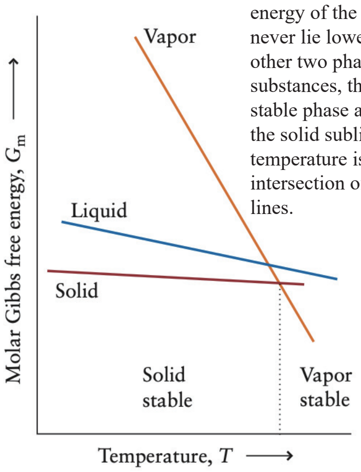
Enthalpy change	**Entropy change**	**Spontaneous?**
exothermic ($\Delta H < 0$)	increase ($\Delta S > 0$)	yes, $\Delta G < 0$
exothermic ($\Delta H < 0$)	decrease ($\Delta S < 0$)	yes, if $\lvert T\Delta S\rvert < \lvert\Delta H\rvert$, $\Delta G < 0$
endothermic ($\Delta H > 0$)	increase ($\Delta S > 0$)	yes, if $T\Delta S > \Delta H$, $\Delta G < 0$
endothermic ($\Delta H > 0$)	decrease ($\Delta S < 0$)	no, $\Delta G > 0$

4.5.2

The Effect of Temperature



The variation of the (molar) Gibbs free energy with temperature for three phases of a substance at a given pressure.
The most stable phase is the phase with lowest molar Gibbs free energy. As the temperature is raised, the solid, liquid, and vapor phases in succession become the most stable.



For some substances and at certain pressures, the molar Gibbs free energy of the liquid phase might never lie lower than those of the other two phases. For such substances, the liquid is never the stable phase and, at constant pressure, the solid sublimes when the temperature is raised to the point of intersection of the solid and vapor lines.

4.5.3

Gibbs Free Energy of Reaction

$$\Delta G = \sum nG_m(\text{products}) - \sum nG_m(\text{reactants})$$

$$\Delta G^\circ = \sum nG_m^\circ(\text{products}) - \sum nG_m^\circ(\text{reactants})$$

ΔG° is fixed for a given reaction and temperature and so does not change as the reaction proceeds.

ΔG depends on the composition of the reaction mixture and so it varies—and might even change sign—as the reaction proceeds.

The **standard Gibbs free energy of formation,** ΔG_f (the "standard free energy of formation"), of a substance is *the standard Gibbs free energy of reaction per mole for the formation of a compound from its elements in their most stable form.*

4.5

Summary & Practice

1. Concept

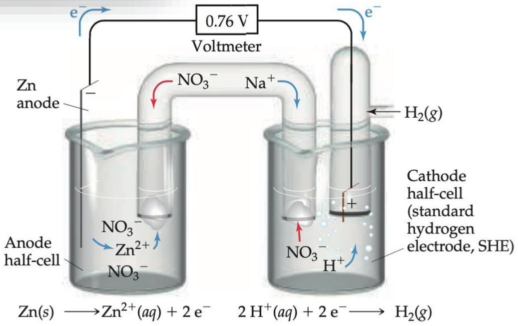
2. Example

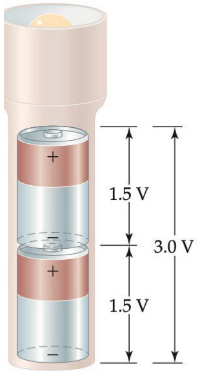
UKChO

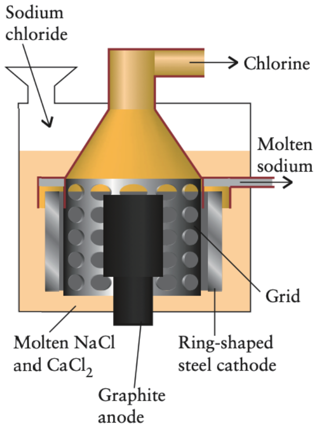
英国化学奥林匹克竞赛

Unit 5

Electrochemistry







Unit 5

Electrochemistry

1.Redox reactions & Electrochemistry

2.Galvanic cells

3.Electrolysis & Chemical power source

5.1

Redox Reactions & Electrochemistry

5.1.1

Oxidation Number

Keeping track of electrons gained by the substance being reduced and electrons lost by the substance being oxidized.

The concept of oxidation numbers (also called *oxidation states*) was devised as a way of doing this. Each atom in a neutral substance or ion is assigned an **oxidation number** (also known as an **oxidation state**).

1. *For an atom in its* ***elemental form****, the oxidation number is always zero.*
2. *For any* ***monatomic ion****, the oxidation number equals the ionic charge.*

5.1.1

Oxidation Number

3. ***Nonmetals*** usually have negative oxidation numbers, although they can sometimes be positive:
    - (**a**) *The oxidation number of* ***oxygen*** *is usually −2 in both ionic and molecular compounds*. The major exception is in compounds called peroxides, which contain the O_2^{2-} ion, giving each oxygen an oxidation number of −1.
    - (**b**) *The oxidation number of* ***hydrogen*** *is usually +1 when bonded to nonmetals and −1 when bonded to metals* (for example, metal hydrides such as sodium hydride, NaH).
    - (**c**) *The oxidation number of* ***fluorine*** *is −1 in all compounds*. The other ***halogens*** have an oxidation number of −1 in most binary compounds. When combined with oxygen, as in oxyanions, however, they have positive oxidation states.
4. ***The sum of the oxidation numbers*** *of all atoms in a neutral compound is zero. The sum of the oxidation numbers in a polyatomic ion equals the charge of the ion.*

5.1.1

Oxidation Number Practice

(**a**) H_2S, (**b**) S_8, (**c**) SCl_2, (**d**) Na_2SO_3, (**e**) SO_4^{2-}.

Practice Exercise 1

In which compound is the oxidation state of oxygen −1?
(**a**) O_2 (**b**) H_2O (**c**) H_2SO_4 (**d**) H_2O_2 (**e**) KCH_3COO

Practice Exercise 2

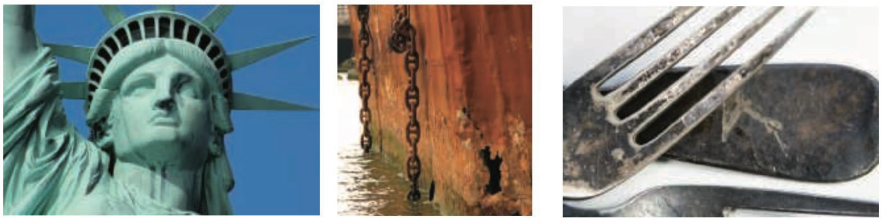
What is the oxidation state of the boldfaced element in
(**a**) $\mathbf{P}_2O_5$, (**b**) Na**H**, (**c**) $\mathbf{Cr}_2O_7^{2-}$, (**d**) **Sn**Br_4, (**e**) Ba$\mathbf{O}_2$?

5.1.2

Oxidation-Reduction Reactions

Electrons are transferred from one reactant to another. Such reactions are called either **oxidation-reduction reactions** or **redox reactions**.

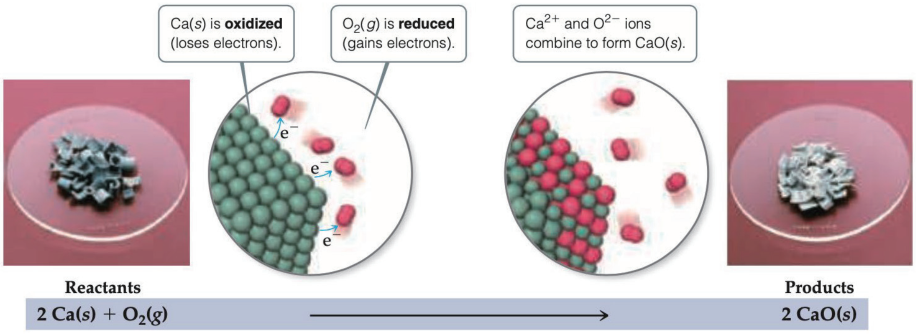
When an atom, ion, or molecule becomes more positively charged (that is, when it loses electrons), we say that it has been   Loss of electrons by a substance is called **oxidation**



5.1.2

Oxidation-Reduction Reactions

When an atom, ion, or molecule becomes more negatively charged (gains electrons), we say that it is *reduced*. The gain of electrons by a substance is called **reduction**.



$Ca(s)$ is **oxidized** (loses electrons).

$O_2(g)$ is **reduced** (gains electrons).

Ca^{2+} and O^{2-} ions combine to form $CaO(s)$.

Reactants

Products

$$2\,Ca(s) + O_2(g) \longrightarrow 2\,CaO(s)$$

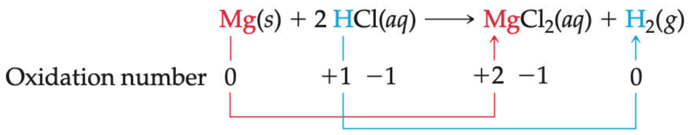
5.1.3 Oxidation of Metals by Acids and Salts

$$A + BX \longrightarrow AX + B$$

displacement reactions

$$Zn(s) + 2\,HBr(aq) \longrightarrow ZnBr_2(aq) + H_2(g)$$

$$Mn(s) + Pb(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq) + Pb(s)$$



$$Mg(s) + 2\,HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$$

Oxidation number $0 \quad +1 \;\; -1 \quad +2 \;\; -1 \quad 0$

5.1.3 Oxidation of Metals by Acids and Salts

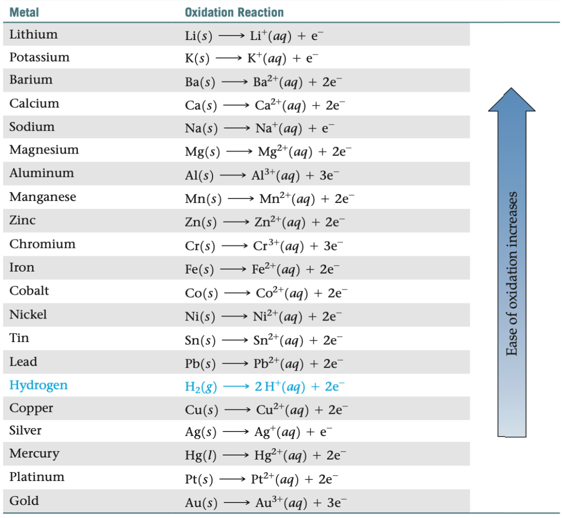
Metals can also be oxidized by aqueous solutions of various salts. Iron metal, for example, is oxidized to Fe^{2+} by aqueous solutions of Ni^{2+} such as $Ni(NO_3)_2(aq)$:

Molecular equation: $Fe(s) + Ni(NO_3)_2(aq) \longrightarrow Fe(NO_3)_2(aq) + Ni(s)$

Net ionic equation: $Fe(s) + Ni^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Ni(s)$

The oxidation of Fe to Fe^{2+} in this reaction is accompanied by the reduction of Ni^{2+} to Ni. Remember: *Whenever one substance is oxidized, another substance must be reduced.*

5.1.4 The Activity Series



Activity Series of Metals in Aqueous Solution

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$
Potassium	$K(s) \longrightarrow K^+(aq) + e^-$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$
Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \longrightarrow 2\,H^+(aq) + 2e^-$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^-$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^-$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$

5.1.5 Half-Reactions

$$\mathrm{Sn^{2+}}(aq) + 2\,\mathrm{Fe^{3+}}(aq) \longrightarrow \mathrm{Sn^{4+}}(aq) + 2\,\mathrm{Fe^{2+}}(aq)$$

$$\textit{Oxidation:}\quad \mathrm{Sn^{2+}}(aq) \longrightarrow \mathrm{Sn^{4+}}(aq) + 2\,\mathrm{e^-}$$

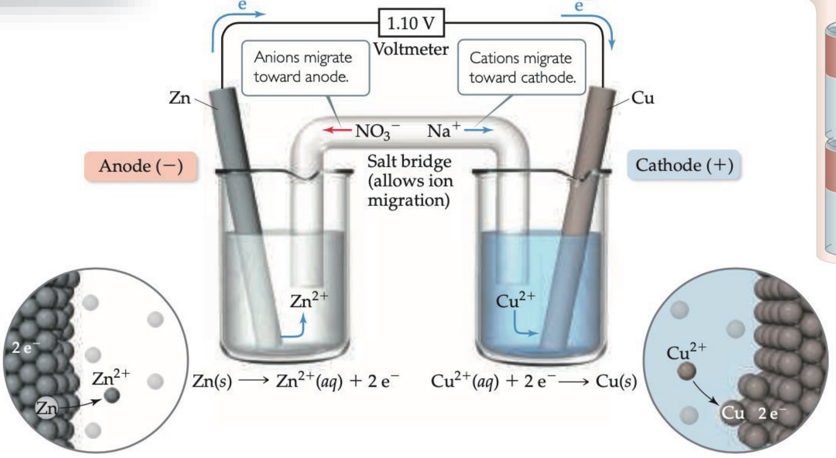
$$\textit{Reduction:}\quad 2\,\mathrm{Fe^{3+}}(aq) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Fe^{2+}}(aq)$$

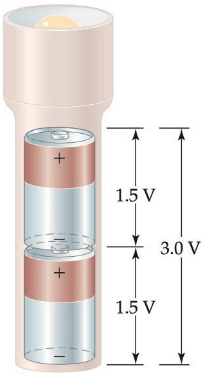
5.1 Summary & Practice

1. Concept

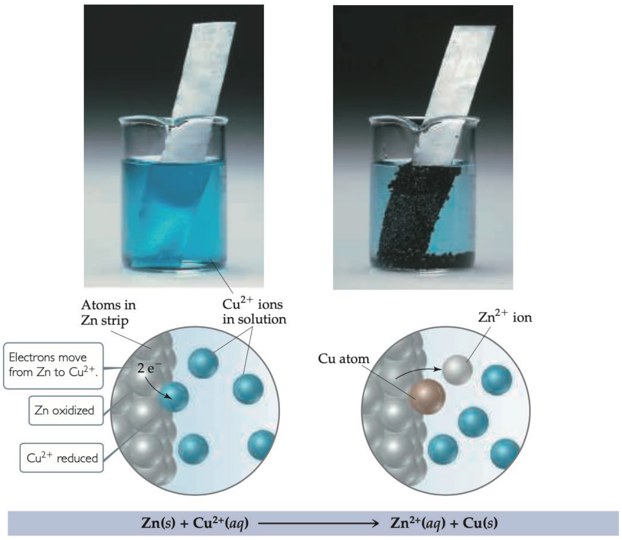
2. Example

5.2 Galvanic Cells

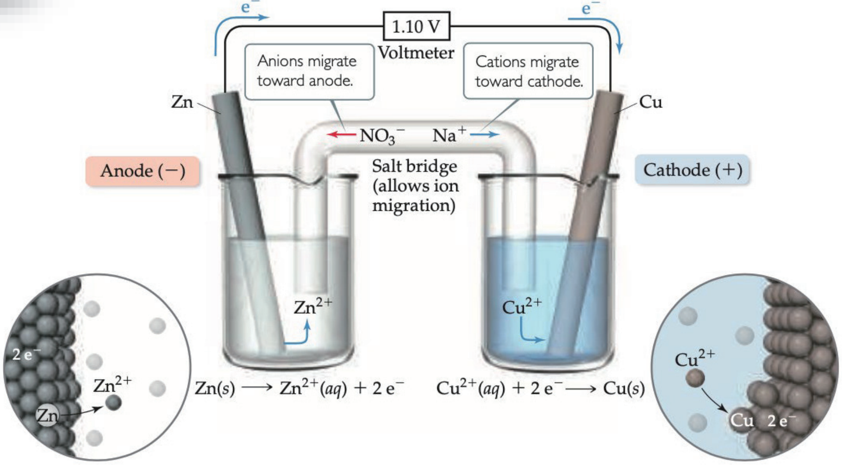




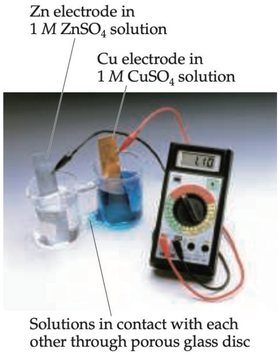
5.2.1 Redox Reaction & Galvanic Cells



5.2.2 The Structure of Galvanic Cells



5.2.3 Electrode in Galvanic Cells



Cathode： gain electron，oxidation number decrease，reduction
Anode：lose electron，oxidation number increase，oxidation

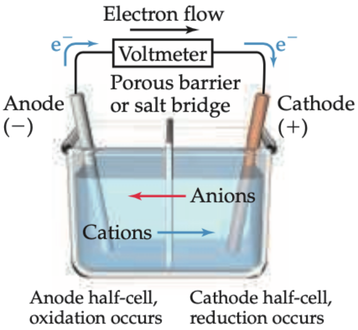
Anode (oxidation half-reaction) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Cathode (reduction half-reaction) $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

The energy released in a spontaneous redox reaction can be used to perform electrical work. This task is accomplished through a **voltaic** (or **galvanic**) **cell**, a device in which the transfer of electrons takes place through an external pathway rather than directly between reactants present in the same reaction vessel.

5.2.4 Free Particles Flow

anions always migrate toward the anode and cations toward the cathode.

electrons flow from the anode through the external circuit to the cathode.



5.2.5 Cell Potentials

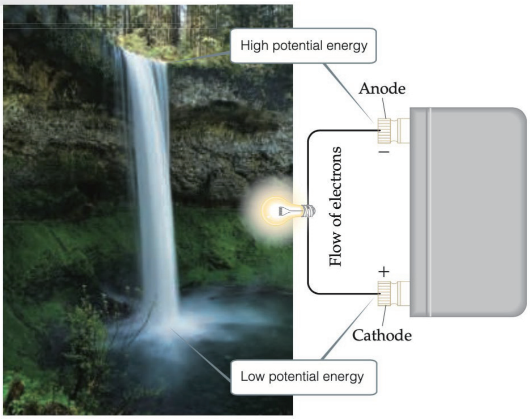
The difference in potential energy per electrical charge (the *potential difference*) between two electrodes is measured in *volts*. One volt (V) is the potential difference required to impart 1 joule (J) of energy to a charge of 1 coulomb (C):

$$1\text{ V} = 1\frac{\text{J}}{\text{C}}$$

The potential difference between the two electrodes of a voltaic cell is called the **cell potential**, denoted *E*cell, also call it the **electromotive** ("causing electron motion") **force**, or **emf**. Because *E*cell is measured in volts, also commonly called the **voltage** of the cell.

5.2.6 Cell Potentials under Standard Conditions

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq, 1\,M) \longrightarrow \mathrm{Zn}^{2+}(aq, 1\,M) + \mathrm{Cu}(s) \qquad E^{\circ}_{\text{cell}} = +1.10\text{ V}$$



The cell potential under standard conditions is called either the **standard cell potential** or **standard emf**

5.2.6 Cell Potentials under Standard Conditions

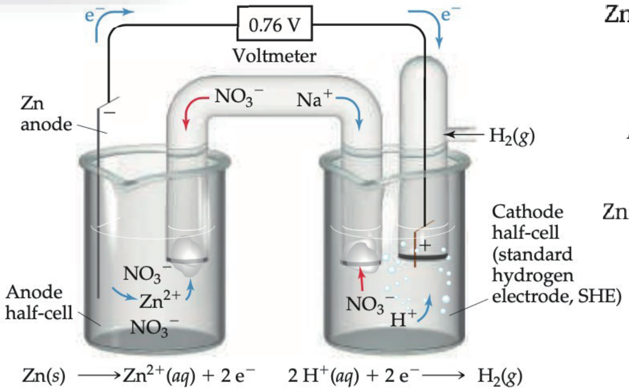
we can assign a standard potential to each half-cell and then use these half-cell potentials to determine E°_{cell}. The cell potential is the difference between two half-cell potentials. By convention, the potential associated with each electrode is chosen to be the potential for *reduction* at that electrode. Thus, standard half-cell potentials are tabulated for reduction reactions, which means they are **standard reduction potentials**, denoted E°_{red}. The standard cell potential, E°_{cell}, is the standard reduction potential of the cathode reaction, E°_{red} (cathode), *minus* the standard reduction potential of the anode reaction, E°_{red} (anode):

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}\,(\text{cathode}) - E^\circ_{\text{red}}\,(\text{anode})$$

$$2\,\text{H}^+(aq, 1\,M) + 2\,\text{e}^- \longrightarrow \text{H}_2(g, 1\text{ atm}) \quad E^\circ_{\text{red}} = 0\text{ V}$$

standard hydrogen electrode
(SHE).

5.2.7 Standard Reduction Potentials



$$\text{Zn}(s) + 2\,\text{H}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{H}_2(g)$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}\,(\text{cathode}) - E^\circ_{\text{red}}\,(\text{anode})$$

$$+0.76\text{ V} = 0\text{ V} - E^\circ_{\text{red}}\,(\text{anode})$$

$$E^\circ_{\text{red}}\,(\text{anode}) = -0.76\text{ V}$$

$$\text{Zn}^{2+}(aq, 1\,M) + 2\,\text{e}^- \longrightarrow \text{Zn}(s) \quad E^\circ_{\text{red}} = -0.76\text{ V}$$

TABLE 20.1 Standard Reduction Potentials in Water at 25°C

E°_{red}(V)	Reduction Half-Reaction
+2.87	$\text{F}_2(g) + 2\,\text{e}^- \longrightarrow 2\,\text{F}^-(aq)$
+1.51	$\text{MnO}_4^-(aq) + 8\,\text{H}^+(aq) + 5\,\text{e}^- \longrightarrow \text{Mn}^{2+}(aq) + 4\,\text{H}_2\text{O}(l)$
+1.36	$\text{Cl}_2(g) + 2\,\text{e}^- \longrightarrow 2\,\text{Cl}^-(aq)$
+1.33	$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\,\text{H}^+(aq) + 6\,\text{e}^- \longrightarrow 2\,\text{Cr}^{3+}(aq) + 7\,\text{H}_2\text{O}(l)$
+1.23	$\text{O}_2(g) + 4\,\text{H}^+(aq) + 4\,\text{e}^- \longrightarrow 2\,\text{H}_2\text{O}(l)$
+1.06	$\text{Br}_2(l) + 2\,\text{e}^- \longrightarrow 2\,\text{Br}^-(aq)$
+0.96	$\text{NO}_3^-(aq) + 4\,\text{H}^+(aq) + 3\,\text{e}^- \longrightarrow \text{NO}(g) + 2\,\text{H}_2\text{O}(l)$
+0.80	$\text{Ag}^+(aq) + \text{e}^- \longrightarrow \text{Ag}(s)$
+0.77	$\text{Fe}^{3+}(aq) + \text{e}^- \longrightarrow \text{Fe}^{2+}(aq)$
+0.68	$\text{O}_2(g) + 2\,\text{H}^+(aq) + 2\,\text{e}^- \longrightarrow \text{H}_2\text{O}_2(aq)$
+0.59	$\text{MnO}_4^-(aq) + 2\,\text{H}_2\text{O}(l) + 3\,\text{e}^- \longrightarrow \text{MnO}_2(s) + 4\,\text{OH}^-(aq)$
+0.54	$\text{I}_2(s) + 2\,\text{e}^- \longrightarrow 2\,\text{I}^-(aq)$
+0.40	$\text{O}_2(g) + 2\,\text{H}_2\text{O}(l) + 4\,\text{e}^- \longrightarrow 4\,\text{OH}^-(aq)$
+0.34	$\text{Cu}^{2+}(aq) + 2\,\text{e}^- \longrightarrow \text{Cu}(s)$
0 [defined]	$2\,\text{H}^+(aq) + 2\,\text{e}^- \longrightarrow \text{H}_2(g)$
−0.28	$\text{Ni}^{2+}(aq) + 2\,\text{e}^- \longrightarrow \text{Ni}(s)$
−0.44	$\text{Fe}^{2+}(aq) + 2\,\text{e}^- \longrightarrow \text{Fe}(s)$
−0.76	$\text{Zn}^{2+}(aq) + 2\,\text{e}^- \longrightarrow \text{Zn}(s)$
−0.83	$2\,\text{H}_2\text{O}(l) + 2\,\text{e}^- \longrightarrow \text{H}_2(g) + 2\,\text{OH}^-(aq)$
−1.66	$\text{Al}^{3+}(aq) + 3\,\text{e}^- \longrightarrow \text{Al}(s)$
−2.71	$\text{Na}^+(aq) + \text{e}^- \longrightarrow \text{Na}(s)$
−3.05	$\text{Li}^+(aq) + \text{e}^- \longrightarrow \text{Li}(s)$

Because electrical potential measures potential energy per electrical charge, standard reduction potentials are intensive properties.

Thus, *changing the stoichiometric coefficient in a half-reaction does not affect the value of the standard reduction potential*

5.2.8 Free Energy, and the Equilibrium Constant

$$\Delta G = -nFE$$

F is the **Faraday constant**

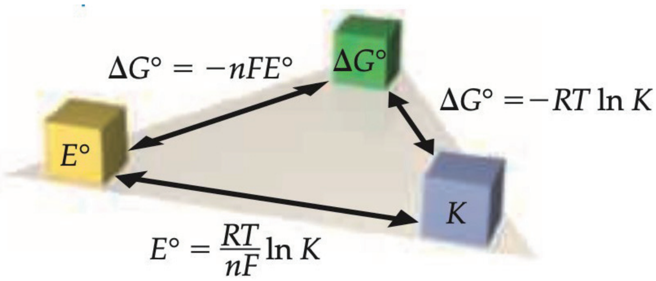
$F = 96{,}485\ \mathrm{C/mol} = 96{,}485\ \mathrm{J/V\text{-}mol}$

$$\Delta G^\circ = -RT \ln K$$

$$E^\circ = \frac{\Delta G^\circ}{-nF} = \frac{-RT\ln K}{-nF} = \frac{RT}{nF}\ln K$$

Michael Faraday. (1791–1867)

5.2.8 Free Energy, and the Equilibrium Constant



5.2.9 The Nernst Equation

$$\Delta G = \Delta G^\circ + RT\ln Q$$

$$-nFE = -nFE^\circ + RT\ln Q$$

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(aq) \longrightarrow \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

$$E = 1.10\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

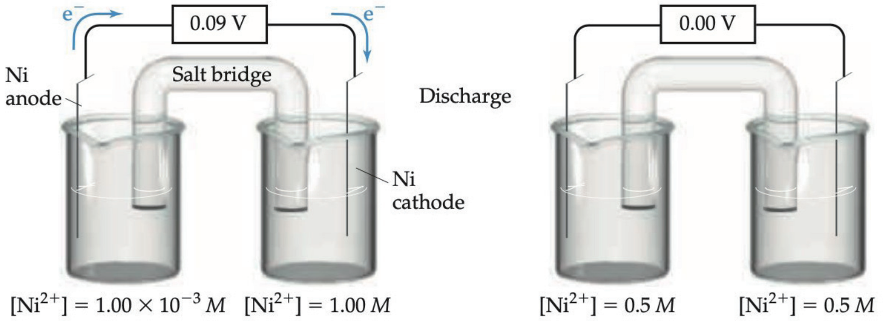
5.2.10

Concentration Cells

$$E = E^\circ - \frac{0.0592\text{ V}}{n}\log Q$$

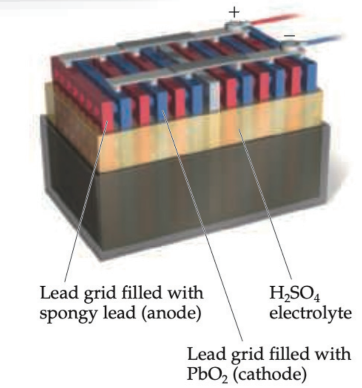
$$= 0 - \frac{0.0592\text{ V}}{2}\log\frac{[\mathrm{Ni}^{2+}]_{\text{dilute}}}{[\mathrm{Ni}^{2+}]_{\text{concentrated}}} = -\frac{0.0592\text{ V}}{2}\log\frac{1.00\times10^{-3}\,M}{1.00\,M}$$

$$= +0.089\text{ V}$$

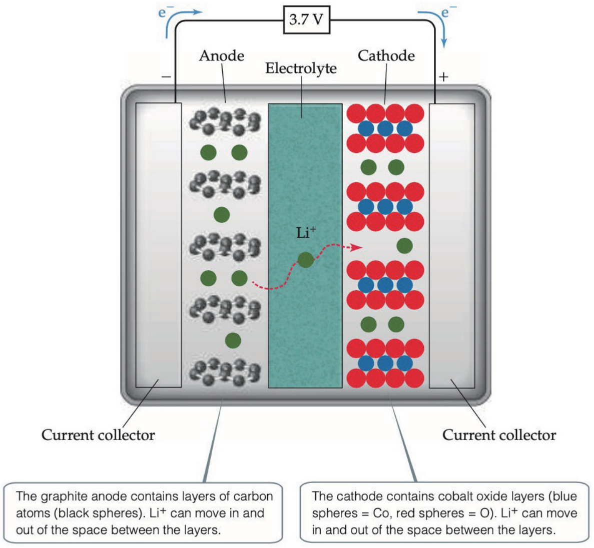


5.2.11

Battery



$2\,\mathrm{PbSO_4}(s) + 2\,\mathrm{H_2O}(l) \longrightarrow \mathrm{PbO_2}(s) + \mathrm{Pb}(s) + 2\,\mathrm{HSO_4^-}(aq) + 2\,\mathrm{H^+}(aq)$



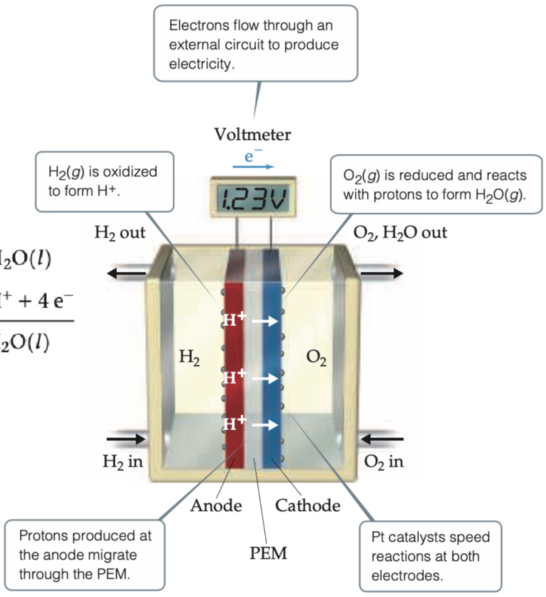
The graphite anode contains layers of carbon atoms (black spheres). Li⁺ can move in and out of the space between the layers.

The cathode contains cobalt oxide layers (blue spheres = Co, red spheres = O). Li⁺ can move in and out of the space between the layers.

5.2.11

Battery

Cathode:	$O_2(g) + 4\,H^+ + 4\,e^-$	$\longrightarrow 2\,H_2O(l)$
Anode:	$2\,H_2(g)$	$\longrightarrow 4\,H^+ + 4\,e^-$
Overall:	$2\,H_2(g) + O_2(g)$	$\longrightarrow 2\,H_2O(l)$



Electrons flow through an external circuit to produce electricity.

$H_2(g)$ is oxidized to form H+.

$O_2(g)$ is reduced and reacts with protons to form $H_2O(g)$.

Protons produced at the anode migrate through the PEM.

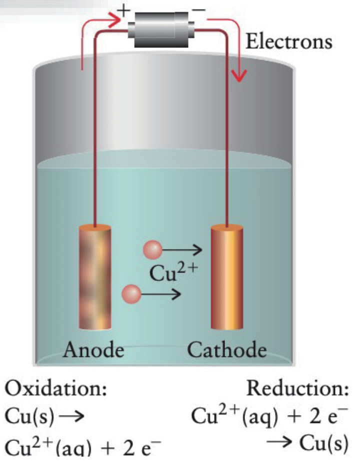
Pt catalysts speed reactions at both electrodes.

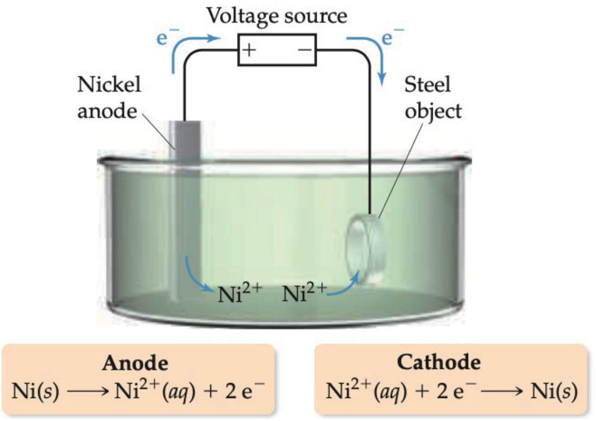
5.2 Summary & Practice

1. Concept

2. Example

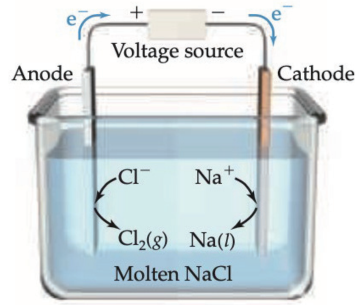
5.3 Electrolysis





5.3.1 Electrolytic Cells

Processes driven by an outside source of electrical energy are called **electrolysis reactions** and take place in **electrolytic cells**.



$2\,Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

$2\,Na^+(l) + 2e^- \longrightarrow 2\,Na(l)$

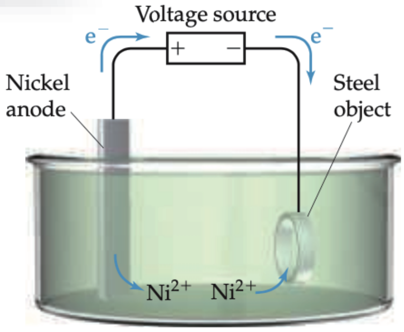
Cathode: $2\,Na^+(l) + 2e^- \longrightarrow 2\,Na(l)$

Anode: $2\,Cl^-(l) \longrightarrow Cl_2(g) + 2e^-$

Overall: $2\,Na^+(l) + 2\,Cl^-(l) \longrightarrow 2\,Na(l) + Cl_2(g)$

5.3.1

Electrolytic Cells



Anode
$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^-$

Cathode
$Ni^{2+}(aq) + 2\,e^- \longrightarrow Ni(s)$

$$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^- \qquad E^\circ_{red} = +1.23\text{ V}$$

$$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \qquad E^\circ_{red} = -0.28\text{ V}$$

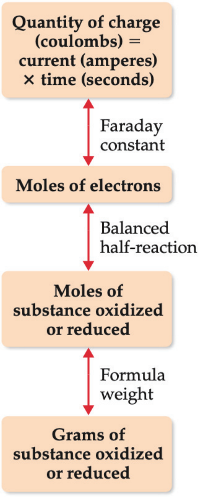
5.3.2

Quantitative Aspects of Electrolysis

$$\text{coulombs} = \text{amperes} \times \text{seconds}$$

$$n = \frac{Q}{F} = \frac{It}{F}$$

The quantity of charge passing through an electrical circuit, such as that in an electrolytic cell, is generally measured in *coulombs*. The charge on 1 mol of electrons is 96,485 C. A coulomb is the quantity of charge passing a point in a circuit in 1 s when the current is 1 ampere (A)



Quantity of charge (coulombs) = current (amperes) × time (seconds)

Faraday constant

Moles of electrons

Balanced half-reaction

Moles of substance oxidized or reduced

Formula weight

Grams of substance oxidized or reduced

Primary cells		
dry	$Zn(s)\mid ZnCl_2(aq), NH_4Cl(aq)\mid MnO(OH)(s)\mid MnO_2(s)\mid$graphite, Anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$ followed by $Zn^{2+}(aq) + 4\,NH_3(aq) \longrightarrow [Zn(NH_3)_4]^{2+}(aq)$ Cathode: $MnO_2(s) + H_2O(l) + e^- \longrightarrow MnO(OH)(s) + OH^-(aq)$ followed by $NH_4^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + NH_3(aq)$	1.5 V
alkaline	$Zn(s)\mid ZnO(s)\mid OH^-(aq)\mid Mn(OH)_2(s)\mid MnO_2(s)\mid$graphite, Anode: $Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$ Cathode: $MnO_2(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow Mn(OH)_2(s) + 2\,OH^-(aq)$	1.5 V
silver	$Zn(s)\mid ZnO(s)\mid KOH(aq)\mid Ag_2O(s)\mid Ag(s)\mid$steel, Anode: $Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$ Cathode: $Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq)$	1.6 V
Secondary cells		
lead–acid	$Pb(s)\mid PbSO_4(s)\mid H^+(aq), HSO_4^-(aq)\mid PbO_2(s)\mid PbSO_4(s)\mid Pb(s)$, Anode: $Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$ Cathode: $PbO_2(s) + 3\,H^+(aq) + HSO_4^-(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$	2 V
nicad	$Cd(s)\mid Cd(OH)_2(s)\mid KOH(aq)\mid Ni(OH)_3(s)\mid Ni(OH)_2(s)\mid Ni(s)$, Anode: $Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-$ Cathode: $2\,Ni(OH)_3(s) + 2\,e^- \longrightarrow 2\,Ni(OH)_2(s) + 2\,OH^-(aq)$	1.25 V
NiMH	$M(s)\mid MH(s)\mid KOH(aq)\mid NiOOH(s)\mid Ni(OH)_2(s)\mid Ni(s)$, Anode: $MH(s)^\dagger + OH^-(aq) \longrightarrow M(s) + H_2O(l) + e^-$ Cathode: $NiOOH(s) + H_2O(l) + e^- \longrightarrow Ni(OH)_2(s) + OH^-$	1.2 V
sodium–sulfur	$Na(l)\mid Na^+$(ceramic electrolyte),S^{2-}(ceramic electrolyte)$\mid S_8(l)$, Anode: $2\,Na(l) \longrightarrow 2\,Na^+$(electrolyte) $+ 2\,e^-$ Cathode: $S_8(l) + 16\,e^- \longrightarrow 8\,S^{2-}$(electrolyte)	2.2 V

5.3 Summary & Practice

1. Concept

2. Example

UKChO

英国化学奥林匹克竞赛

Unit 6

General Review of Inorganic Chemistry

UKChO

英国化学奥林匹克竞赛

Unit 7 Structure Determines Properties

1.Introduction

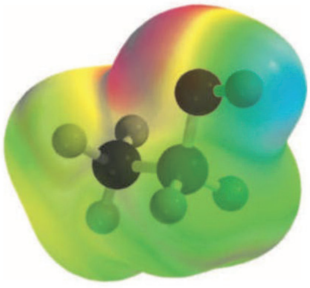
2.Isomer

3.Nomenclature

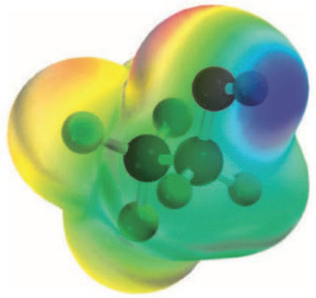
7.1 Structure Determines Properties

X = H: Ethanol
X = F: 2,2,2-Trifluoroethanol

X = H: Conjugate base of ethanol
X = F: Conjugate base of 2,2,2-trifluoroethanol



Ethanol (CH_3CH_2OH)



2,2,2-Trifluoroethanol (CF_3CH_2OH)

7.1.1

What is Organic Chemistry

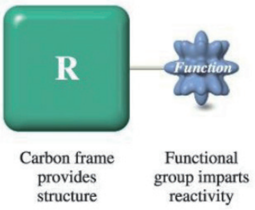
Organic chemistry is the chemistry of the compounds of carbon.

- The compounds of carbon are central to life on this planet.
- Every living organism is made of organic compounds.
- Consider what the world would be like if all the carbon and carbon compounds were removed suddenly. The result would be somewhat like the barren surface of the moon.
- Life is organic chemistry.

7.1.2

Organic Compound

A goal of organic chemistry is to relate the structure of a molecule to the reactions that it can undergo. We can then study the steps by which each type of reaction takes place, and we can learn to create new molecules by applying those processes.



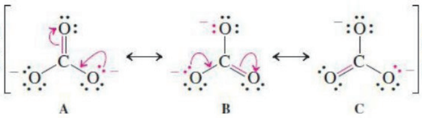
Thus, it makes sense to classify organic molecules according to the subunits and bonds that determine their chemical reactivity: These determinants are groups of atoms called functional groups.

7.1.3

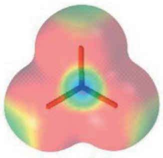
Resonance

Resonance Forms of the Carbonate Ion

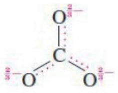
Square brackets, "[ ]" and double-headed arrows, "⟷", are used to depict resonance forms



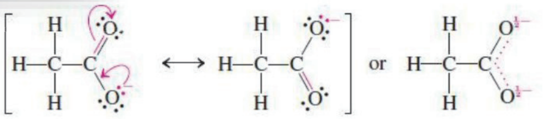
Red arrows ↷ denote the movement of electron pairs: "electron pushing"



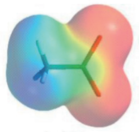
Carbonate ion



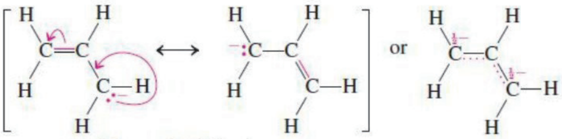
7.1.3 Resonance



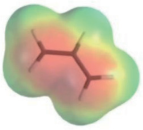
Acetate ion



Acetate ion

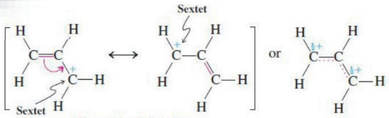


2-Propenyl (allyl) anion

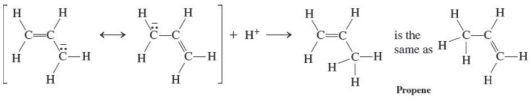


2-Propenyl anion

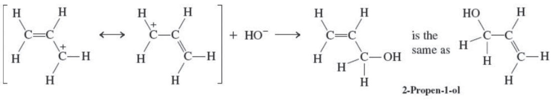
7.1.3 Resonance



2-Propenyl (allyl) cation

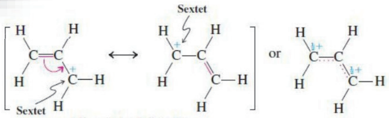


Propene

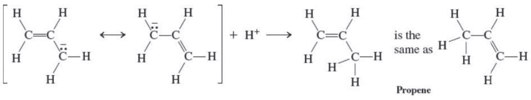


2-Propen-1-ol

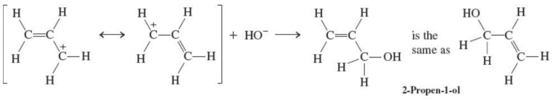
7.1.3 Resonance



2-Propenyl (allyl) cation



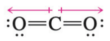
Propene



2-Propen-1-ol

7.1.4 Molecular Dipole Moments

The molecular dipole moment is the resultant of all of the individual bond dipole moments of a substance

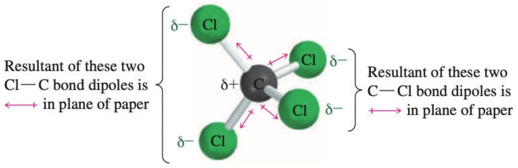

Carbon dioxide

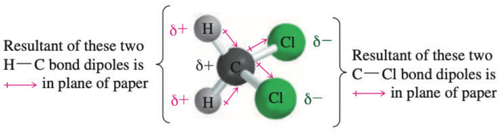
Dipole moment = 0 D

Which of the following compounds would you expect to have a dipole moment? If the molecule has a dipole moment, specify its direction.

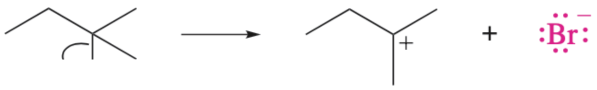
(a) BF_3
(b) H_2O
(c) CH_4
(d) CH_3Cl
(e) CH_2O
(f) HCN

7.1.4 Molecular Dipole Moments



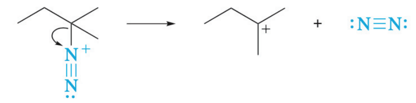


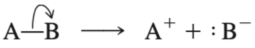
7.1.5 Curved Arrows, Arrow Pushing, and Chemical Reactions

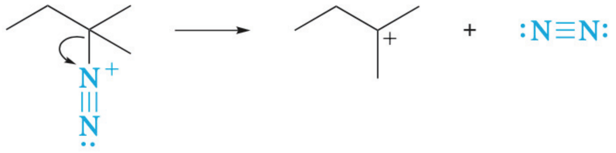


ocation Bromide ion

$AB \longrightarrow A^+ + B^-$


A diazonium ion A carbocation Nitrogen


$A{-}B \longrightarrow A^+ + :B^-$


A diazonium ion A carbocation Nitrogen

7.1.5

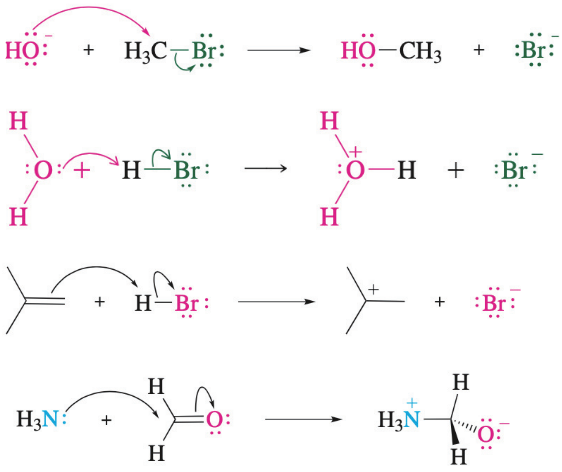
Curved Arrows, Arrow Pushing, and Chemical Reactions

The reverse of a dissociation is a combination, such as the formation of a covalent bond between a cation A^+ and an anion $:B^-$.

Here the tail of the curved arrow begins at the middle of the unshared electron pair of $:B^-$ and the head points to the location of the new bond—in this case the open space just before A^+. *Electrons flow from sites of higher electron density to lower.* The unshared electron pair of $:B^-$ becomes the shared pair in the A—B bond.

7.1.5

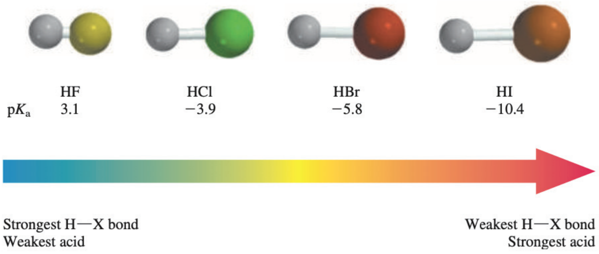
Curved Arrows, Arrow Pushing, and Chemical Reactions



7.1.6

How Structure Affects Acid Strength

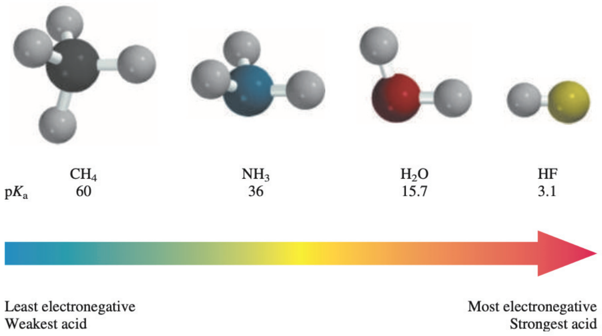
Bond Strength. The effect of bond strength is easy to see by comparing the acidities of the hydrogen halides.



7.1.6

How Structure Affects Acid Strength

Electronegativity. The effect of electronegativity on acidity is evident in the following series involving bonds between hydrogen and the second-row elements C, N, O, and F.



7.1.6

How Structure Affects Acid Strength

(a) Which is the stronger acid: $(CH_3)_3\overset{+}{N}H$ or $(CH_3)_2\overset{+}{\underset{..}{O}}H$?

(b) Which is the stronger base: $(CH_3)_3N\colon$ or $(CH_3)_2\ddot{O}\colon$?

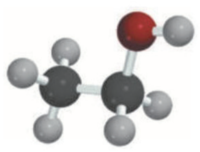
Sample Solution (a) The ionizable proton is bonded to N in $(CH_3)_3\overset{+}{N}H$ and to O in $(CH_3)_2\overset{+}{\underset{..}{O}}H$.

Nitrogen and oxygen are in the same row of the periodic table, so their relative electronegativities are the determining factor. Oxygen is more electronegative than nitrogen; therefore $(CH_3)_2\overset{+}{\underset{..}{O}}H$ is a stronger acid than $(CH_3)_3\overset{+}{N}H$.

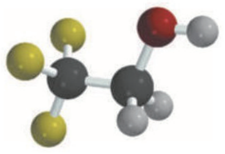
7.1.6

How Structure Affects Acid Strength

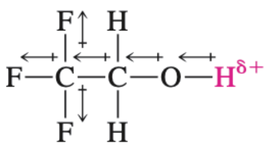
	HO—H	CH_3O—H	CH_3CH_2O—H	$(CH_3)_2CHO$—H	$(CH_3)_3CO$—H
	Water	Methanol	Ethanol	Isopropyl alcohol	*tert*-Butyl alcohol
pK_a	15.7	15.2	16	17	18



CH_3CH_2O—H
Ethanol
pK_a 16



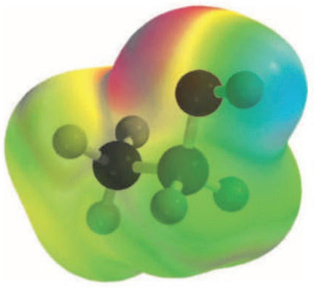
CF_3CH_2O—H
2,2,2-Trifluoroethanol
11.3



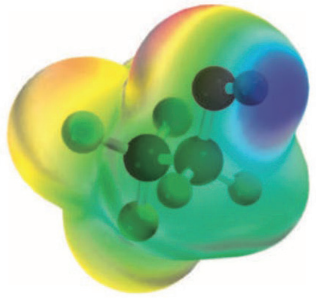
7.1.6 How Structure Affects Acid Strength

X = H: Ethanol
X = F: 2,2,2-Trifluoroethanol

X = H: Conjugate base of ethanol
X = F: Conjugate base of 2,2,2-trifluoroethanol



Ethanol (CH_3CH_2OH)

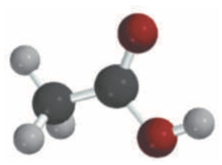


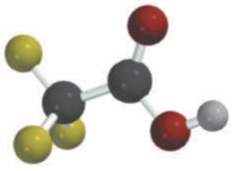
2,2,2-Trifluoroethanol (CF_3CH_2OH)

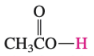
7.1.6 How Structure Affects Acid Strength

Structural effects that are transmitted through bonds are called **inductive effects.** A substituent *induces* a polarization in the bonds between it and some remote site.

The same kind of inductive effects that make CF_3CH_2OH a stronger acid than CH_3CH_2OH makes the trifluoro derivative of acetic acid more than 4 pK_a units stronger than acetic acid.

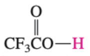






$CH_3\overset{\overset{O}{\|}}{C}O{-}H$

Acetic acid



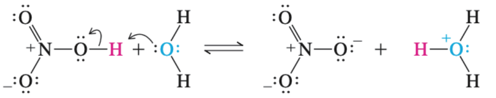
$CF_3\overset{\overset{O}{\|}}{C}O{-}H$

Trifluoroacetic acid

	Acetic acid	Trifluoroacetic acid
pK_a	4.7	0.50

7.1.6 How Structure Affects Acid Strength

Electron Delocalization in the Conjugate Base. With a pK_a of -1.4, nitric acid is almost completely ionized in water. If we look at the Lewis formula of nitric acid in light of what we have said about inductive effects, we can see why. The N atom in nitric acid is not only electronegative in its own right, but bears a formal charge of $+1$, which enhances its ability to attract electrons away from the —OH group. But inductive effects are only part of the story. When nitric acid transfers its proton to water, nitrate ion is produced.



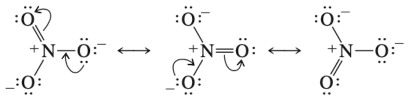
Nitric acid (acid)

Water (base)

Nitrate ion (conjugate base)

Hydronium ion (conjugate acid)

Nitrate ion is stabilized by electron delocalization, which we can represent in terms of resonance between three equivalent contributing structures:

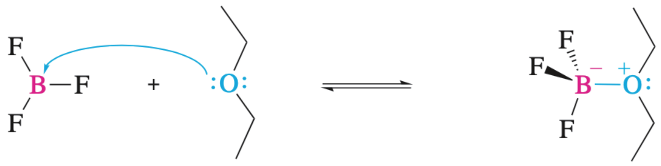


7.1.7

Acids and Bases: The Lewis View


Lewis acid Lewis base

Lewis acid Lewis base

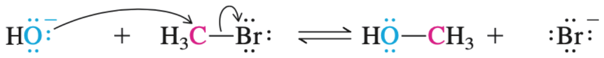

Boron trifluoride (Lewis acid)

Diethyl ether (Lewis base)

"Boron trifluoride etherate" (Lewis acid/Lewis base complex)

7.1.7

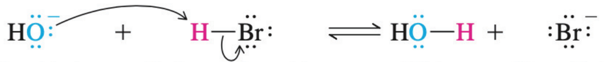
Acids and Bases: The Lewis View


Hydroxide ion (Lewis base)

Bromomethane (Lewis acid)

Methanol

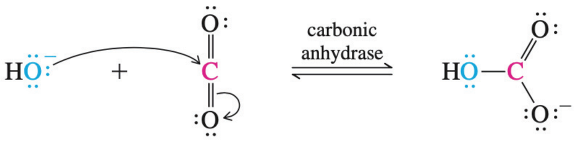
Bromide ion


Hydroxide ion (Lewis base)

Hydrogen bromide (Lewis acid)

Water

Bromide ion



Hydroxide ion (Lewis base)

Carbon dioxide (Lewis acid)

Hydrogen carbonate ion

7.1

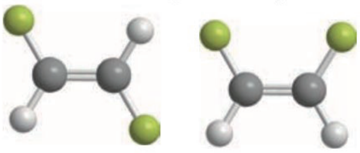
Summary & Practice

1. Concept

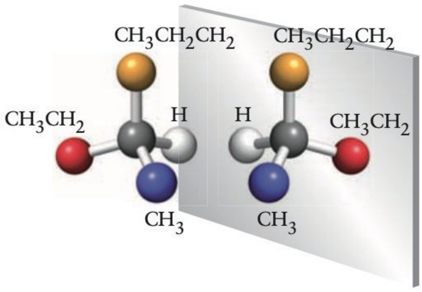
2. Example

7.2 Isomer

Same atoms, same partners
different arrangements in space



Geometrical isomers



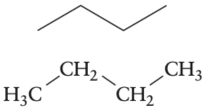
7.2.1 Isomer

Different compounds that have the same molecular formula are classified as **isomers.**

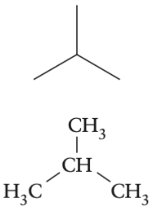
Isomers can be either **constitutional isomers** (differ in connectivity) or **stereoisomers** (differ in arrangement of atoms in space).

Constitutional isomers are also sometimes called **structural isomers.**

7.2.1 Structural Isomers



24 Butane, C_4H_{10}



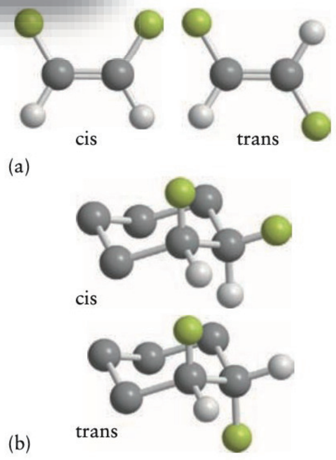
25 Methylpropane, C_4H_{10}

Molecules that are **structural isomers** are built from the same atoms, but the atoms are connected differently; that is, the molecules have a different **connectivity.**

Write the condensed structural formulas for the five isomeric alkanes of molecular formula C_6H_{14}.

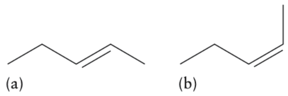
7.2.2

Stereoisomers (geometrical isomers)



In **stereoisomers,** the molecules have the same connectivity but the atoms are arranged differently in space.

Geometrical isomers, in which atoms have different arrangements on either side of a double bond or above and below the ring of a cycloalkane or cycloalkene



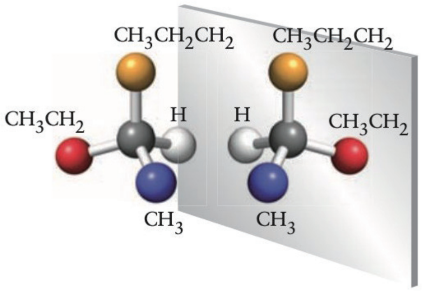
26

7.2.3

Stereoisomers (optical isomers)

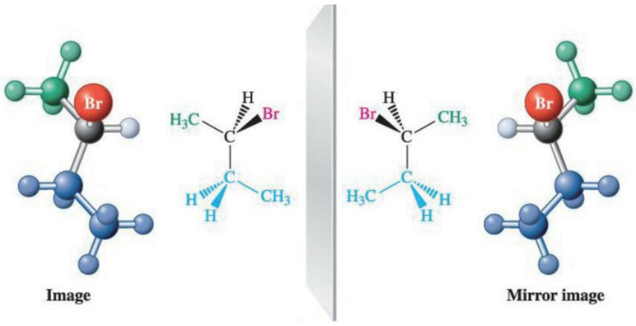
Optical isomers are two compounds with molecules that are exact mirror images of each other but are not superimposable.

Chiral molecule, a molecule that can be superimposed on its mirror image, just as you could superimpose a pair of eyeglasses on its mirror image.



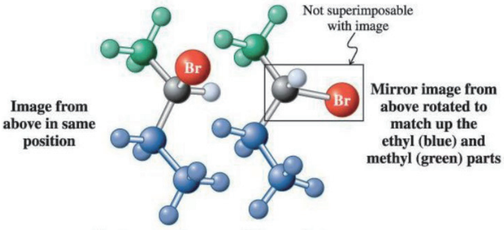
7.2.4

Chiral Molecules

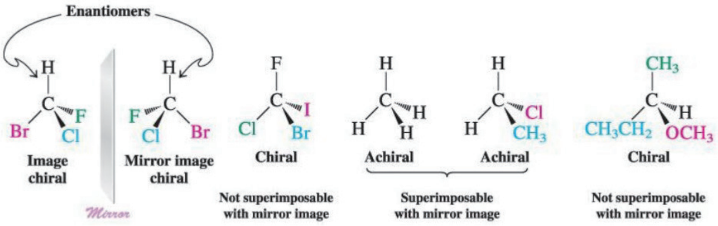


7.2.4

Chiral Molecules

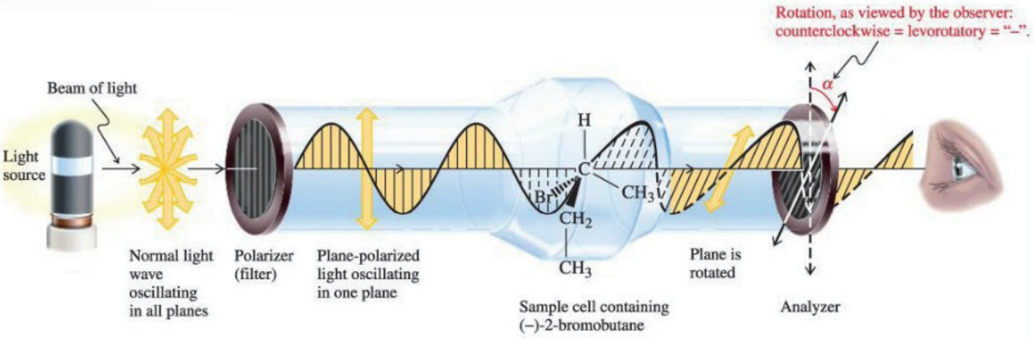


The two enantiomers of 2-bromobutane are nonsuperimposable



7.2.4

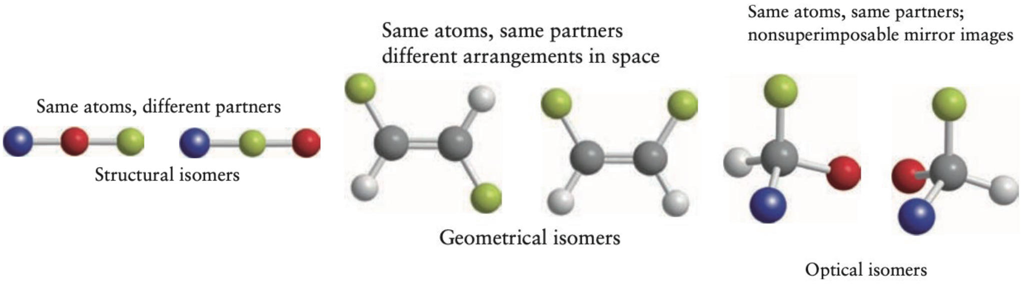
Optical Activity



7.2.5

Isomer Summary

Structural isomers have identical molecular formulas, but their atoms are linked to different neighbors. Geometrical isomers have the same molecular and structural formulas but different arrangements in space. Molecules with four different groups attached to a single carbon atom are chiral; they are optical isomers.

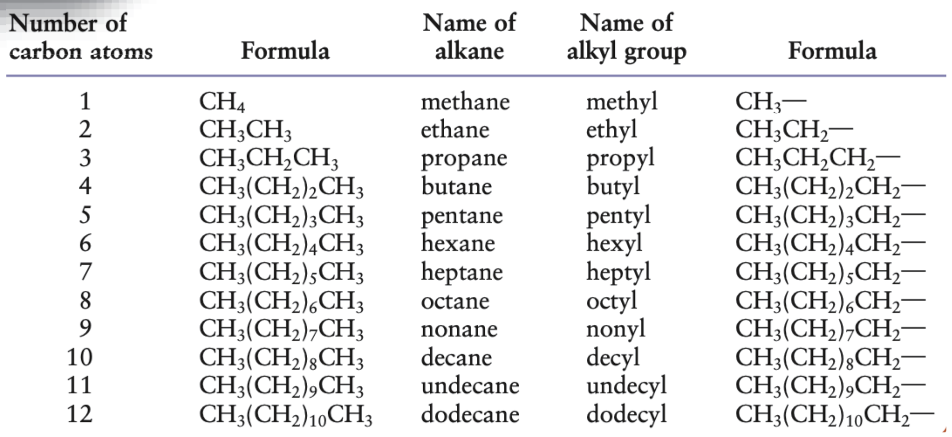


7.2 Summary & Practice

1. Concept

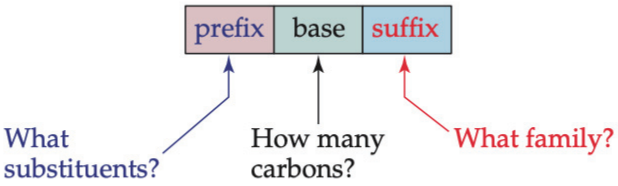
2. Example

7.3 Nomenclature



Number of carbon atoms	Formula	Name of alkane	Name of alkyl group	Formula
1	CH_4	methane	methyl	$CH_3—$
2	CH_3CH_3	ethane	ethyl	$CH_3CH_2—$
3	$CH_3CH_2CH_3$	propane	propyl	$CH_3CH_2CH_2—$
4	$CH_3(CH_2)_2CH_3$	butane	butyl	$CH_3(CH_2)_2CH_2—$
5	$CH_3(CH_2)_3CH_3$	pentane	pentyl	$CH_3(CH_2)_3CH_2—$
6	$CH_3(CH_2)_4CH_3$	hexane	hexyl	$CH_3(CH_2)_4CH_2—$
7	$CH_3(CH_2)_5CH_3$	heptane	heptyl	$CH_3(CH_2)_5CH_2—$
8	$CH_3(CH_2)_6CH_3$	octane	octyl	$CH_3(CH_2)_6CH_2—$
9	$CH_3(CH_2)_7CH_3$	nonane	nonyl	$CH_3(CH_2)_7CH_2—$
10	$CH_3(CH_2)_8CH_3$	decane	decyl	$CH_3(CH_2)_8CH_2—$
11	$CH_3(CH_2)_9CH_3$	undecane	undecyl	$CH_3(CH_2)_9CH_2—$
12	$CH_3(CH_2)_{10}CH_3$	dodecane	dodecyl	$CH_3(CH_2)_{10}CH_2—$

7.3.1 Naming Alkanes



prefix | base | suffix

What substituents?

How many carbons?

What family?

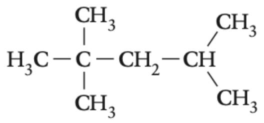
7.3.1

Naming Alkanes

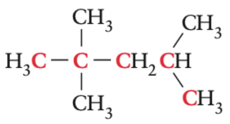
Number of carbon atoms	Formula	Name of alkane	Name of alkyl group	Formula
1	CH_4	methane	methyl	$CH_3—$
2	CH_3CH_3	ethane	ethyl	$CH_3CH_2—$
3	$CH_3CH_2CH_3$	propane	propyl	$CH_3CH_2CH_2—$
4	$CH_3(CH_2)_2CH_3$	butane	butyl	$CH_3(CH_2)_2CH_2—$
5	$CH_3(CH_2)_3CH_3$	pentane	pentyl	$CH_3(CH_2)_3CH_2—$
6	$CH_3(CH_2)_4CH_3$	hexane	hexyl	$CH_3(CH_2)_4CH_2—$
7	$CH_3(CH_2)_5CH_3$	heptane	heptyl	$CH_3(CH_2)_5CH_2—$
8	$CH_3(CH_2)_6CH_3$	octane	octyl	$CH_3(CH_2)_6CH_2—$
9	$CH_3(CH_2)_7CH_3$	nonane	nonyl	$CH_3(CH_2)_7CH_2—$
10	$CH_3(CH_2)_8CH_3$	decane	decyl	$CH_3(CH_2)_8CH_2—$
11	$CH_3(CH_2)_9CH_3$	undecane	undecyl	$CH_3(CH_2)_9CH_2—$
12	$CH_3(CH_2)_{10}CH_3$	dodecane	dodecyl	$CH_3(CH_2)_{10}CH_2—$

7.3.1

Naming Alkanes

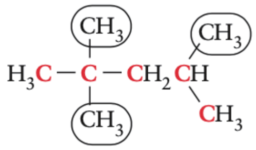


(a) Count carbon atoms in the longest chain.



The longest carbon chain (in red) has 5 carbon atoms. The molecule is a substituted pentane

Identify and count substituents.

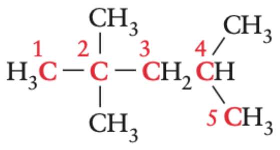


There are 3 methyl groups (CH_3¬) on the longest chain

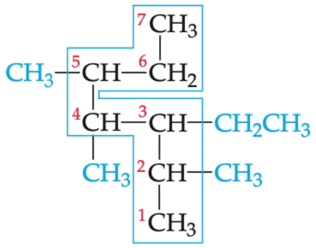
7.3.1

Naming Alkanes

Number the backbone carbon atoms to give the lowest numbers to the substituents.

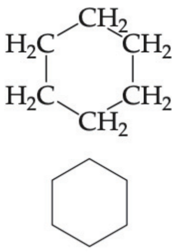


2,2,4-trimethylpentane



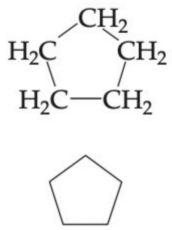
7.3.2 Naming Cycloalkane

Alkanes that form rings, or cycles, are called **cycloalkanes**



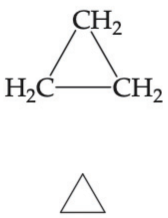
Cyclohexane

Each vertex represents one CH$_2$ group



Cyclopentane

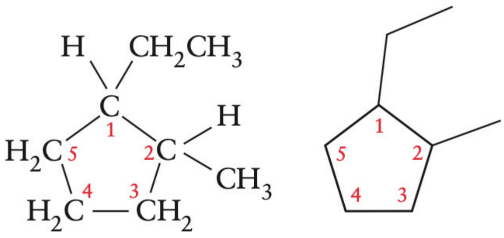
Five vertices = five CH$_2$ groups



Cyclopropane

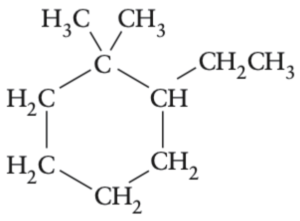
Three vertices = three CH$_2$ groups

7.3.2 Naming Cycloalkane



1-Ethyl-2-methylcyclopentane

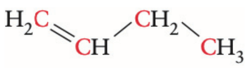
2-ethyl-1,1-dimethylcyclohexane



7.3.3 Naming Alkenes

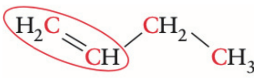
Name the alkene $CH_3CH_2CH{=}CH_2$

(a) ***Step 1.*** Count carbon atoms in the longest chain.



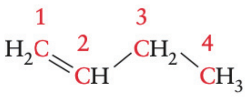
The longest chain (in red) is 4, indicating the root but-.

Step 2. Identify and count substituents and multiple bonds.



There are no substituents, but there is a double bond, so the suffix is -ene.

Step 3. Number the backbone carbon atoms to give the lowest numbers to the location of the double bond.



$CH_3CH_2CH{=}CH_2$ is 1-butene (not 3-butene).

7.3.3 Summary & Practice

1. Concept

2. Example

UKChO

英国化学奥林匹克竞赛

Unit 8 Hydrocarbon

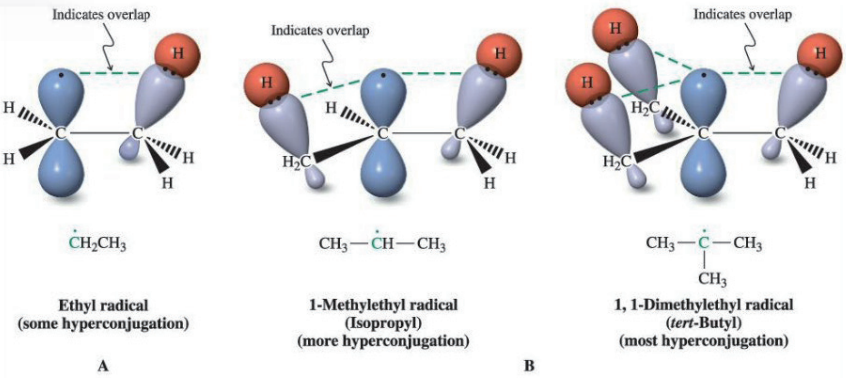
1.Alkane

2. Cycloalkanes

3. Alkenes

4. Benzene and aromaticity

8.1 Alkane



Ethyl radical
(some hyperconjugation)
A

1-Methylethyl radical
(Isopropyl)
(more hyperconjugation)
B

1, 1-Dimethylethyl radical
(*tert*-Butyl)
(most hyperconjugation)

8.1.1

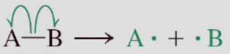
Strength of Alkane Bonds: Radicals

$$\mathrm{H{-}H} \xrightarrow{\text{Bond breaking}} \mathrm{H\cdot + H\cdot} \qquad \Delta H^\circ = DH^\circ = 104\ \text{kcal mol}^{-1}\ (435\ \text{kJ mol}^{-1})$$

Endothermic: heat is consumed when bonds are broken

Radicals are formed by homolytic cleavage

Homolytic Cleavage: Bonding Electrons Separate



$$\mathrm{A{-}B} \longrightarrow \mathrm{A\cdot + \cdot B}$$

Radicals

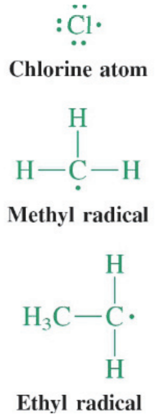
Heterolytic Cleavage: Bonding Electrons Move as Pair

$$\mathrm{A{-}B} \longrightarrow \mathrm{A^+ + {:}B^-}$$

Ions

8.1.1

Strength of Alkane Bonds: Radicals



Chlorine atom

Methyl radical

Ethyl radical

Increasing size of the halogen →

Decreasing electronegativity of the halogen →

Decreasing polarity of the H—X or C—X bond →

Increasing bond length →

Decreasing strength of the H—X or C—X bond →

	$\overset{\delta^+\ \delta^-}{\mathrm{H{-}F}}$	$\overset{\delta^+\ \delta^-}{\mathrm{H{-}Cl}}$	$\overset{\delta^+\ \delta^-}{\mathrm{H{-}Br}}$	$\overset{\delta^+\ \delta^-}{\mathrm{H{-}I}}$	
DH° =	136	103	87	71	kcal mol^{-1}
	$CH_3{-}F$	$CH_3{-}Cl$	$CH_3{-}Br$	$CH_3{-}I$	
DH° =	110	85	70	57	kcal mol^{-1}

8.1.1

Strength of Alkane Bonds: Radicals

C–H Bond Strength in Alkanes

	$CH_3{-}H$	>	$RCH_2{-}H$	>	$R_2CH{-}H$	>	$R_3C{-}H$	
	Methyl		Primary		Secondary		Tertiary	
DH° =	105		101		98.5		96.5	kcal mol^{-1}

Decreasing bond strength, DH° →

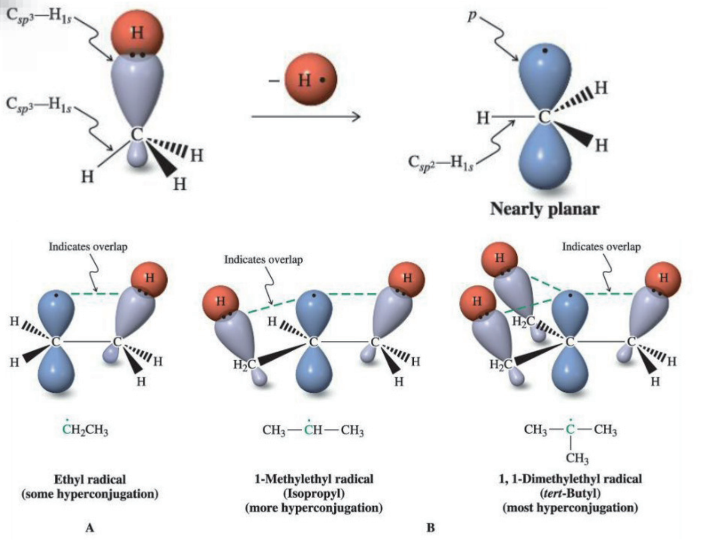
Radical Stabilities

Increasing stability →

$\cdot CH_3$	<	$\cdot CH_2R$	<	$\cdot CHR_2$	<	$\cdot CR_3$
Methyl		Primary		Secondary		Tertiary

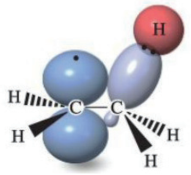
Decreasing DH° of alkane R–H →

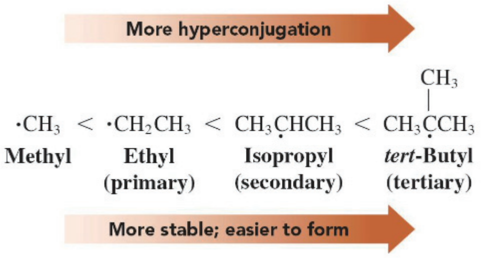
8.1.2 Structure of Alkyl Radicals: Hyperconjugation



8.1.2 Structure of Alkyl Radicals: Hyperconjugation

Hyperconjugative Overlap in Ethyl Radical





More hyperconjugation

$$\cdot CH_3 < \cdot CH_2CH_3 < CH_3\dot{C}HCH_3 < CH_3\underset{\cdot}{\overset{CH_3}{C}}CH_3$$

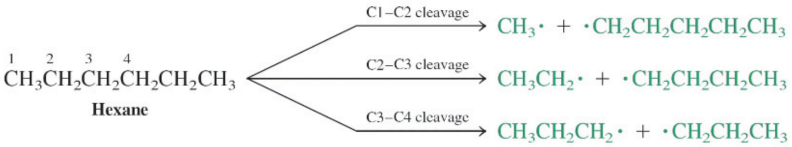
Methyl	Ethyl (primary)	Isopropyl (secondary)	*tert*-Butyl (tertiary)

More stable; easier to form

8.1.3 Conversion of Petroleum: Pyrolysis

Pyrolysis of Hexane

Examples of cleavage into radicals:



$$\overset{1}{C}H_3\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2CH_2CH_3$$

Hexane

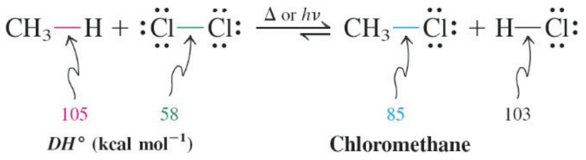
$$\xrightarrow{\text{C1–C2 cleavage}} CH_3\cdot + \cdot CH_2CH_2CH_2CH_2CH_3$$

$$\xrightarrow{\text{C2–C3 cleavage}} CH_3CH_2\cdot + \cdot CH_2CH_2CH_2CH_3$$

$$\xrightarrow{\text{C3–C4 cleavage}} CH_3CH_2CH_2\cdot + \cdot CH_2CH_2CH_3$$

$$\text{Dodecane} \xrightarrow{\text{Zeolite, 482°C, 2 min}} \underset{17\%}{C_3} + \underset{31\%}{C_4} + \underset{23\%}{C_5} + \underset{18\%}{C_6} + \underset{11\%}{\text{other products}}$$

8.1.4 Chlorination of Methane: The Radical Chain Mechanism



Chlorine converts methane into chloromethane

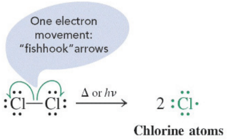
When methane and chlorine gas are mixed in the dark at room temperature, no reaction occurs. The mixture must be heated to a temperature above 300°C or irradiated with ultraviolet light (denoted by hv) before a reaction takes place.

One of the two initial products is chloromethane, derived from methane in which a hydrogen atom is removed and replaced by chlorine. The other product of this transformation is hydrogen chloride.

Further substitution leads to dichloromethane (methylene chloride), CH_2Cl_2, trichloromethane (chloroform), $CHCl_3$; and tetrachloromethane (carbon tetrachloride), CCl_4.

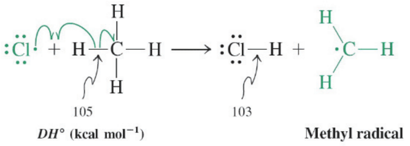
8.1.4 Chlorination of Methane: The Radical Chain Mechanism

Initiation: Homolytic cleavage of the Cl–Cl bond



$$\Delta H^\circ = DH^\circ(Cl_2) = +58\ \text{kcal mol}^{-1}\ (+243\ \text{kJ mol}^{-1})$$

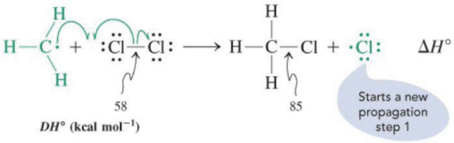
Propagation step 1: Abstraction of an H atom by :Cl·



$$\Delta H^\circ = DH^\circ(CH_3\text{–}H) - DH^\circ(H\text{–}Cl) = +2\ \text{kcal mol}^{-1}\ (+8\ \text{kJ mol}^{-1})$$

8.1.4 Chlorination of Methane: The Radical Chain Mechanism

Propagation step 2: Abst[illegible]n of a Cl atom by · CH3· CH_3

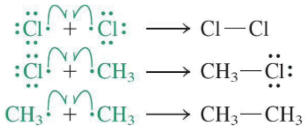


$$\Delta H^\circ = DH^\circ(Cl_2) - DH^\circ(CH_3\text{–}Cl) = -27\ \text{kcal mol}^{-1}\ (-113\ \text{kJ mol}^{-1})$$

	ΔH° [kcal mol^{-1}(kJ mol^{-1})]
$:\ddot{Cl}\cdot + CH_4 \longrightarrow CH_3\cdot + H\ddot{Cl}:$	+2 (+8)
$CH_3\cdot + Cl_2 \longrightarrow CH_3\ddot{Cl}: + :\ddot{Cl}\cdot$	−27 (−113)
$CH_4 + Cl_2 \longrightarrow CH_3\ddot{Cl}: + H\ddot{Cl}:$	−25 (−105)

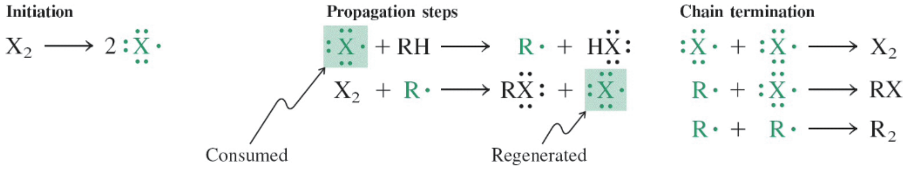
8.1.4 Chlorination of Methane: The Radical Chain Mechanism

Chain termination: Radical–radical combination



radical chain mechanism.

A Radical Chain Mechanism

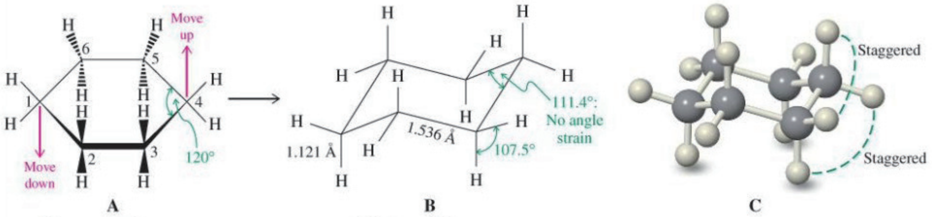


8.1 Summary & Practice

1. Concept

2. Example

8.2 Cycloalkanes

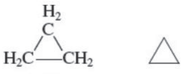


Planar cyclohexane
(120° bond angles;
12 eclipsing hydrogens)

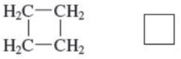
Chair cyclohexane
(Nearly tetrahedral bond angles;
no eclipsing hydrogens)

8.2.1

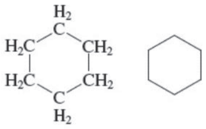
Names of Cycloalkanes



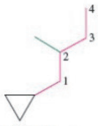
Cyclopropane



Cyclobutane

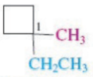


Cyclohexane



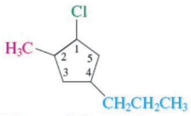
(2-Methylbutyl)cyclopropane

(No ring numbering and ring takes precedence: not (2-methylbutyl)cyclopropane and not 1-cyclopropyl-2-methylbutane)



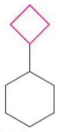
1-Ethyl-1-methylcyclobutane

(Alphabetical: not 1-methyl-1-ethylcyclobutane)



1-Chloro-2-methyl-4-propylcyclopentane

(Alphabetical: not 2-chloro-1-methyl-4-propylcyclopentane)

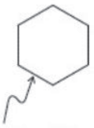


Cyclobutylcyclohexane

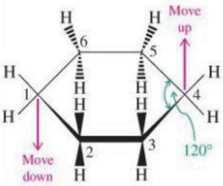
(Smaller ring is substituent: not cyclohexylcyclobutane)

8.2.2

Cyclohexane

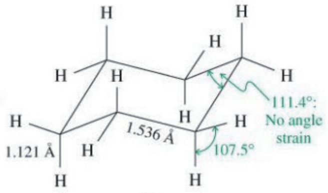


$DH° = 88$ kcal mol^{-1}



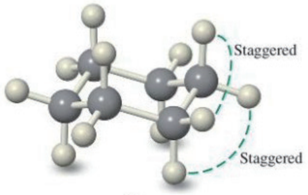
A

Planar cyclohexane
(120° bond angles;
12 eclipsing hydrogens)



B

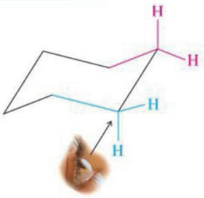
Chair cyclohexane
(Nearly tetrahedral bond angles;
no eclipsing hydrogens)

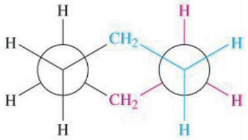


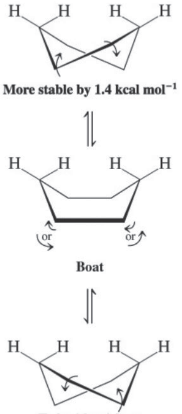
C

8.2.2

Cyclohexane



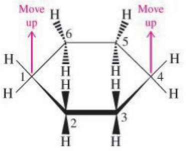




More stable by 1.4 kcal mol^{-1}

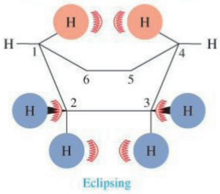
Boat

Twist (skew) boat
More stable by 1.4 kcal mol^{-1}

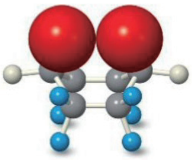


Planar cyclohexane

Steric repulsion: transannular strain



Boat cyclohexane

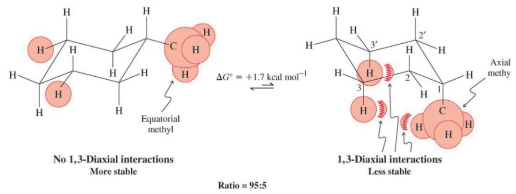


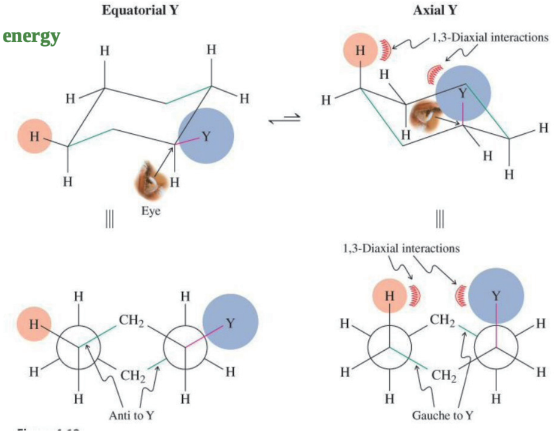
Chair to boat = +6.9 kcal mol^{-1}

8.2.3

Substituted Cyclohexane

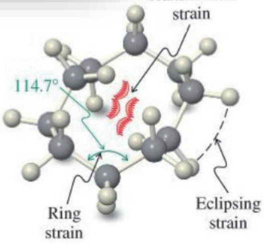
Axial and equatorial methylcyclohexanes are not equivalent in energy



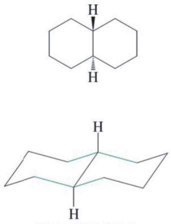


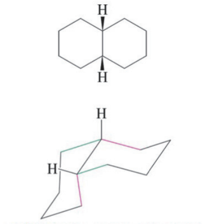
8.2.4

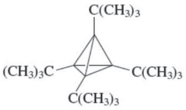
Larger Cycloalkanes



Cyclodecane

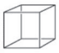






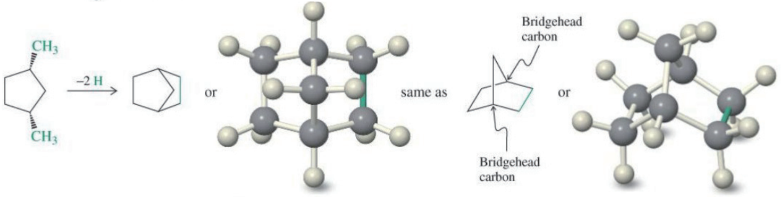
Tetrakis(1,1-dimethylethyl)-tetrahedrane
Strain = 129 kcal mol^{-1}

Tetrahedrane (C_4H_4)
Strain = 137 kcal mol^{-1}



Cubane (C_8H_8)
Strain = 166 kcal mol^{-1}

Dodecahedrane ($C_{20}H_{20}$)
Strain = 61 kcal mol^{-1}

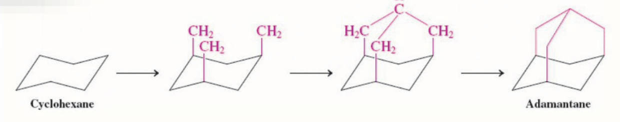


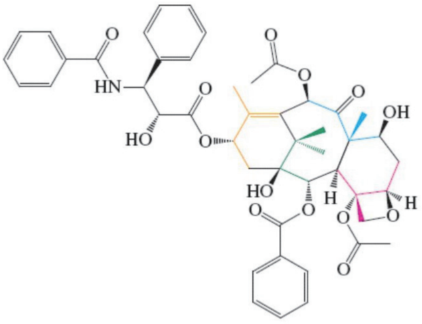
Norbornane **Norbornane**

8.2.4

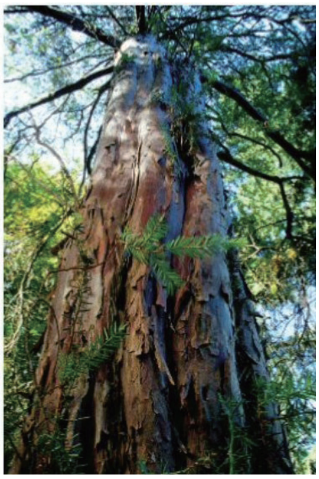
Larger Cycloalkanes

The Pacific yew tree: the source of taxol.





Taxol

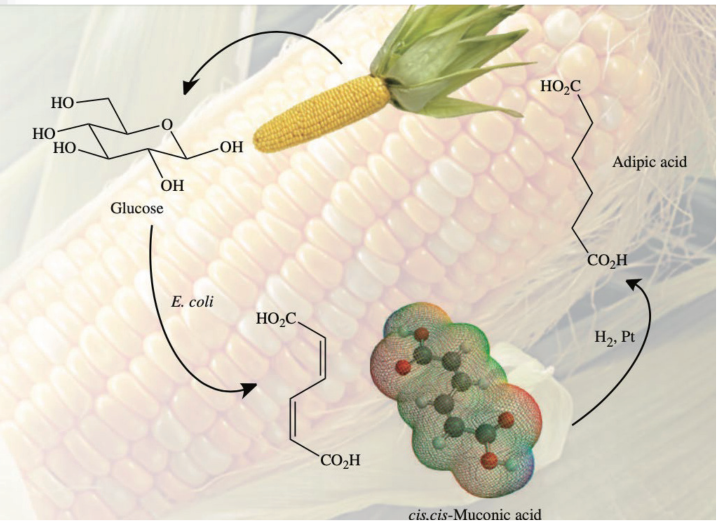


8.2 Summary & Practice

1. Concept

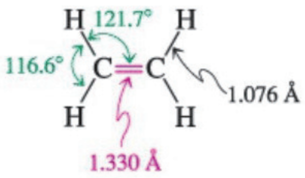
2. Example

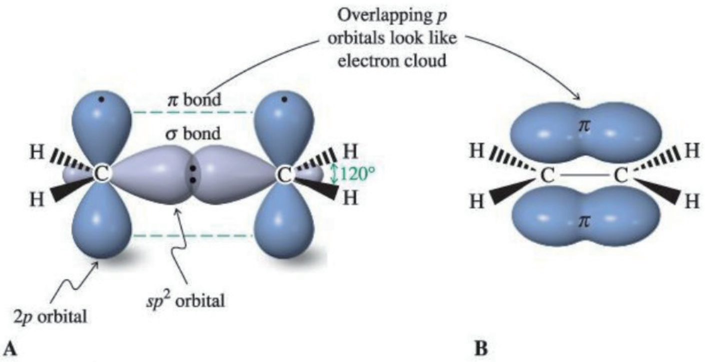
8.3 Alkenes



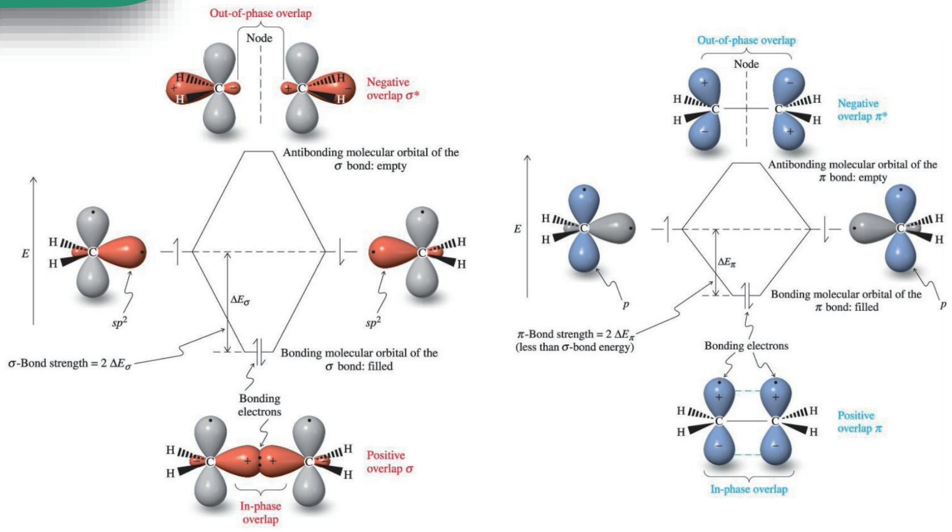
8.3.1 Bonding in Ethene: The Pi Bond

The double bond consists of sigma and pi components

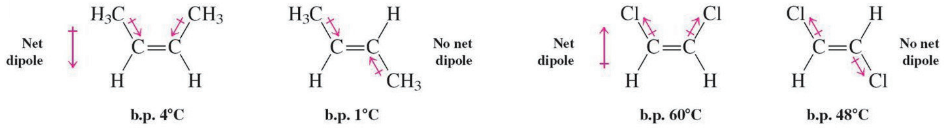




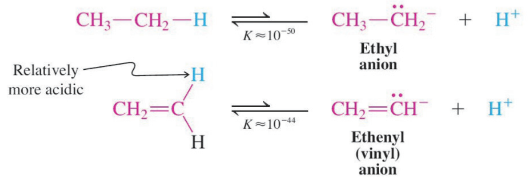
8.3.2 The pi bond in ethene is relatively weak



8.3.3 Polarization in Alkenes: Alkyl Groups are Inductive Electron Donor

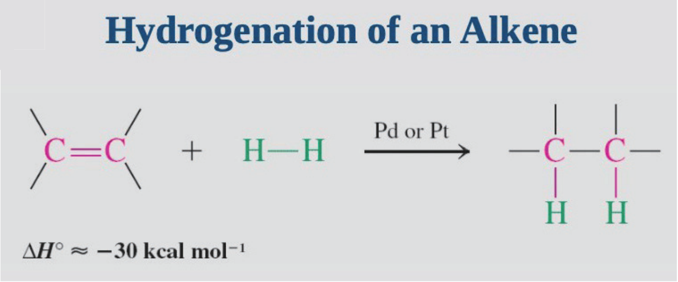


Acidity of the Ethenyl Hydrogen



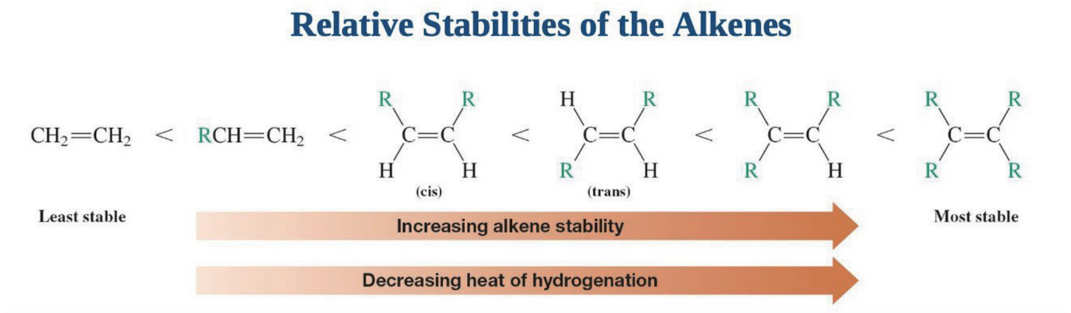
$$CH_2=CHCl + 2\,Li \xrightarrow{(CH_3CH_2)_2O} \underset{60\%}{CH_2=CHLi} + LiCl$$

8.3.4 Catalytic Hydrogenation of Alkenes

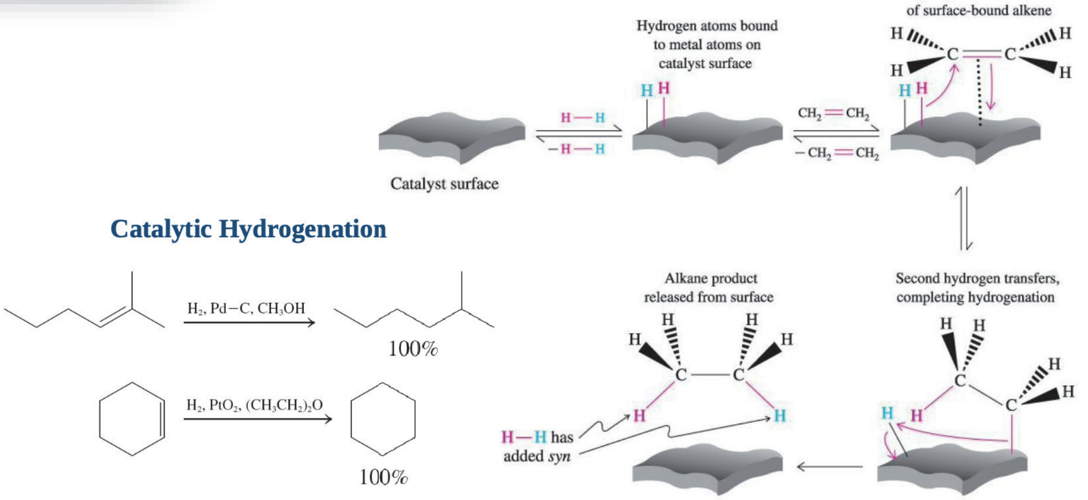


When an alkene and hydrogen gas are mixed in the presence of catalysts such as palladium or platinum, two hydrogen atoms add to the double bond to give the saturated alkane.
This reaction, which is called **hydrogenation,** is very exothermic.

8.3.4 Catalytic Hydrogenation of Alkenes

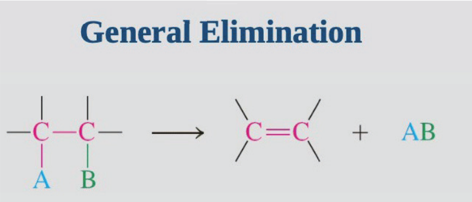


8.3.4 Catalytic Hydrogenation of Alkenes

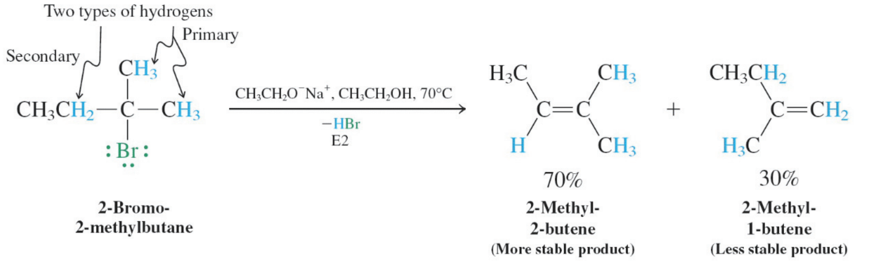


8.3.4 Preparation of Alkenes

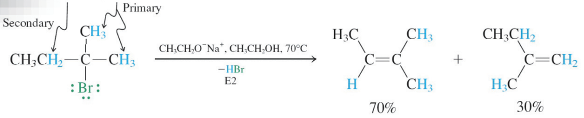
Alkenes from Haloalkanes and Alkyl Sulfonates: Bimolecular Elimination



E2 Reaction of 2-Bromo-2-methylbutane with Ethoxide



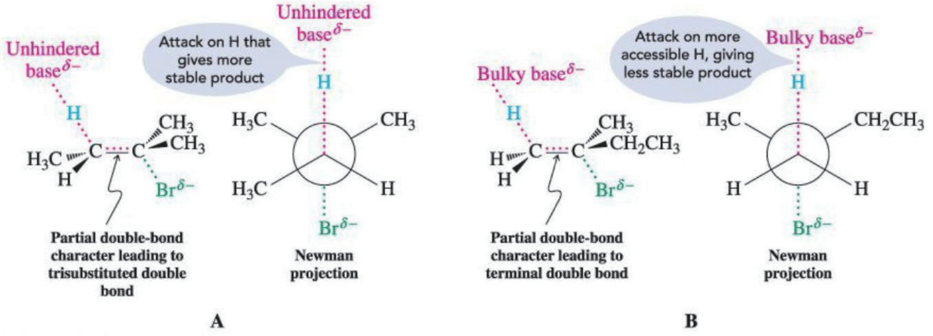
8.3.4 Preparation of Alkenes



2-Bromo-
2-methylbutane

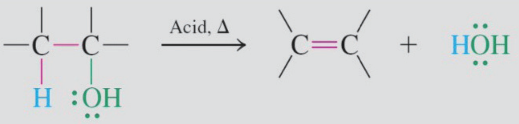
2-Methyl-
2-butene
(More stable product)

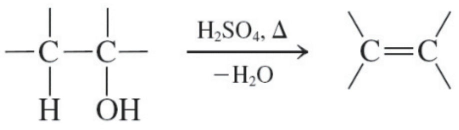
2-Methyl-
1-butene
(Less stable product)



8.3.5 Preparation of Alkenes:Dehydration of Alcohols

Acid-Mediated Dehydration of Alcohols





Most stable alkene is major product
Primary: E2 mechanism
Secondary, tertiary: E1 mechanism
Carbocations may rearrange

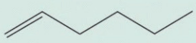
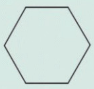
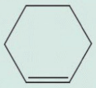
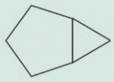
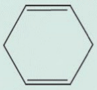
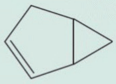
Order of reactivity: primary < secondary < tertiary

8.3.6 Degree of Unsaturation

Degree of unsaturation

$$\frac{2n_C + 2 - n_N - n_H - n_X}{2}$$

The **degree of unsaturation** is defined as the sum of the numbers of rings and π bonds present in the molecule.

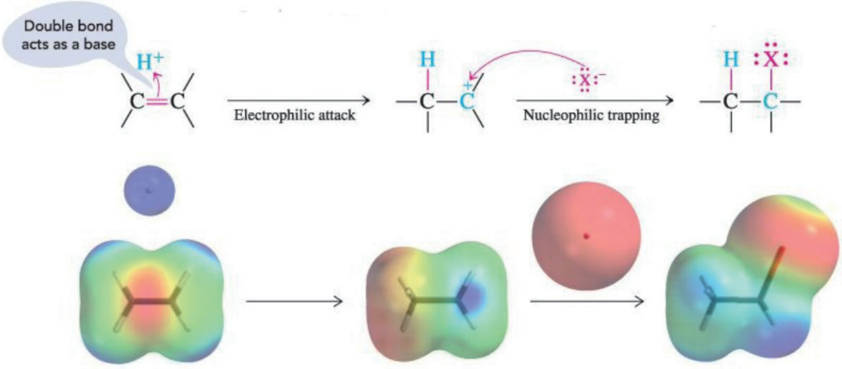
Representative Structures	Degree of Unsaturation
	0
 (one π bond) ;  (one ring)	1
 (two π bonds) ;  (one π bond + one ring) ;  (two rings)	2
 (three π bonds) ;  (two π bonds + one ring) ;  (one π bond + two rings)	3

8.3.6

Electrophilic Addition of Hydrogen Halides

Electrophilic attack by protons gives carbocations

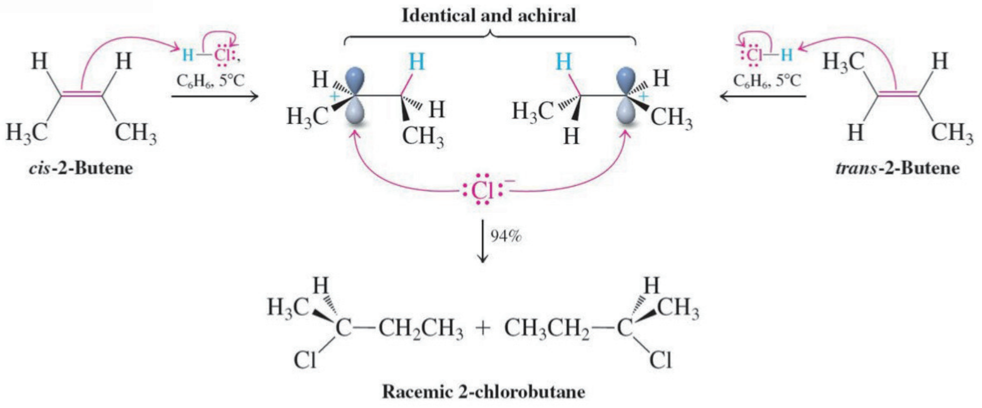
Mechanism of Electrophilic Addition of HX to Alkenes



8.3.6

Electrophilic Addition of Hydrogen Halides

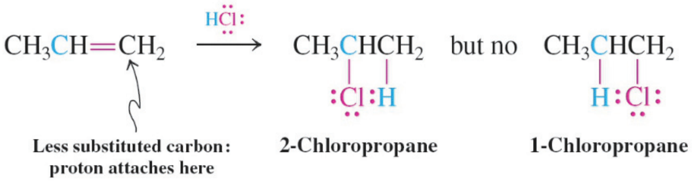
Nucleophilic trapping of carbocations is nonstereoselective



8.3.7

The Markovnikov Rule

Regioselective Electrophilic Addition to Propene

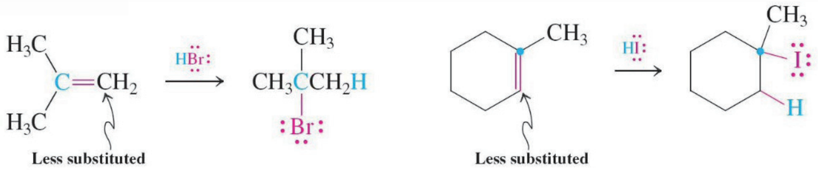


We can see from these examples that, if the carbon atoms participating in the double bond are not equally substituted, the proton from the hydrogen halide attaches itself to the less substituted carbon.

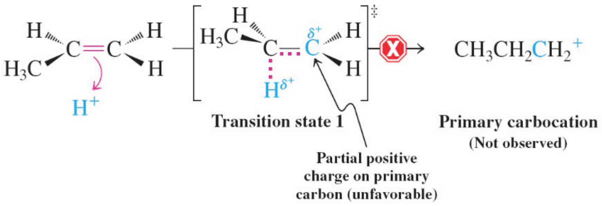
As a consequence, the halogen ends up at the more substituted carbon. This phenomenon, referred to as the **Markovnikov rule**,

8.3.7 The Markovnikov Rule

Two Further Examples of Regioselective Additions



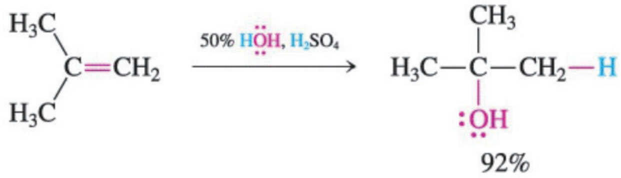
Protonation of Propene at C2—More Substituted Carbon (Does Not Occur)



8.3.8 Alcohol Synthesis by Electrophilic Hydration

The elements of water, H and OH, add across the double bond, an **electrophilic hydration**. The addition follows the Markovnikov rule in that H^+ adds to the less substituted carbon and the OH group ends up at the more substituted one.

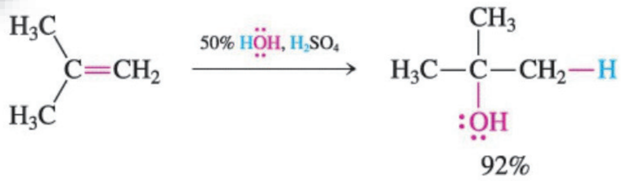
Electrophilic Hydration



92%

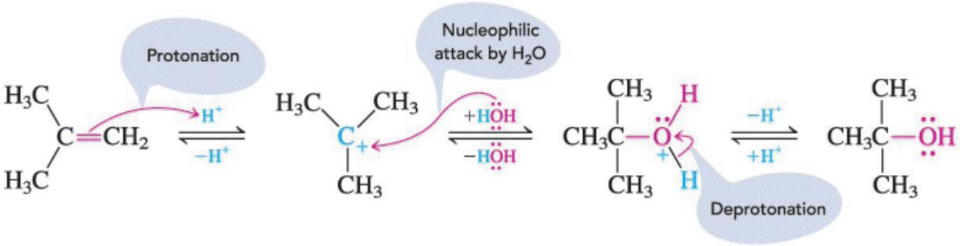
2-Methylpropene **2-Methyl-2-propanol**

8.3.8 Alcohol Synthesis by Electrophilic Hydration



92%

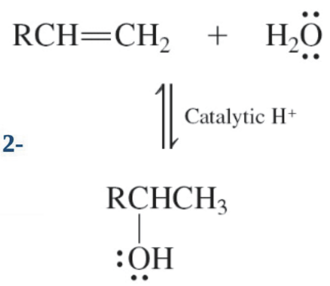
2-Methylpropene **2-Methyl-2-propanol**



8.3.9

Alkene Hydration and Alcohol Dehydration

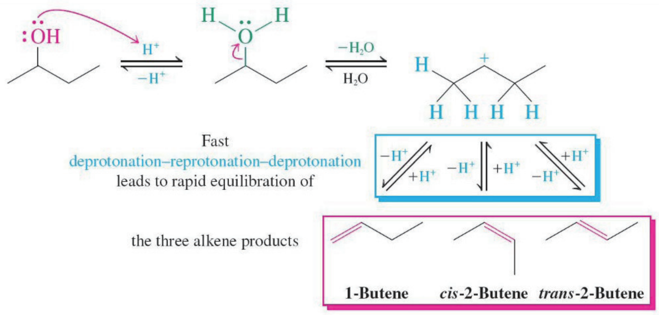
$$\text{Alkene} + H_2O \underset{\text{Conc. } H_2SO_4\text{, high temperature}}{\overset{H_2SO_4\text{, excess } H_2O\text{, low temperature}}{\rightleftharpoons}} \text{Alcohol}$$



$$RCH{=}CH_2 + H_2\ddot{O} \xrightleftharpoons{\text{Catalytic } H^+} \underset{:\ddot{O}H}{RCHCH_3}$$

Hydration–Dehydration Equilibrium

Thermodynamic Control in the Acid-Catalyzed Dehydration of 2-Butanol



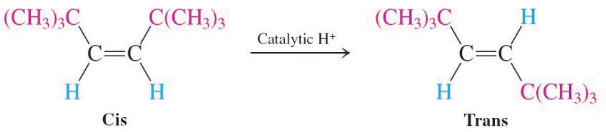
Fast deprotonation–reprotonation–deprotonation leads to rapid equilibration of

the three alkene products

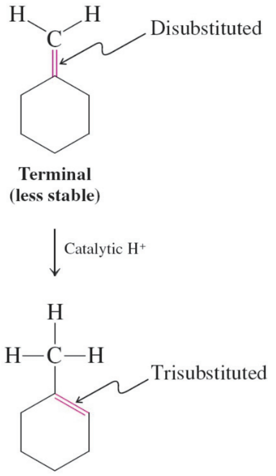
1-Butene ***cis*-2-Butene** ***trans*-2-Butene**

8.3.10

Acid-Catalyzed Equilibration of Alkenes



Cis **Trans**



Terminal (less stable)

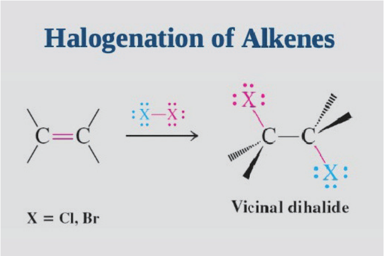
Internal (more stable)

8.3.11

Electrophilic Addition of Halogens

Bromination takes place through *anti* addition

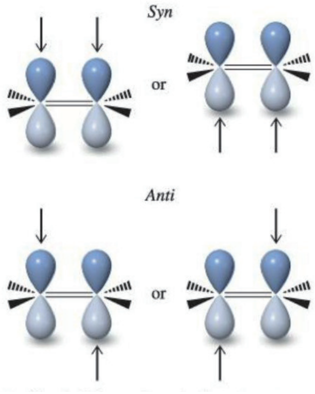
Remember: Two Topologies of Alkene Addition



Halogenation of Alkenes

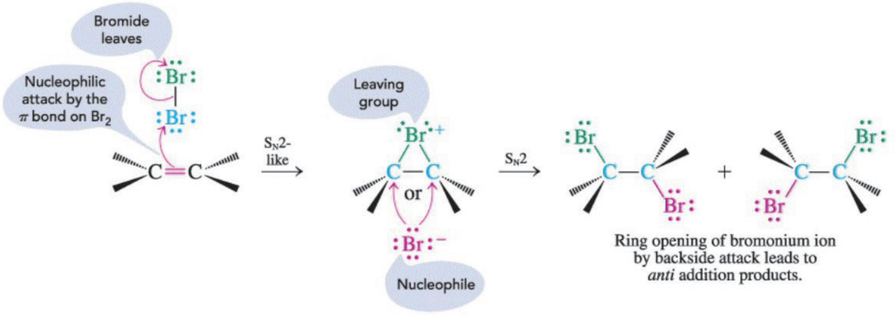
X = Cl, Br

Vicinal dihalide



8.3.11 Electrophilic Addition of Halogens

Formation and Nucleophilic Opening of a Cyclic Bromonium Ion

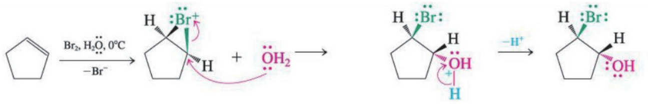


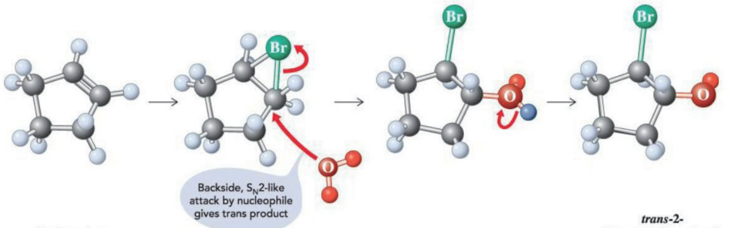
Ring opening of bromonium ion by backside attack leads to *anti* addition products.

8.3.12 The Generality of Electrophilic Addition

The bromonium ion can be trapped by other nucleophiles

The creation of a bromonium ion in alkene brominations suggests that, in the presence of other nucleophiles, competition might be observed in the trapping of the intermediate. For example, bromination of cyclopentene in water as solvent gives the vicinal bromoalcohol (common name, bromohydrin). In this case, the bromonium ion is attacked by water, which is present in large excess and therefore outcompeting bromide in this step. The net transformation is the *anti* addition of Br and OH to the double bond. The other product formed is HBr. The corresponding chloroalcohols (chlorohydrins) can be made from chlorine in water through a chloronium ion intermediate.



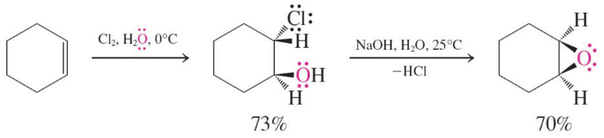


Cyclopentene

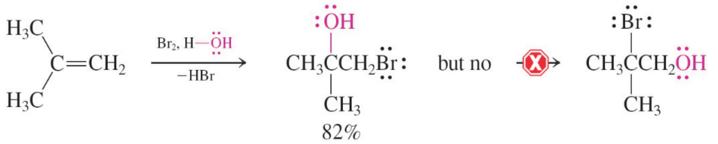
trans-2-Bromocyclopentanol

8.3.12 Electrophilic Addition of Halogens

Oxacyclopropane Formation from an Alkene Through the Haloalcohol



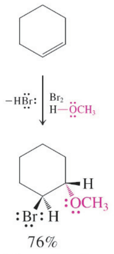
Halonium ion opening can be regioselective



1-Bromo-2-methyl-2-propanol

2-Bromo-2-methyl-1-propanol

Vicinal Haloether Synthesis

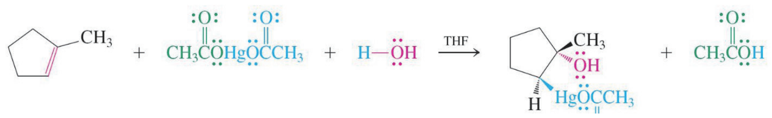


trans-1-Bromo-2-methoxycyclohexane

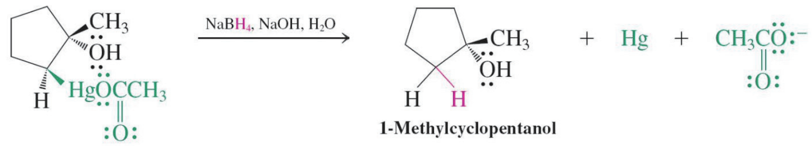
8.3.13 Oxymercuration–Demercuration

oxymercuration–demercuration, in which mercuric acetate acts as the reagent. In the first step (oxymercuration), treatment of an alkene with this species in the presence of water leads to the corresponding addition product.

Oxymercuration



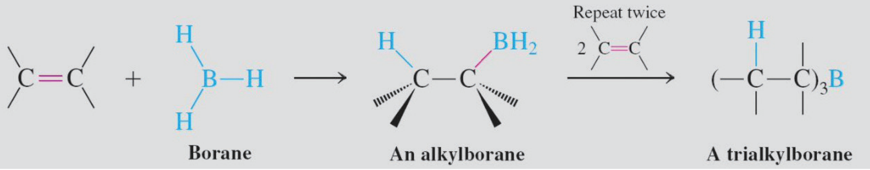
Demercuration



8.3.14 Hydroboration–Oxidation (anti-Markovnikov addition)

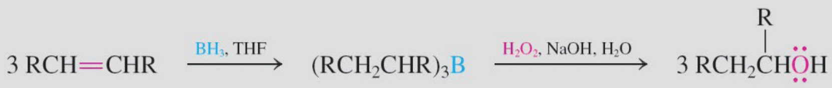
The boron–hydrogen bond adds across double bonds

Hydroboration of Alkenes



The oxidation of alkylboranes gives alcohols

Hydroboration–Oxidation Sequence

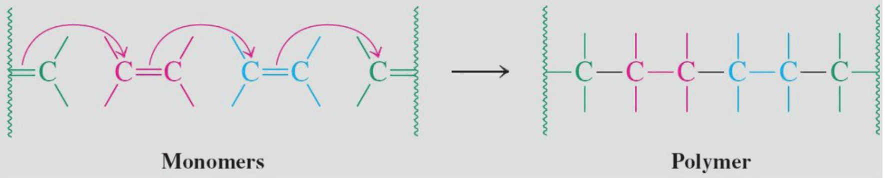


$$3\,\mathrm{RCH{=}CHR} \xrightarrow{\mathrm{BH_3,\ THF}} (\mathrm{RCH_2CHR})_3\mathrm{B} \xrightarrow{\mathrm{H_2O_2,\ NaOH,\ H_2O}} 3\,\mathrm{RCH_2}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{H\ddot{O}H}$$

8.3.15 Dimerization, Oligomerization, Polymerization of Alkenes

Is it possible for alkenes to react with one another? Indeed it is, but only in the presence of an appropriate catalyst—for example, an acid, a radical, a base, or a transition metal.
In this reaction the unsaturated centers of the alkene monomer are linked to form dimers, trimers, **oligomers**, and ultimately **polymers**, substances of great industrial importance.

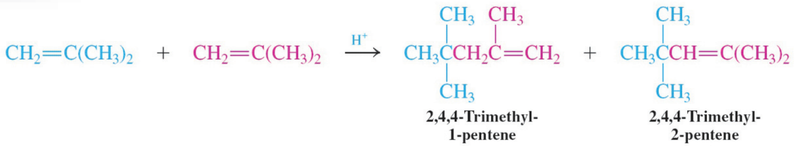
Polymerization



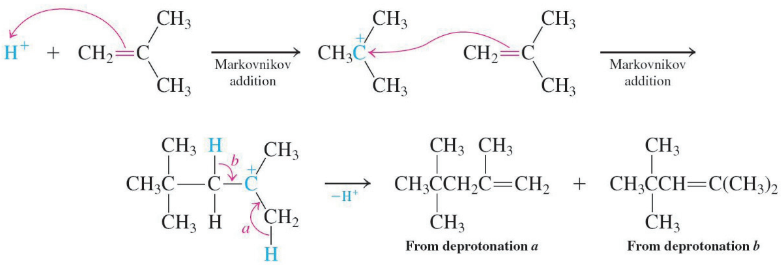
8.3.15

Dimerization, Oligomerization, Polymerization of Alkenes

Dimerization of 2-Methylpropene



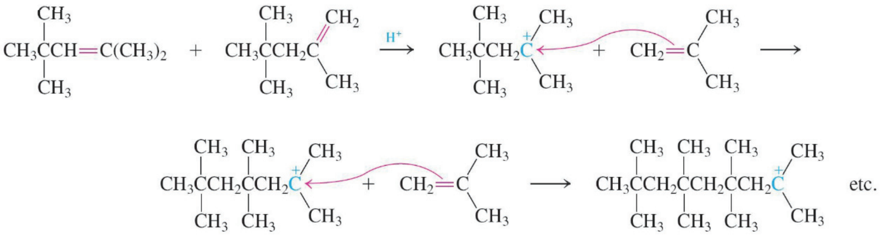
Mechanism of Acid-Catalyzed Dimerization of 2-Methylpropene



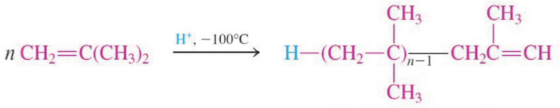
8.3.15

Dimerization, Oligomerization, Polymerization of Alkenes

Oligomerization of the 2-Methylpropene Dimers



Polymerization of 2-Methylpropene



Poly(2-methylpropene)
(Polyisobutylene)

8.3

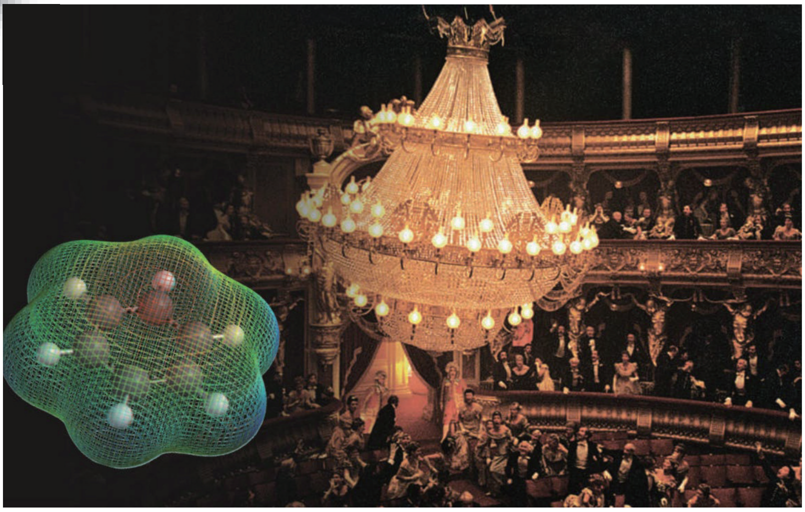
Summary & Practice

1. Concept

2. Example

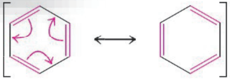
8.4

Benzene and aromaticity

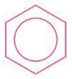


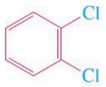
8.4.1

Naming the Benzenes



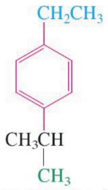
is the same as



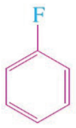


1,2-Dichlorobenzene
(*o*-Dichlorobenzene)

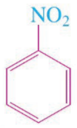
1-Bromo-3-nitrobenzene
(*m*-Bromonitrobenzene)



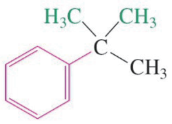
1-Ethyl-4-(1-methylethyl)benzene
(*p*-Ethylisopropylbenzene)



Fluorobenzene

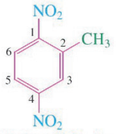


Nitrobenzene

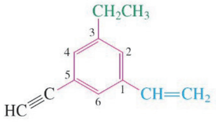


(1,1-Dimethylethyl)benzene
(*tert*-Butylbenzene)

1-Bromo-2,3-dimethylbenzene
(Alphabetical; not
3-bromo-1,2-dimethylbenzene)



2-Methyl-1,4-dinitrobenzene



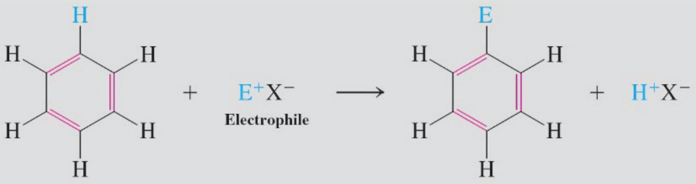
1-Ethenyl-3-ethyl-5-ethynylbenzene

8.4.2

Electrophilic Aromatic Substitution

Benzene undergoes substitution reactions with electrophiles

Electrophilic Aromatic Substitution



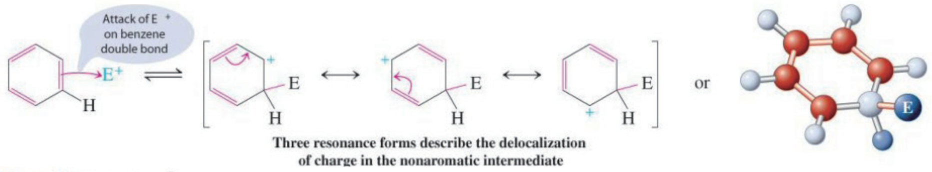
Electrophilic aromatic substitution in benzene proceeds by addition of the electrophile followed by proton loss

8.4.2

Electrophilic Aromatic Substitution

Mechanism of Electrophilic Aromatic Substitution

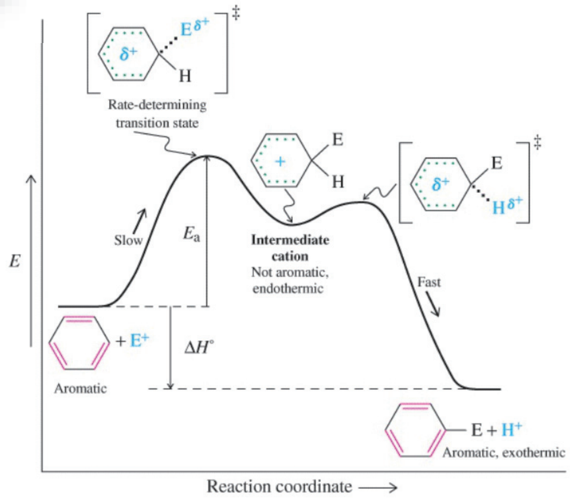
Step 1. Electrophilic attack



Step 2. Proton loss

8.4.2

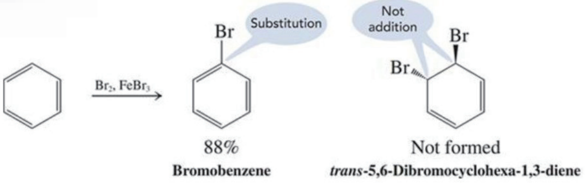
Electrophilic Aromatic Substitution



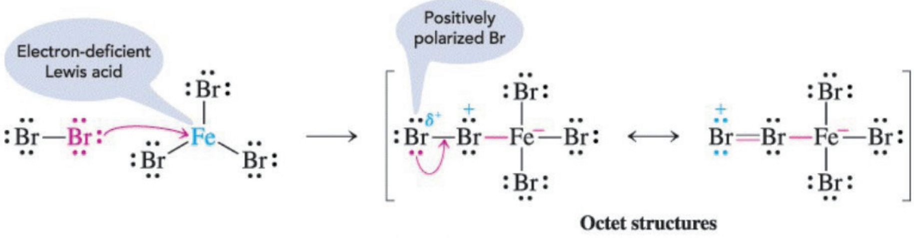
8.4.3

Halogenation of Benzene

Bromination of Benzene

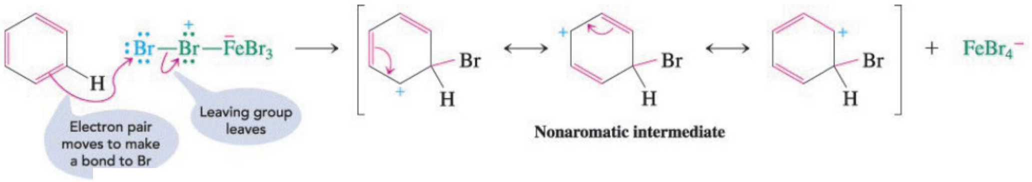


Activation of Bromine by the Lewis Acid $FeBr_3$ Catalyst



8.4.3 Halogenation of Benzene

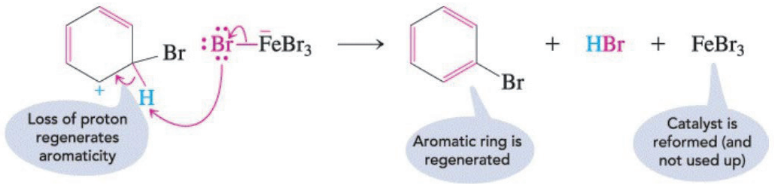
Electrophilic Attack on Benzene by Activated Bromine


Electron pair moves to make a bond to Br

Leaving group leaves

Nonaromatic intermediate

Bromobenzene Formation by Proton Transfer


Loss of proton regenerates aromaticity

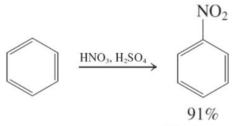
Aromatic ring is regenerated

Catalyst is reformed (and not used up)

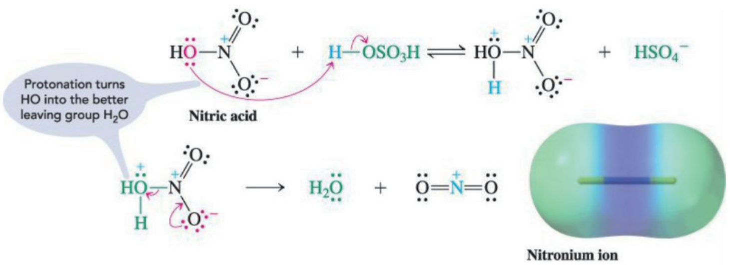
8.4.4 Nitration and Sulfonation of Benzene

Benzene is subject to electrophilic attack by the nitronium ion

Nitration of Benzene


Nitrobenzene

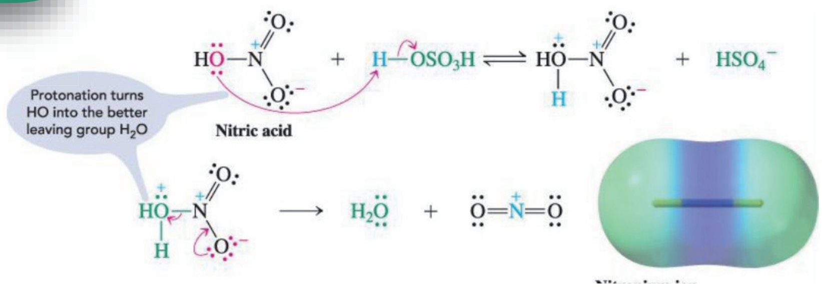
Activation of Nitric Acid by Sulfuric Acid


Protonation turns HO into the better leaving group H_2O

Nitric acid

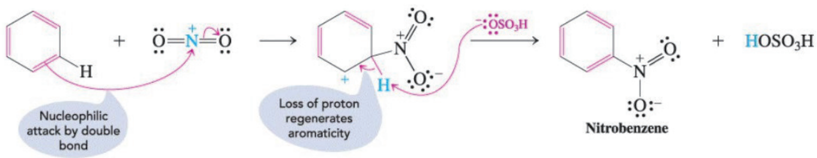
Nitronium ion

8.4.4 Nitration and Sulfonation of Benzene


Protonation turns HO into the better leaving group H_2O

Nitric acid

Mechanism of Aromatic Nitration by the Nitronium ion


Nucleophilic attack by double bond

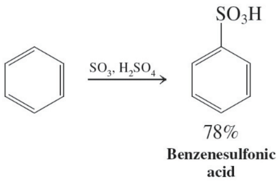
Loss of proton regenerates aromaticity

Nitrobenzene

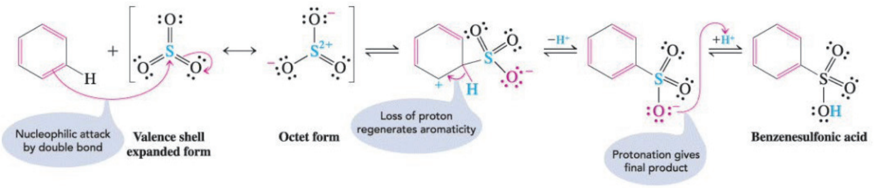
8.4.4 Nitration and Sulfonation of Benzene

Sulfonation is reversible

Sulfonation of Benzene

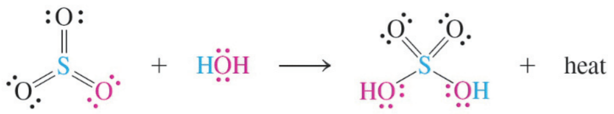


Mechanism of Aromatic Sulfonation

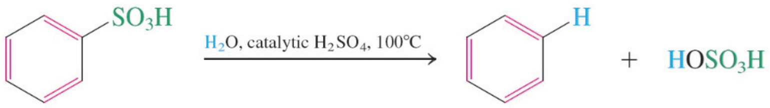


8.4.4 Nitration and Sulfonation of Benzene

Hydration of SO_3



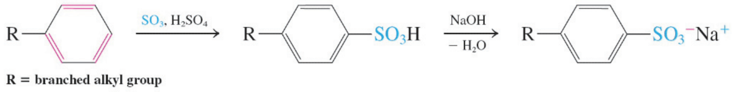
Reverse Sulfonation: Hydrolysis



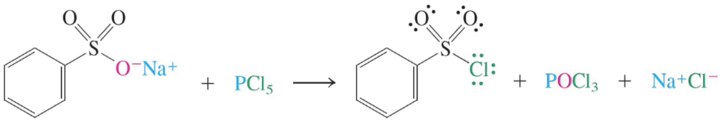
8.4.4 Nitration and Sulfonation of Benzene

Benzenesulfonic acids have important uses

Aromatic Detergent Synthesis



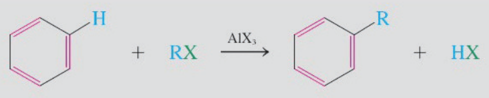
Preparation of Benzenesulfonyl Chloride



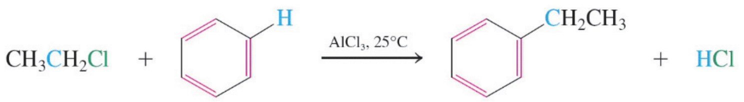
8.4.5 Friedel-Crafts Alkylation

In 1877, Friedel and Crafts discovered that a haloalkane reacts with benzene in the presence of an aluminum halide. The resulting products are the alkylbenzene and hydrogen halide. This reaction, which can be carried out in the presence of other Lewis acid catalysts, is called the **Friedel-Crafts alkylation** of benzene.

Friedel-Crafts Alkylation



Friedel-Crafts Alkylation of Benzene with Chloroethane

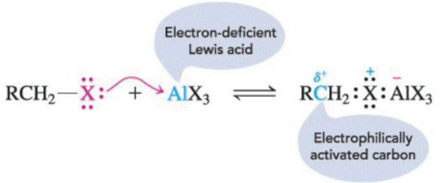


37%
Ethylbenzene

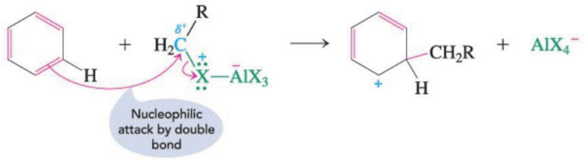
8.4.5 Friedel-Crafts Alkylation

Mechanism of Friedel-Crafts Alkylation with Primary Haloalkanes

Step 1. Haloalkane activation

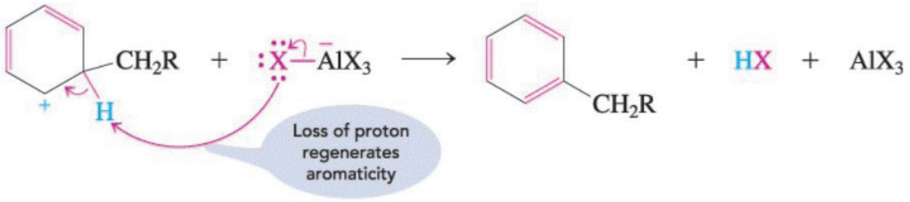


Step 2. Electrophilic attack by activated haloalkane



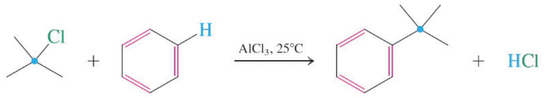
8.4.5 Friedel-Crafts Alkylation

Step 3. Proton loss



8.4.5 Friedel-Crafts Alkylation

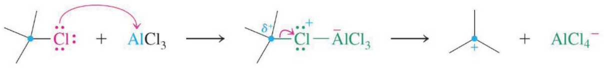
Friedel-Crafts Alkylation of Benzene with 2-Chloro-2-methylpropane (*tert*-Butyl Chloride)



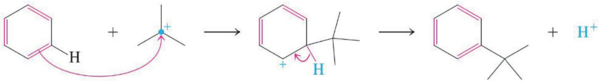
90%
1,1-Dimethylethylbenzene
(tert-Butylbenzene)

Mechanism of the Friedel-Crafts tert-Butylation of Benzene with 2-Chloro-2-methylpropane (*tert*-Butyl Chloride)

Formation of tertiary carbocation

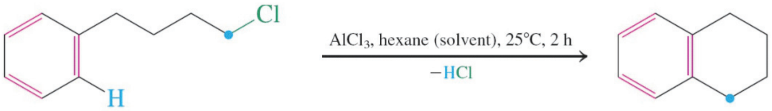


Electrophilic aromatic substitution



8.4.5 Friedel-Crafts Alkylation

An Intramolecular Friedel-Crafts Alkylation



93%
Tetralin
(Common name)

Friedel-Crafts alkylations can be carried out with any starting material that functions as a precursor to a carbocation, such as an alcohol or alkene

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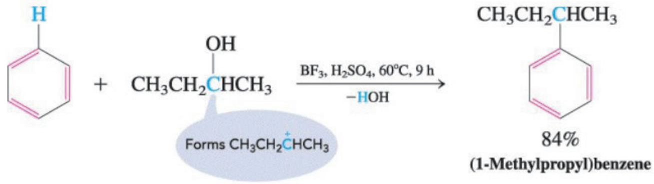
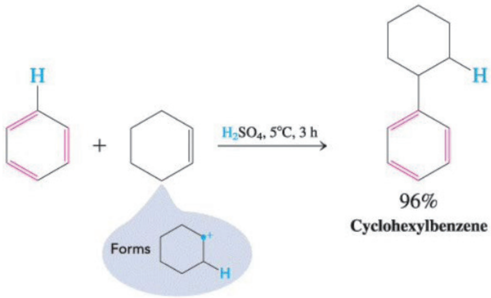
8.4.5 Friedel-Crafts Alkylation

Friedel-Crafts Alkylations Using Other Carbocation Precursors

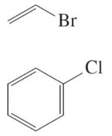


84%
(1-Methylpropyl)benzene



96%
Cyclohexylbenzene

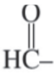
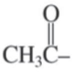
Unreactive Halides in the Friedel-Crafts Alkylation

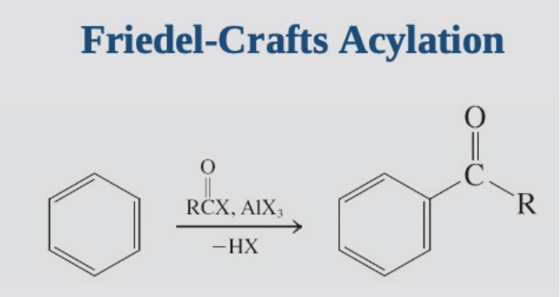


8.4.6

Friedel-Crafts Acylation

The second electrophilic aromatic substitution that forms carbon-carbon bonds is **Friedel-Crafts acylation.**

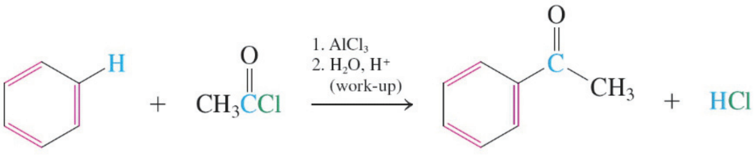
IUPAC retains the common naming of formyl for  $\mathrm{H\overset{\overset{O}{\|}}{C}-}$ and acetyl for  $\mathrm{CH_3\overset{\overset{O}{\|}}{C}-}$



8.4.6

Friedel-Crafts Acylation

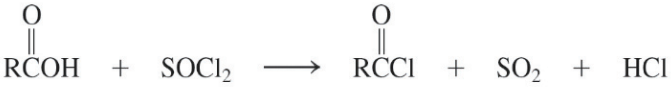
Friedel-Crafts Acylation of Benzene with Acetyl Chloride



61%

1-Phenylethanone
(Acetophenone)

Preparation of an Acyl Chloride



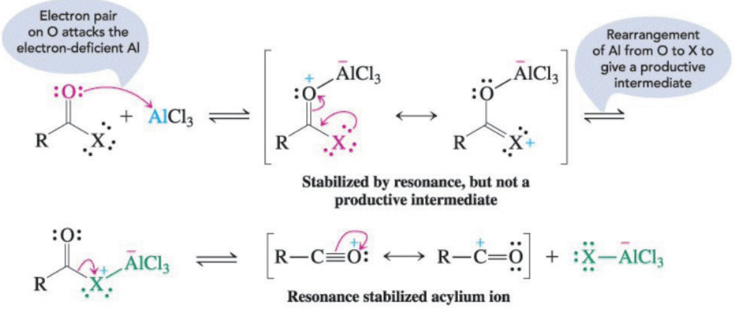
$$\mathrm{R\overset{\overset{O}{\|}}{C}OH + SOCl_2 \longrightarrow R\overset{\overset{O}{\|}}{C}Cl + SO_2 + HCl}$$

8.4.6

Friedel-Crafts Acylation

Acyl halides react with Lewis acids to produce acylium ions

Acylium Ions from Acyl Halides

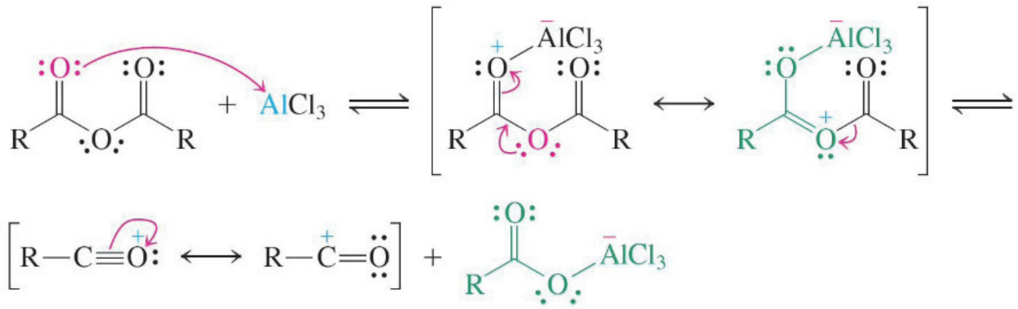


Stabilized by resonance, but not a productive intermediate

Resonance stabilized acylium ion

8.4.6 Friedel-Crafts Acylation

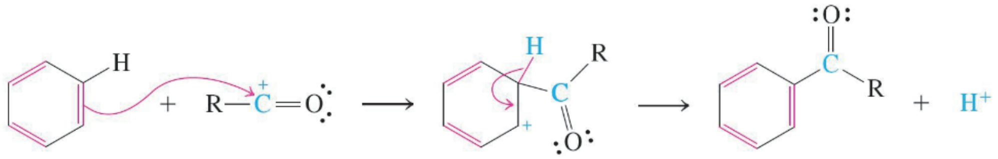
Acylium Ions from Carboxylic Anhydrides



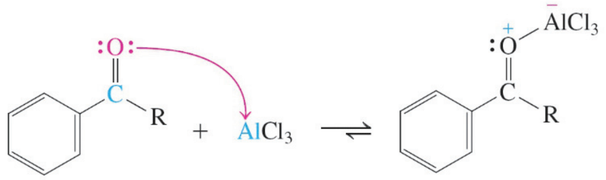
8.4.6 Friedel-Crafts Acylation

Acylium ions undergo electrophilic aromatic substitution

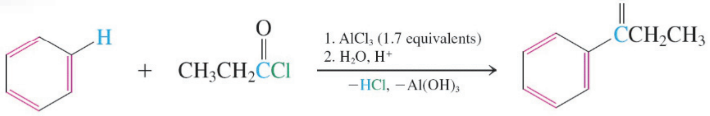
Electrophilic Acylation



Lewis Acid Complexation with 1-Phenylalkanones

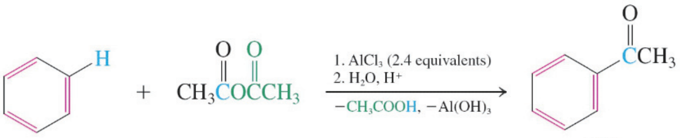


8.4.6 Friedel-Crafts Acylation



84%

1-Phenyl-1-propanone (Propiophenone)

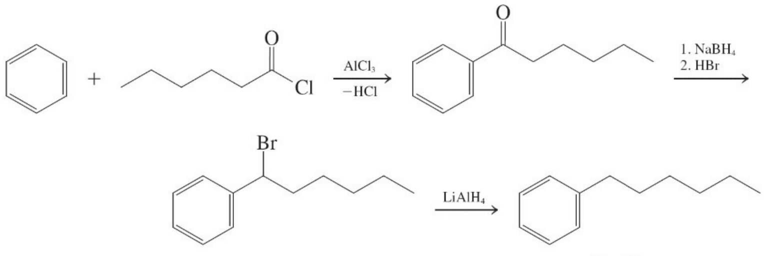


85%

1-Phenylethanone (Acetophenone)

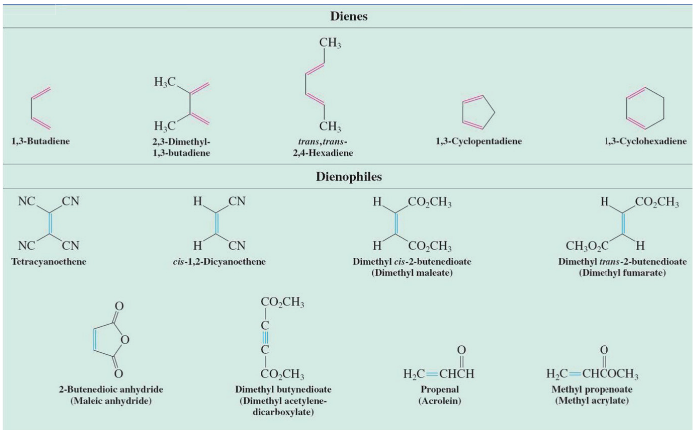
8.4.6 Friedel-Crafts Acylation

Preparation of Hexylbenzene by Hexanoylation–Reduction of Benzene



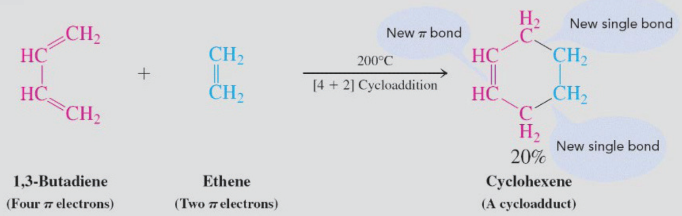
8.4.7 Diels-Alder Cycloaddition

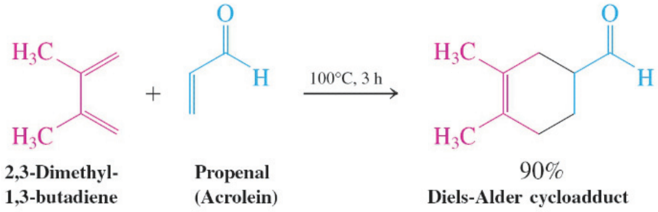
Typical Dienes and Dienophiles in the Diels-Alder Reaction



8.4.7 Diels-Alder Cycloaddition

Diels-Alder Cycloaddition of Ethene and 1,3-Butadiene





8.4 Summary & Practice

1. Concept

2. Example

UKChO

英国化学奥林匹克竞赛

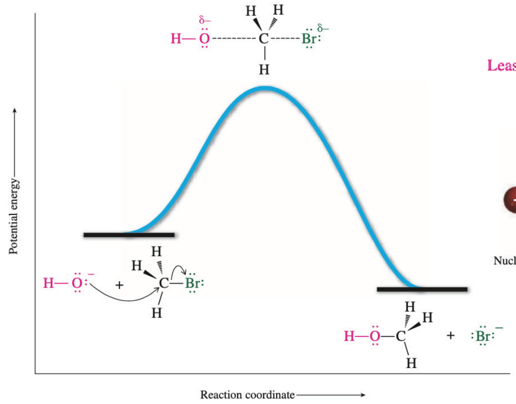
Unit 9A Haloalkane

1.Nucleophilic Substitution

2. Further Reactions of Haloalkane

3. Elimination of Haloalkane

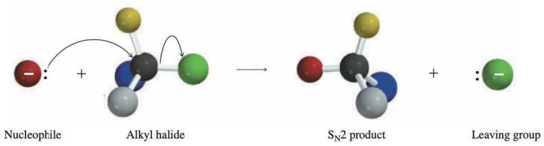
9.1 Nucleophilic Substitution



Increasing rate of substitution by nucleophiles

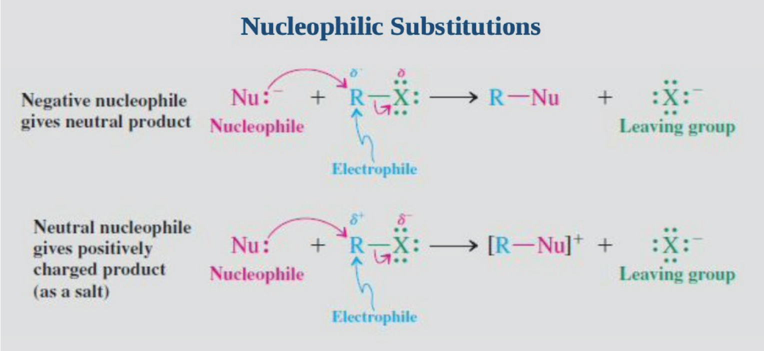
RF << RCl < RBr < RI

Least reactive — Most reactive



9.1.1 Nucleophilic Substitution

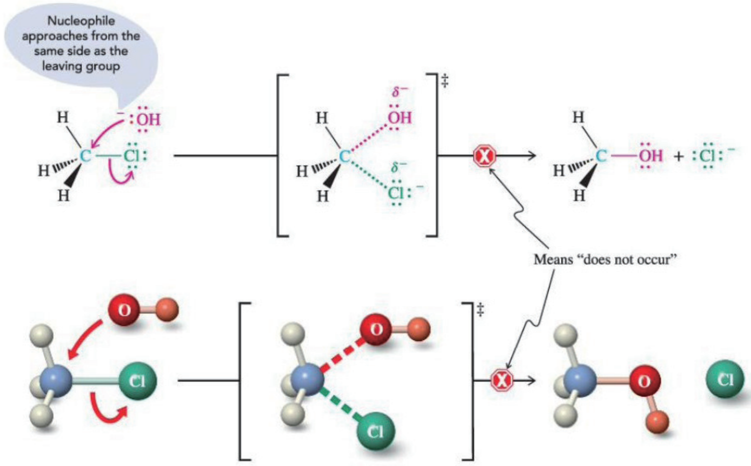
Haloalkanes contain an electrophilic carbon atom, which may react with nucleophiles—substances that contain an unshared electron pair. The nucleophilic reagent can be an anion, such as hydroxide or a neutral species, such as ammonia (:NH3). In this process, which we call **nucleophilic substitution,** the reagent attacks the haloalkane and replaces the halide



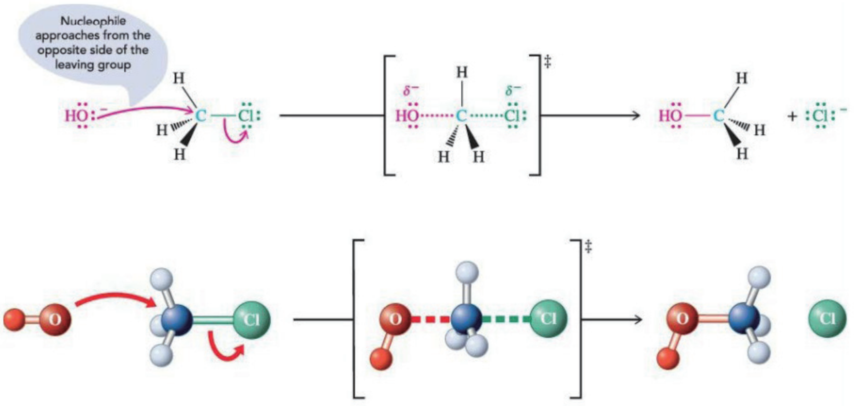
9.1.2 Reaction Mechanisms

$$\begin{array}{c} CH_3Cl + NaOH \\ \big\downarrow H_2O,\ \Delta \\ CH_3OH + NaCl \end{array}$$

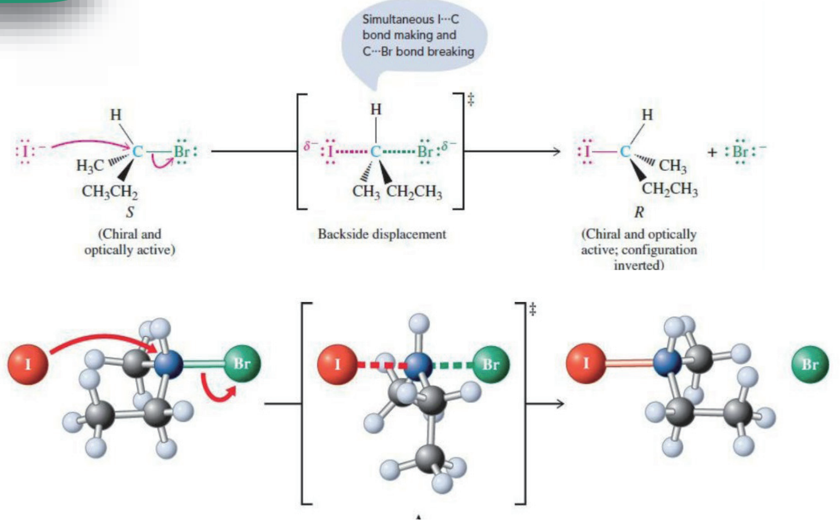
"Δ" means that the reaction mixture is heated.



9.1.2 Reaction Mechanisms

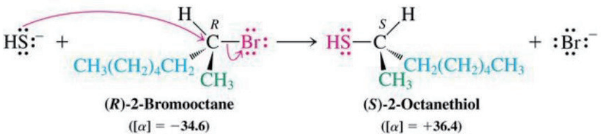


9.1.3 S_N2 reaction

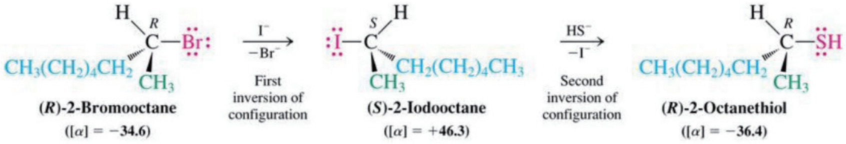


9.1.3 S_N2 reaction

Inversion of Configuration of an Optically Pure Compound by SN2 Reaction



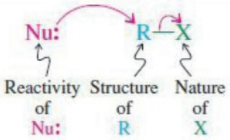
Using Double Inversion to Give Net Retention of Configuration



9.1.4 The Leaving Group

Leaving-group ability is a measure of the ease of its displacement

Some Variables Affecting the SN2



Leaving-Group Ability

$I^- > Br^- > Cl^- > F^-$

Best Worst

Increasing

Basicity

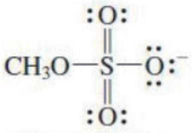
$I^- < Br^- < Cl^- < F^-$

Least Most

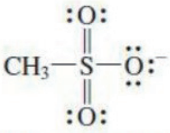
Decreasing

9.1.4 The Leaving Group

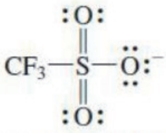
Sulfate and Sulfonate Leaving Groups


$CH_3O-S(=O)_2-O^-$

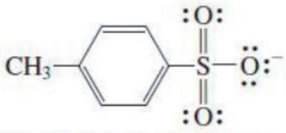
Methyl sulfate ion


$CH_3-S(=O)_2-O^-$

Methanesulfonate ion
(Mesylate ion)


$CF_3-S(=O)_2-O^-$

Trifluoromethanesulfonate ion
(Triflate ion)



4-Methylbenzenesulfonate ion
(*p*-Toluenesulfonate ion,
tosylate ion)

9.1.5 Nucleophile

Increasing negative charge increases nucleophilicity

$CH_3\ddot{C}l: + H\ddot{O}:^- \longrightarrow CH_3\ddot{O}H + :\ddot{C}l:^-$ Fast

$CH_3\ddot{C}l: + H_2\ddot{O} \longrightarrow CH_3\ddot{O}H_2^+ + :\ddot{C}l:^-$ Very slow

$CH_3\ddot{C}l: + H_2\ddot{N}:^- \longrightarrow CH_3\ddot{N}H_2 + :\ddot{C}l:^-$ Very fast

$CH_3\ddot{C}l: + H_3N: \longrightarrow CH_3NH_3^+ + :\ddot{C}l:^-$ Slower

---

9.1.5 Nucleophile

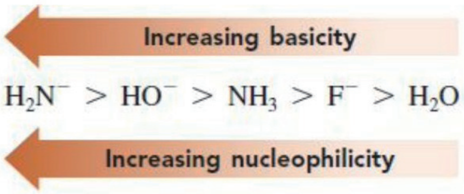
Nucleophilicity decreases to the right in the periodic table

$CH_3CH_2\ddot{B}r: + H_3N: \longrightarrow CH_3CH_2NH_3^+ + :\ddot{B}r:^-$ Fast

$CH_3CH_2\ddot{B}r: + H_2\ddot{O} \longrightarrow CH_3CH_2\ddot{O}H_2^+ + :\ddot{B}r:^-$ Very slow

$CH_3CH_2\ddot{B}r: + H_2\ddot{N}:^- \longrightarrow CH_3CH_2\ddot{N}H_2 + :\ddot{B}r:^-$ Very fast

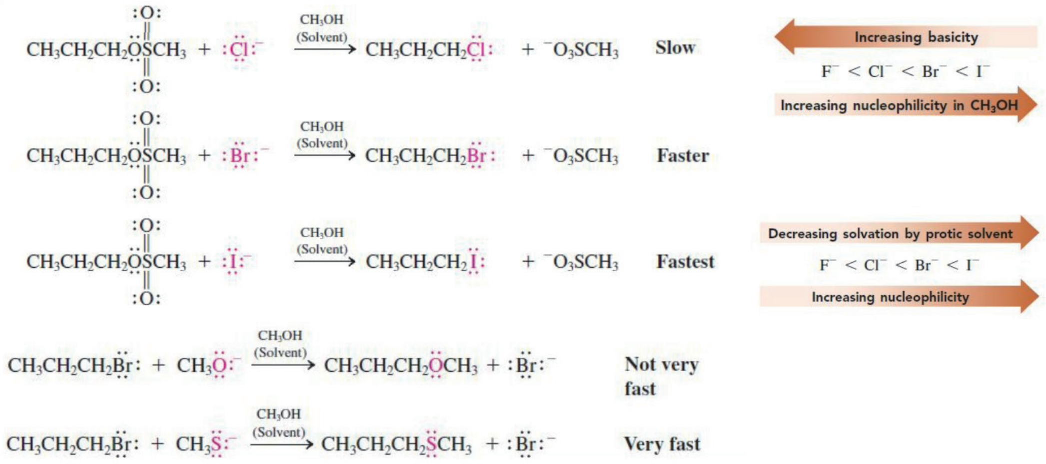
$CH_3CH_2\ddot{B}r: + H\ddot{O}:^- \longrightarrow CH_3CH_2\ddot{O}H + :\ddot{B}r:^-$ Slower



$H_2N^- > HO^- > NH_3 > F^- > H_2O$

9.1.5 Nucleophile

Solvation impedes nucleophilicity



$CH_3CH_2CH_2OSO_2CH_3 + Cl^- \xrightarrow[\text{(Solvent)}]{CH_3OH} CH_3CH_2CH_2Cl + {}^-O_3SCH_3$ **Slow**

$CH_3CH_2CH_2OSO_2CH_3 + Br^- \xrightarrow[\text{(Solvent)}]{CH_3OH} CH_3CH_2CH_2Br + {}^-O_3SCH_3$ **Faster**

$CH_3CH_2CH_2OSO_2CH_3 + I^- \xrightarrow[\text{(Solvent)}]{CH_3OH} CH_3CH_2CH_2I + {}^-O_3SCH_3$ **Fastest**

$CH_3CH_2CH_2Br + CH_3O^- \xrightarrow[\text{(Solvent)}]{CH_3OH} CH_3CH_2CH_2OCH_3 + Br^-$ **Not very fast**

$CH_3CH_2CH_2Br + CH_3S^- \xrightarrow[\text{(Solvent)}]{CH_3OH} CH_3CH_2CH_2SCH_3 + Br^-$ **Very fast**

Increasing basicity

$F^- < Cl^- < Br^- < I^-$

Increasing nucleophilicity in CH_3OH

Decreasing solvation by protic solvent

$F^- < Cl^- < Br^- < I^-$

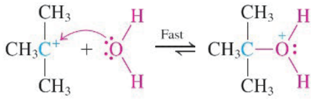
Increasing nucleophilicity

9.1 Summary & Practice

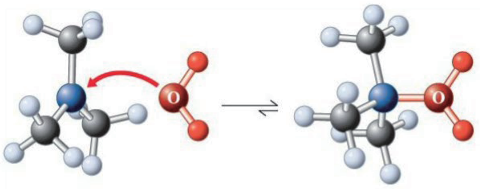
1. Concept

2. Example

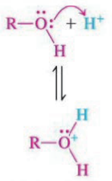
9.2 Further Reactions of Haloalkane



$(CH_3)_3C^+ + H_2O \overset{\text{Fast}}{\rightleftharpoons} (CH_3)_3C{-}O^+H_2$



An alkyloxonium ion

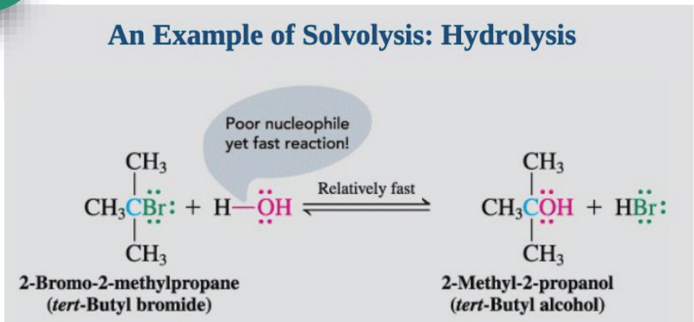


$R{-}OH + H^+ \rightleftharpoons R{-}O^+H_2$

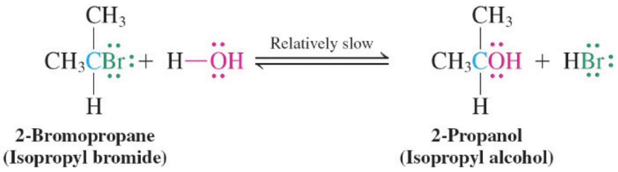
Alkyloxonium ion

9.2.1

Tertiary and Secondary Haloalkanes



$$CH_3\overset{CH_3}{\underset{CH_3}{C}}Br + H{-}OH \underset{}{\overset{\text{Relatively fast}}{\rightleftharpoons}} CH_3\overset{CH_3}{\underset{CH_3}{C}}OH + HBr$$

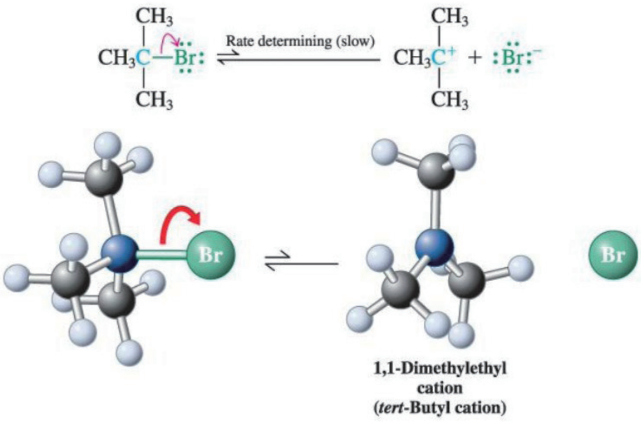


$$CH_3\overset{CH_3}{\underset{H}{C}}Br + H{-}OH \overset{\text{Relatively slow}}{\rightleftharpoons} CH_3\overset{CH_3}{\underset{H}{C}}OH + HBr$$

9.2.2

Unimolecular Nucleophilic Substitution

Dissociation of Halide to Form a Carbocation

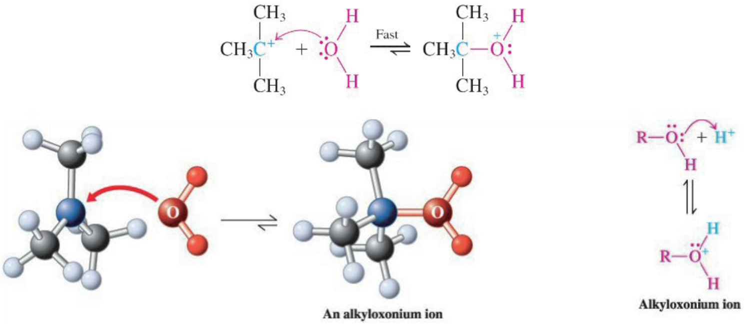


$$CH_3\overset{CH_3}{\underset{CH_3}{C}}{-}Br \overset{\text{Rate determining (slow)}}{\rightleftharpoons} CH_3\overset{CH_3}{\underset{CH_3}{C^+}} + :Br:^-$$

9.2.2

Unimolecular Nucleophilic Substitution

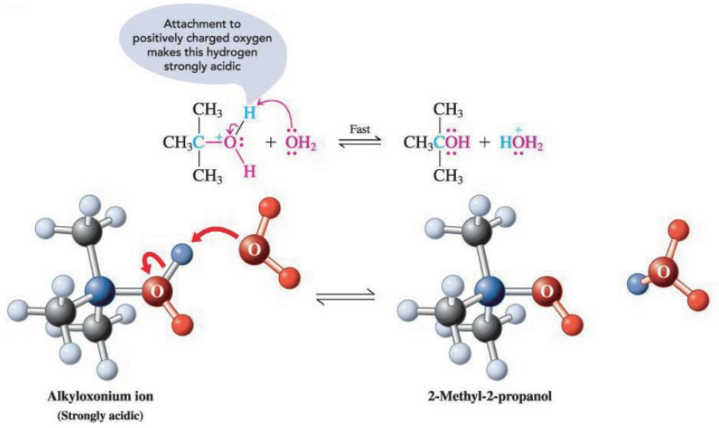
Nucleophilic Attack by Water



$$CH_3\overset{CH_3}{\underset{CH_3}{C^+}} + :\overset{H}{\underset{H}{O}} \overset{\text{Fast}}{\rightleftharpoons} CH_3\overset{CH_3}{\underset{CH_3}{C}}{-}\overset{+}{\overset{H}{\underset{H}{O}}}:$$

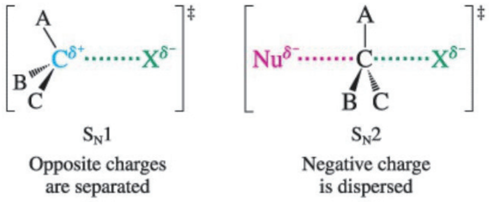
9.2.2 Unimolecular Nucleophilic Substitution

Deprotonation



9.2.3 Effects of Solvent, Leaving Group, and Nucleophile on Unimolecular Substitution

Polar solvents accelerate the SN1



Effect of Solvent on the Rate of an SN1S_N1 Reaction

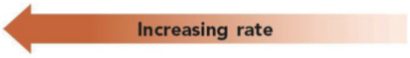
	Relative rate
$(CH_3)_3CBr \xrightarrow[\text{More polar solvent}]{100\%\ H_2O} (CH_3)_3COH + HBr$	400,000
$(CH_3)_3CBr \xrightarrow[\text{Less polar solvent}]{90\%\ \text{acetone},\ 10\%\ H_2O} (CH_3)_3COH + HBr$	1

9.2.3 Effects of Solvent, Leaving Group, and Nucleophile on Unimolecular Substitution

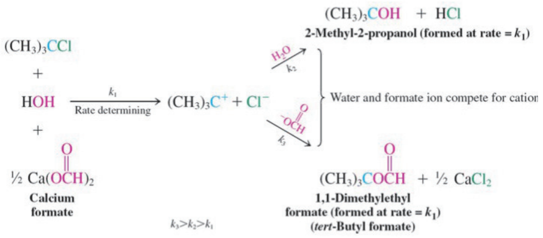
The SN1 reaction speeds up with better leaving groups

Relative Rate of Solvolysis of RX (R = Tertiary Alkyl)

X=—OSO2R′>—I>—Br>—Cl$X = —OSO_2R' > —I > —Br > —Cl$



The strength of the nucleophile affects the product distribution but not the reaction rate



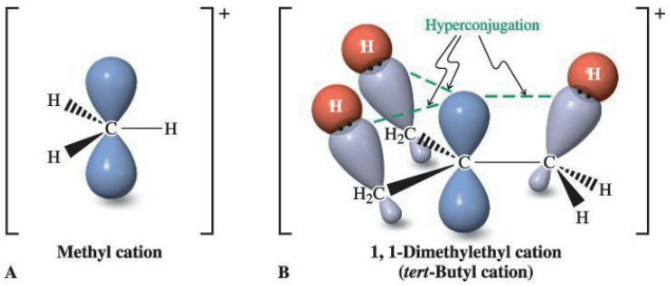
9.2.4 Carbocation Stability

Relative Stability of Carbocations

$CH_3CH_2CH_2\overset{+}{C}H_2 < CH_3CH_2\overset{+}{C}HCH_3 < (CH_3)_3\overset{+}{C}$

Primary < Secondary < Tertiary

Increasing carbocation stability



Methyl cation

A

B

1, 1-Dimethylethyl cation
(*tert*-Butyl cation)

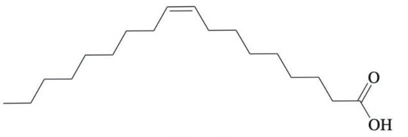
9.2 Summary & Practice

1. Concept

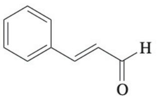
2. Example

9.3 Elimination

Oleic acid is prepared from olive oil.

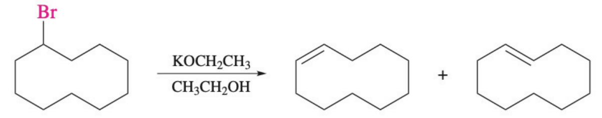


Oleic acid



Cinnamaldehyde

Cinnamaldehyde gives cinnamon its flavor.



Bromocyclodecane

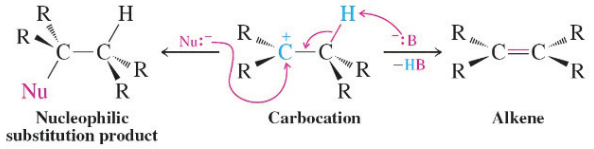
cis-Cyclodecene
(*Z*)-cyclodecene
(85%)

trans-Cyclodecene
(*E*)-cyclodecene
(15%)

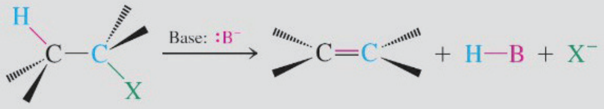
9.3.1

Unimolecular Elimination: E1

Competition Between Nucleophilic and Basic Attack on a Carbocation

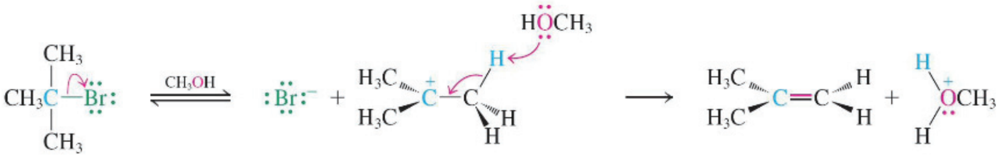


Elimination



9.3.2

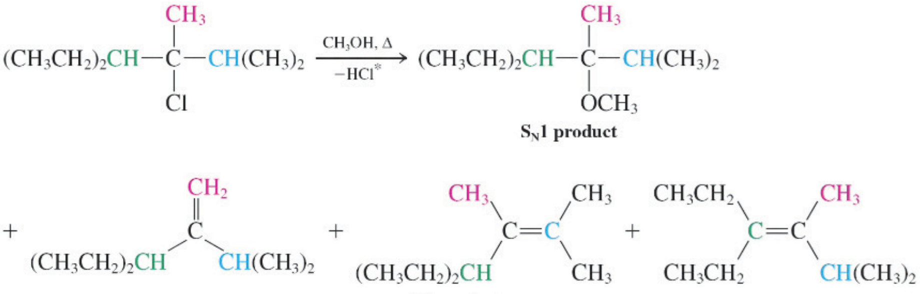
Reaction Mechanism



9.3.3

Product

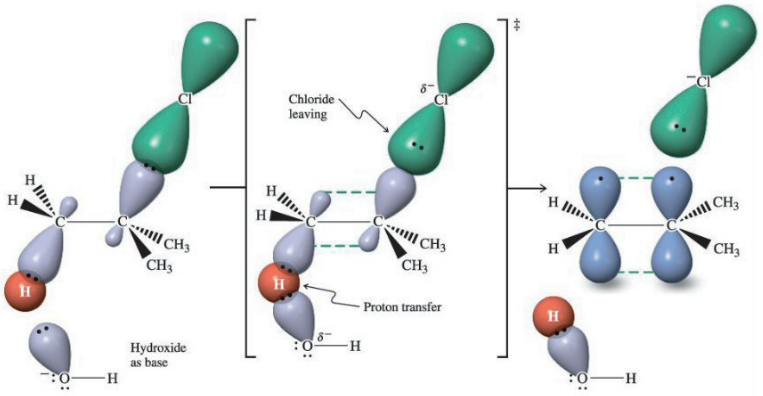
The E1E1 Reaction Can Give Product Mixtures



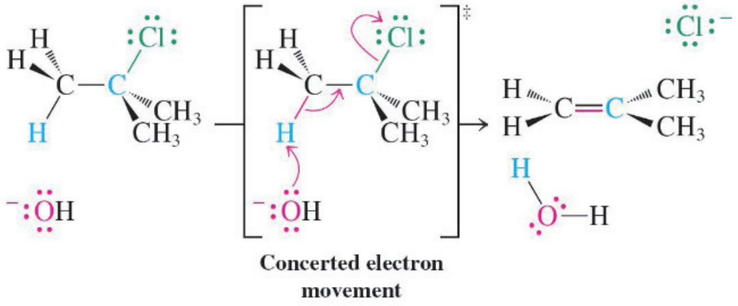
E1 products

9.3.4 Bimolecular Elimination: E2

E2 reactions proceed in one step



9.3.4 Bimolecular Elimination: E2



9.3 Summary & Practice

1. Concept

2. Example

UKChO

英国化学奥林匹克竞赛

授课教师：杨行

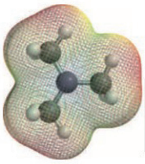
Unit 9B Alcohol

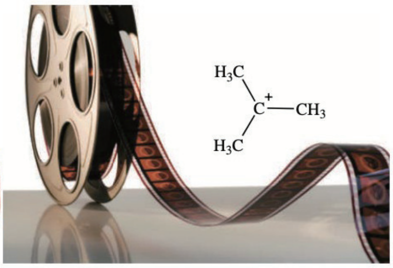
4.Synthesis of Alcohols

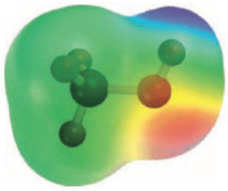
5.Reaction of Alcohols

6.Ester

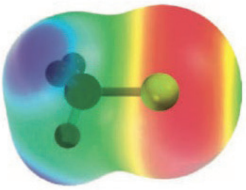
9.4 Synthesis of Alcohols







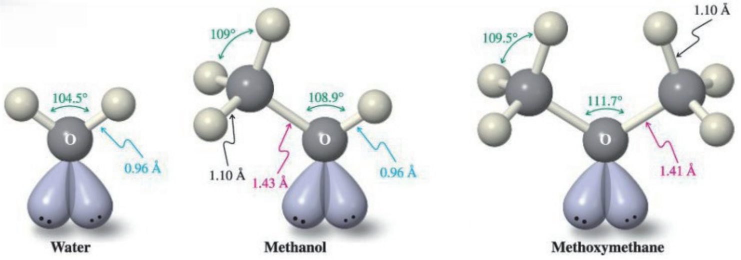
Methanol (CH_3OH)



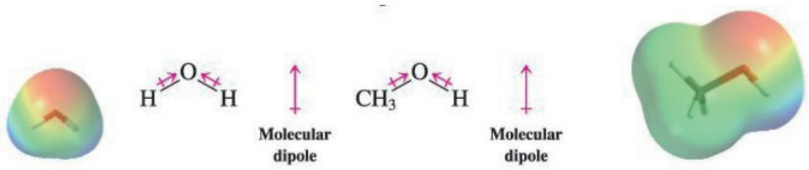
Chloromethane (CH_3Cl)

9.4.1 Structural and Physical Properties of Alcohols

The structure of alcohols resembles that of water

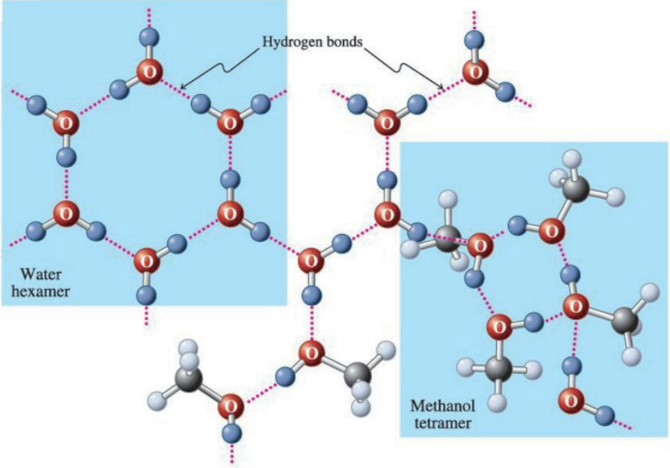


Bond and Molecular Dipoles of Water and Methanol



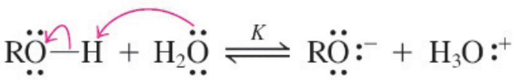
9.4.1 Structural and Physical Properties of Alcohols

Hydrogen bonding raises the boiling points and water solubilities of alcohols



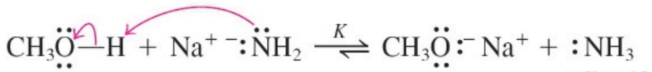
9.4.2 Alcohols as Acids and Bases

The acidity of alcohols resembles that of water



$$R\ddot{\underset{\cdot\cdot}{O}}\!-\!H + H_2\ddot{\underset{\cdot\cdot}{O}} \overset{K}{\rightleftharpoons} R\ddot{\underset{\cdot\cdot}{O}}{:}^- + H_3O{:}^+$$

Alkoxide ion



$$CH_3\ddot{\underset{\cdot\cdot}{O}}\!-\!H + Na^+\ {}^-{:}\ddot{N}H_2 \overset{K}{\rightleftharpoons} CH_3\ddot{\underset{\cdot\cdot}{O}}{:}^-\,Na^+ + {:}NH_3$$

$pK_a = 15.5$

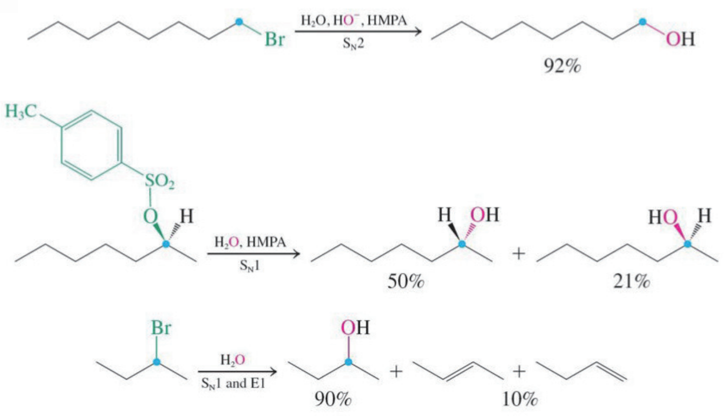
Sodium amide

Sodium methoxide

$pK_a = 35$

9.4.3 Synthesis of Alcohols by Nucleophilic Substitution

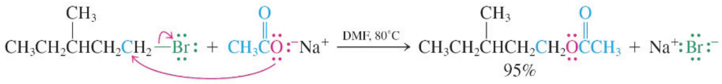
Alcohols by Nucleophilic Substitution



9.4.3 Synthesis of Alcohols by Nucleophilic Substitution

Alcohols from Haloalkanes by Acetate Substitution—Hydrolysis

Step 1. Acetate formation (SN2S_N2 reaction)

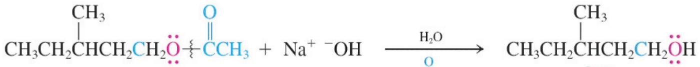


$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2{-}\ddot{\underset{..}{Br}}: + CH_3\overset{O}{\overset{\|}{C}}\ddot{\underset{..}{O}}:^-Na^+ \xrightarrow{DMF,\ 80^\circ C} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\ddot{\underset{..}{O}}\overset{O}{\overset{\|}{C}}CH_3 + Na^+ :\ddot{\underset{..}{Br}}:^-$$

95%

1-Bromo-3-methylpentane **3-Methylpentyl acetate** (An ester)

Step 2. Conversion into the alcohol (ester hydrolysis)



$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\ddot{\underset{..}{O}}\wr\overset{O}{\overset{\|}{C}}CH_3 + Na^+ \ {}^-OH \xrightarrow[-CH_3\overset{O}{\overset{\|}{C}}O^-Na^+]{H_2O} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\ddot{\underset{..}{O}}H$$

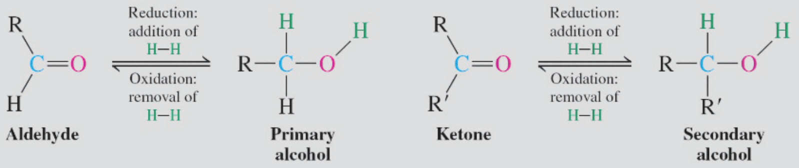
85%

3-Methyl-1-pentanol

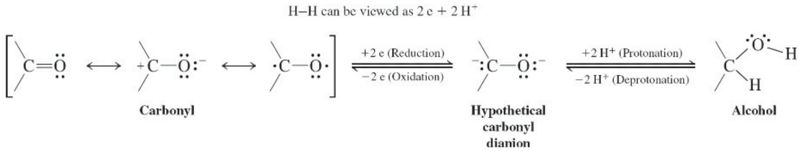
In Summary Alcohols may be prepared from haloalkanes by nucleophilic substitution, provided the haloalkane is readily available and side reactions such as elimination do not interfere.

9.4.4 Oxidation–Reduction Relation Between Alcohols and Carbonyl Compounds

The Redox Relation Between Alcohols and Carbonyl Compounds



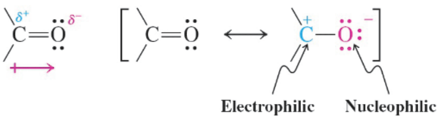
Hydrogenation-Dehydrogenation Viewed As Coupled Electron–Proton Transfer

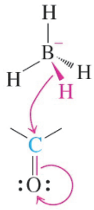


9.4.4

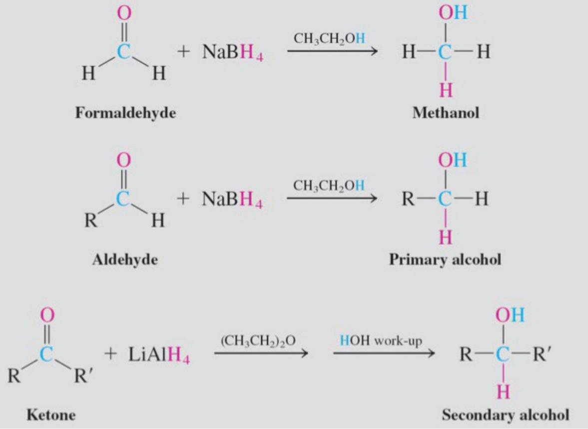
Oxidation–Reduction Relation Between Alcohols and Carbonyl Compounds

Alcohols can form by hydride reduction of the carbonyl group





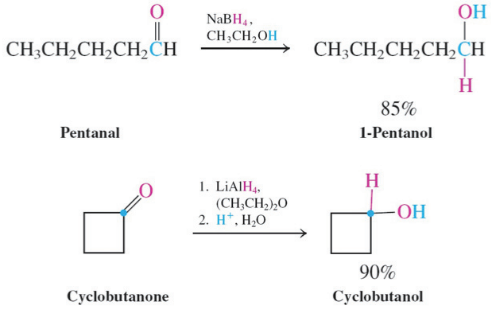
General Hydride Reductions of Aldehydes and Ketones to Alcohols



9.4.4

Oxidation–Reduction Relation Between Alcohols and Carbonyl Compounds

Examples of Hydride Reductions of Aldehydes and Ketones to Alcohols



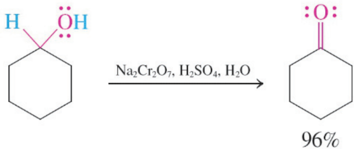
$$CH_3CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}H \xrightarrow[CH_3CH_2OH]{NaBH_4,} CH_3CH_2CH_2CH_2\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}H$$

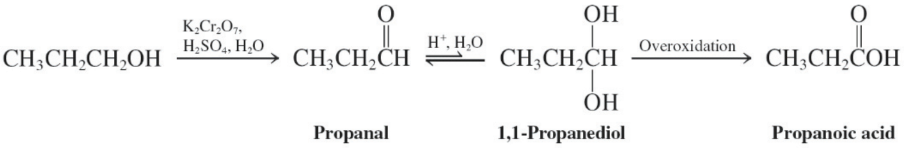
9.4.5

Chromium reagents for alcohol oxidation

Oxidation of a Secondary Alcohol to a Ketone with Aqueous Cr(VI)

Cr(VI)





$$CH_3CH_2CH_2OH \xrightarrow[H_2SO_4,\ H_2O]{K_2Cr_2O_7,} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}H \overset{H^+,\ H_2O}{\rightleftharpoons} CH_3CH_2\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}H \xrightarrow{\text{Overoxidation}} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}OH$$

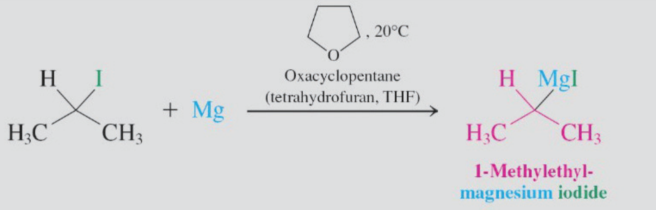
9.4.6 Organometallic Reagents

Alkyllithium and alkylmagnesium reagents are prepared from haloalkanes

$$CH_3Br + 2\,Li \xrightarrow{(CH_3CH_2)_2O\ \text{(ethoxyethane)},\ 0^\circ-10^\circ C} CH_3Li + LiBr$$

Methyl-lithium

Alkylmagnesium (Grignard) Synthesis

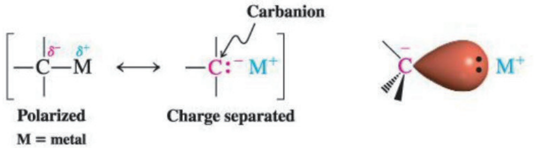


1-Methylethyl-magnesium iodide

9.4.6 Organometallic Reagents

The alkylmetal bond is strongly polar

Carbon–Metal Bond in Alkyllithium and Alkylmagnesium Compounds



Alkoxide Formation with Methyllithium

$$(CH_3)_3C\overset{\delta^-}{O}-\overset{\delta^+}{H} + \overset{\delta^+}{Li}-\overset{\delta^-}{CH_3} \longrightarrow (CH_3)_3CO^-\ Li^+ + H-CH_3$$

2-Methyl-2-propanol (*tert*-Butylalcohol) $pK_a = 18$

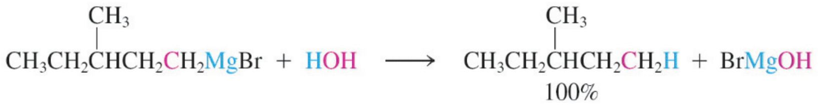
Methyllithium

Lithium *tert*-butoxide

Methane $pK_a \simeq 50$

9.4.6 Organometallic Reagents

Decomposition of an Organometallic Reagent by Hydrolysis

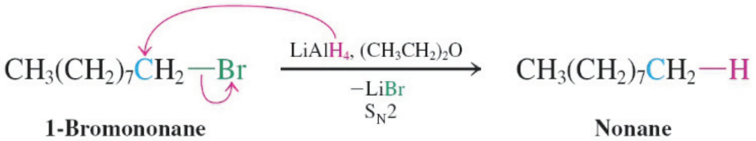


$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2MgBr + HOH \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_2H + BrMgOH$$

100%

3-Methylpentylmagnesium bromide

3-Methylpentane



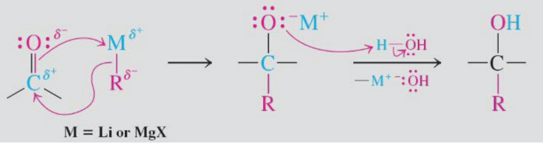
$$CH_3(CH_2)_7CH_2-Br \xrightarrow[-LiBr,\ S_N2]{LiAlH_4,\ (CH_3CH_2)_2O} CH_3(CH_2)_7CH_2-H$$

1-Bromononane

Nonane

9.4.7 Organometallic Reagents in the Synthesis of Alcohols

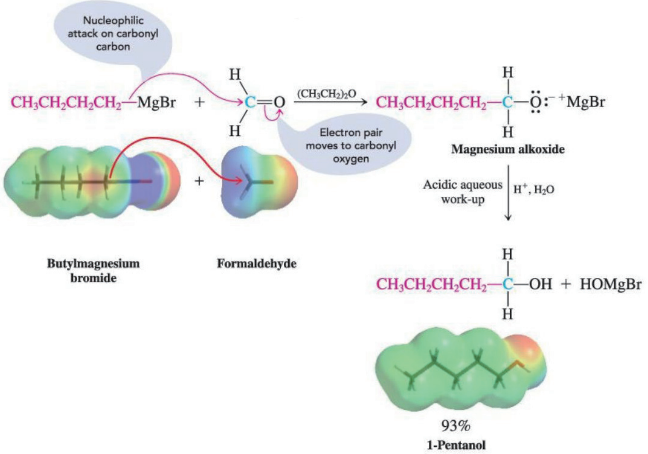
Alcohol Syntheses from Aldehydes, Ketones, and Organometallics



M = Li or MgX

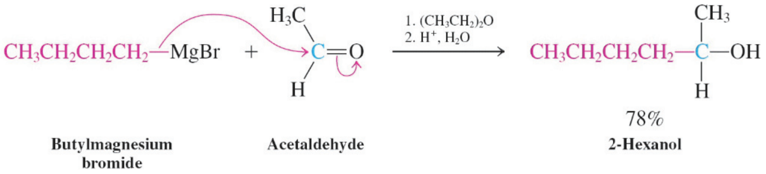
9.4.7 Organometallic Reagents in the Synthesis of Alcohols

Formation of a Primary Alcohol from a Grignard Reagent and Formaldehyde



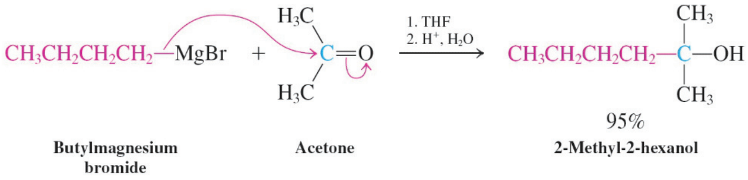
9.4.7 Organometallic Reagents in the Synthesis of Alcohols

Formation of a Secondary Alcohol from a Grignard Reagent and an Aldehyde



$$CH_3CH_2CH_2CH_2{-}MgBr + (H_3C)(H)C{=}O \xrightarrow[2.\ H^+,\ H_2O]{1.\ (CH_3CH_2)_2O} CH_3CH_2CH_2CH_2{-}C(CH_3)(H){-}OH$$

Formation of a Tertiary Alcohol from a Grignard Reagent and a Ketone



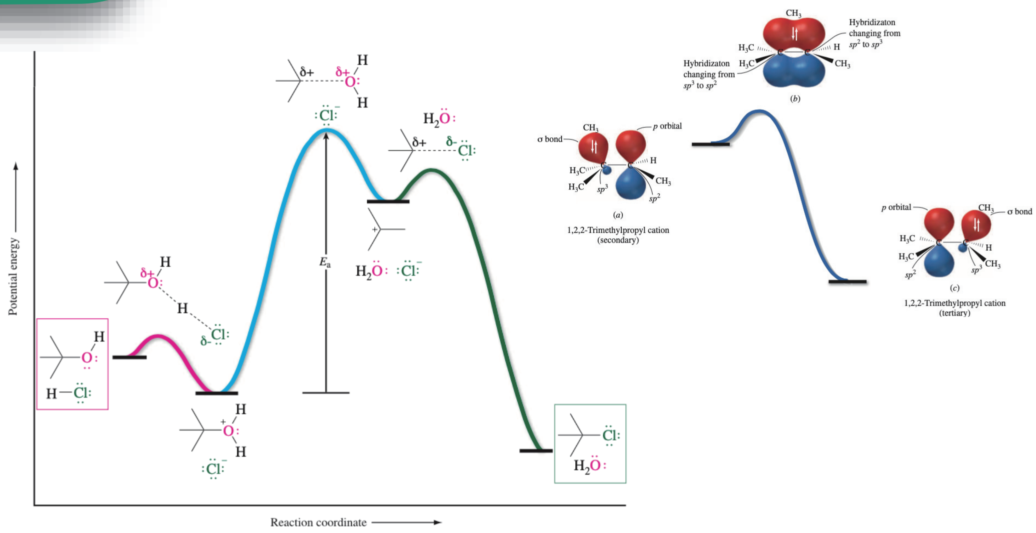
$$CH_3CH_2CH_2CH_2{-}MgBr + (H_3C)_2C{=}O \xrightarrow[2.\ H^+,\ H_2O]{1.\ THF} CH_3CH_2CH_2CH_2{-}C(CH_3)_2{-}OH$$

9.4 Summary & Practice

1. Concept

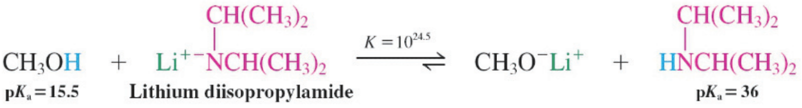
2. Example

9.5 Reaction of Alcohols



9.5.1 Reactions of Alcohols with Base

Three Ways of Making Methoxide from Methanol



$$\underset{pK_a = 15.5}{CH_3OH} + \underset{\text{Lithium diisopropylamide}}{Li^{+}\,{}^{-}\overset{\overset{CH(CH_3)_2}{|}}{N}CH(CH_3)_2} \xrightleftharpoons{K = 10^{24.5}} CH_3O^{-}Li^{+} + \underset{pK_a = 36}{H\overset{\overset{CH(CH_3)_2}{|}}{N}CH(CH_3)_2}$$

$$\underset{pK_a = 15.5}{CH_3OH} + \underset{\text{Butyllithium}}{CH_3CH_2CH_2CH_2Li} \xrightleftharpoons{K = 10^{34.5}} CH_3O^{-}Li^{+} + \underset{pK_a = 50}{CH_3CH_2CH_2CH_2H}$$

$$\underset{pK_a = 15.5}{CH_3OH} + \underset{\text{Potassium hydride}}{K^{+}H^{-}} \xrightleftharpoons{K = 10^{22.5}} CH_3O^{-}K^{+} + \underset{pK_a = 38}{H{-}H}$$

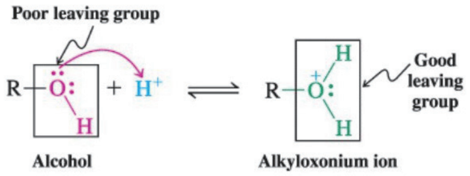
9.5.1 Reactions of Alcohols with Base

Alkoxides from Alcohols and Alkali Metals

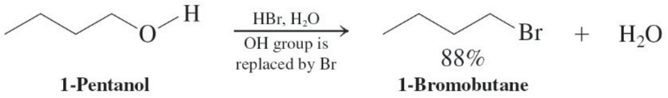
$$2\ CH_3CH_2OH + 2\ Na \rightarrow 2\ CH_3CH_2O^-Na^+ + H_2$$
$$2\ (CH_3)_3COH + 2\ K \rightarrow 2\ (CH_3)_3CO^-K^+ + H_2$$

9.5.2 Reactions of Alcohols with Strong Acids

Protonation of Hydroxy Turns It into a Good Leaving Group

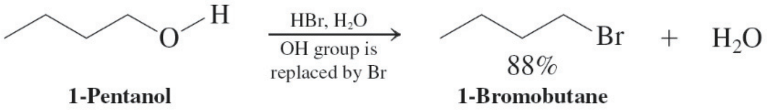


Primary Bromoalkane Synthesis from an Alcohol

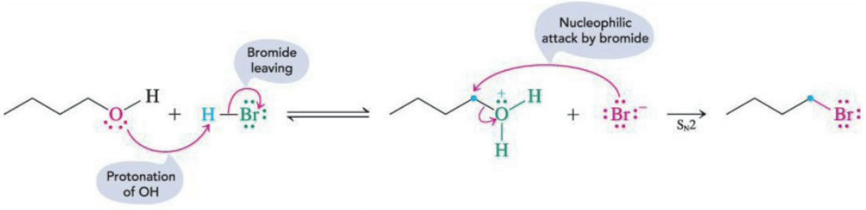


9.5.2 Reactions of Alcohols with Strong Acids

Primary Bromoalkane Synthesis from an Alcohol



Mechanism of Primary Bromoalkane Synthesis from an Alcohol

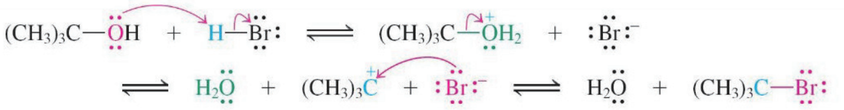


9.5.3 Reactions of Alcohols with Strong Acids

Conversion of 2-Methyl-2-propanol into 2-Bromo-2-methylpropane

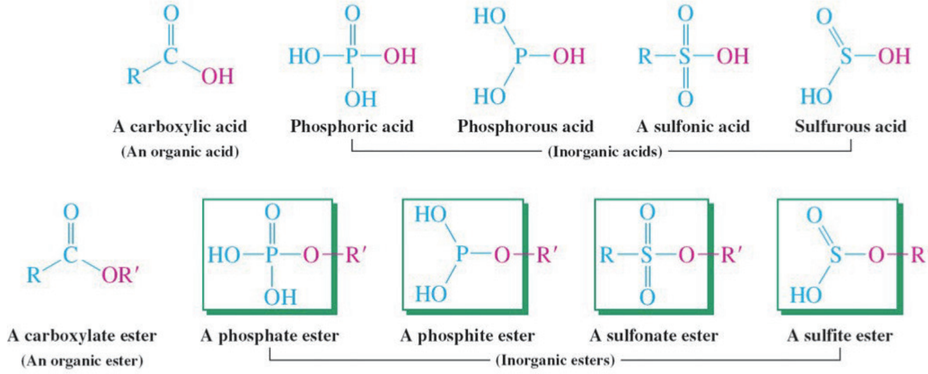
$$(CH_3)_3COH + \underset{\text{Excess}}{HBr} \rightleftharpoons (CH_3)_3CBr + H_2O$$

Mechanism of the SN1^{S_N1} Reaction of Tertiary Alcohols with Hydrogen Halides



9.5.4 Esters from Alcohols

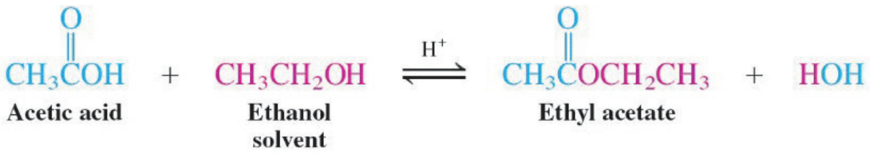
Organic and Inorganic Esters



9.5.4 Esters from Alcohols

Alcohols react with carboxylic acids to give organic esters

Esterification

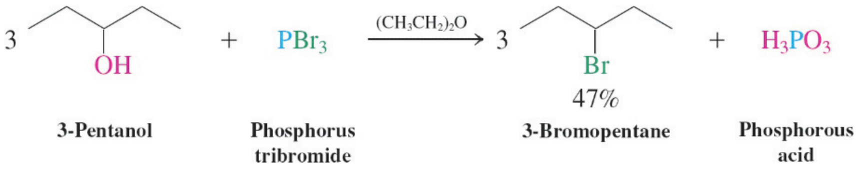


$$\underset{\text{Acetic acid}}{CH_3\overset{O}{\overset{\|}{C}}OH} + \underset{\substack{\text{Ethanol}\\\text{solvent}}}{CH_3CH_2OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3} + HOH$$

9.5.5 Haloalkane Synthesis

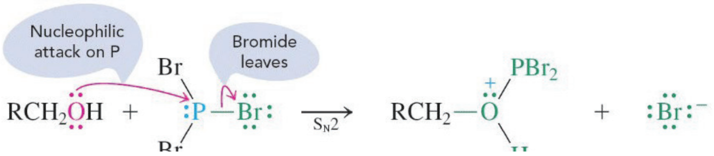
Haloalkanes can be made from alcohols through inorganic esters

Bromoalkane Synthesis by Using PBr3

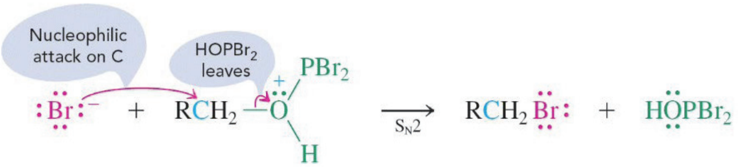


9.5.5 Haloalkane Synthesis

Step 1



Step 2

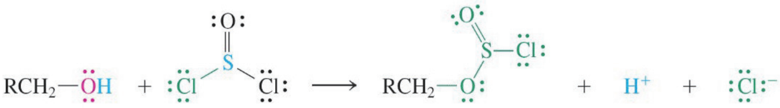


9.5.5 Haloalkane Synthesis

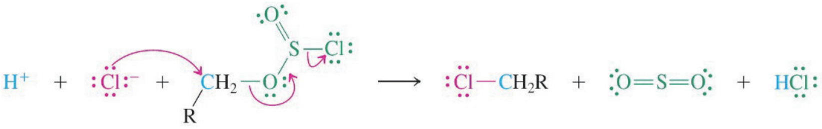
Chloroalkane Synthesis with SOCl2

$$CH_3CH_2CH_2OH + SOCl_2 \longrightarrow \underset{91\%}{CH_3CH_2CH_2Cl} + O{=}S{=}O + HCl$$

Step 1

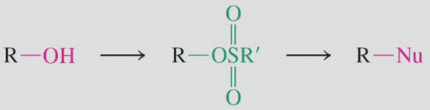


Step 2



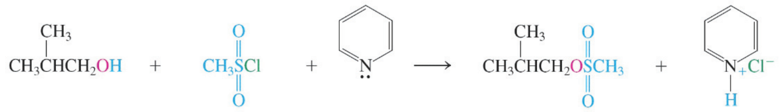
9.5.5 Haloalkane Synthesis

Sulfonate Intermediates in Nucleophilic Displacement of the Hydroxy Group in Alcohols



$$R-OH \longrightarrow R-O\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}R' \longrightarrow R-Nu$$

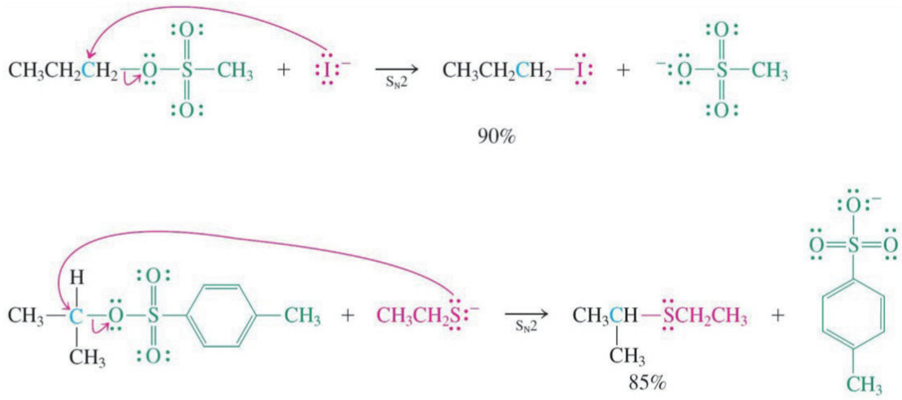
Synthesis of an Alkyl Sulfonate



2-Methyl-1-propanol · **Methanesulfonyl chloride (Mesyl chloride)** · **Pyridine** · **2-Methylpropyl methanesulfonate (2-Methylpropyl mesylate)** · **Pyridinium hydrochloride**

9.5.5 Haloalkane Synthesis

Substitution Reactions of Alkyl Sulfonates

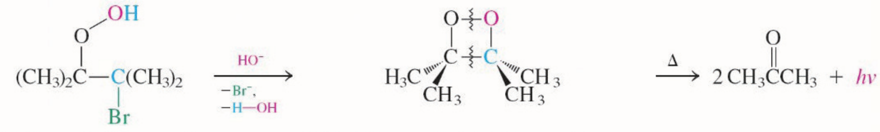


9.5.5 Williamson Ether Synthesis

Ethers are prepared by SN2 reactions

Williamson Ether Syntheses

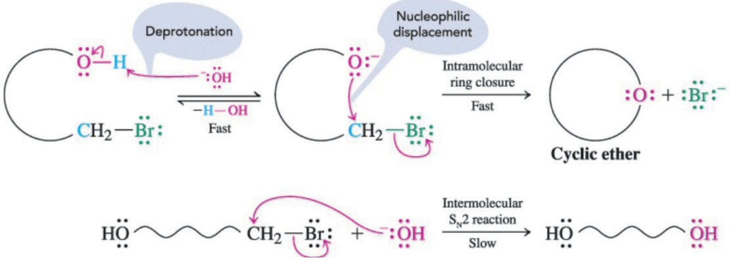
60% (butanol solvent)
95% (DMSO solvent)
1-Butoxybutane



A 2-bromohydroperoxide · **3,3,4,4-Tetramethyl-1,2-dioxacyclobutane (A 1,2-dioxetane)** · **Acetone**

9.5.5 Williamson Ether Synthesis

Cyclic ethers can be prepared by intramolecular Williamson synthesis

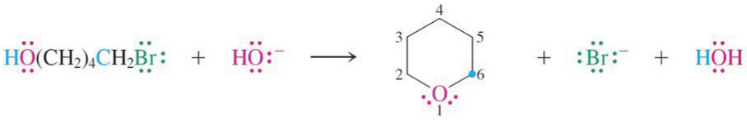


9.5.5 Williamson Ether Synthesis

Cyclic ethers can be prepared by intramolecular Williamson synthesis

Cyclic Ether Synthesis

Oxacyclopropane
(Oxirane, ethylene oxide)



Oxacyclohexane
(Tetrahydropyran)

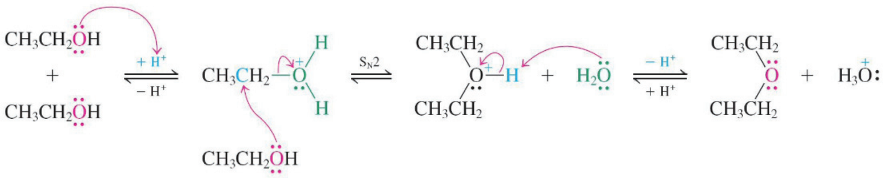
9.5.5 Synthesis of Ethers: Alcohols and Mineral Acids

Alcohols give ethers by both SN2 and SN1 mechanisms

Symmetrical Ether Synthesis from a Primary Alcohol with Strong Acid

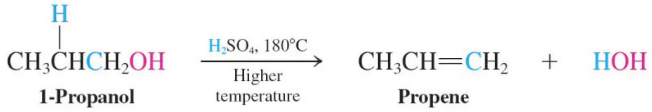
$$2\,CH_3CH_2OH \xrightarrow[\text{High temperature}]{H_2SO_4,\ 130^\circ C} CH_3CH_2OCH_2CH_3 + HOH$$

Mechanism of Ether Synthesis from Primary Alcohols: Protonation and SN2



9.5.5 Synthesis of Ethers: Alcohols and Mineral Acids

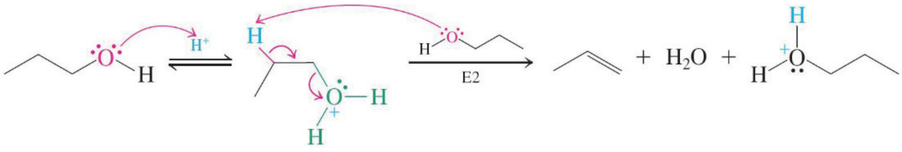
Alkene Synthesis from a Primary Alcohol and Strong Acid at Elevated Temperature: E2



$$CH_3\overset{\overset{\displaystyle H}{|}}{C}HCH_2OH \xrightarrow[\text{Higher temperature}]{H_2SO_4,\ 180°C} CH_3CH{=}CH_2 + HOH$$

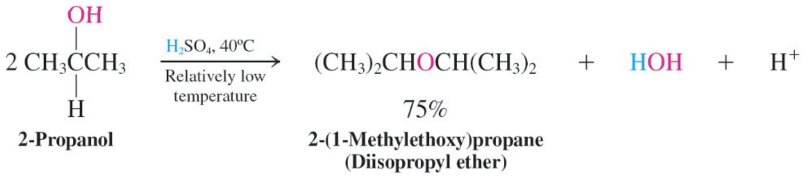
1-Propanol **Propene**

E2 Mechanism for the Acid-Catalyzed Dehydration of 1-Propanol



9.5.5 Synthesis of Ethers: Alcohols and Mineral Acids

Symmetrical Ether Synthesis from a Secondary Alcohol



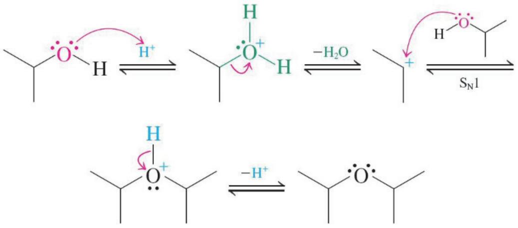
$$2\ CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}CH_3 \xrightarrow[\text{Relatively low temperature}]{H_2SO_4,\ 40°C} (CH_3)_2CHOCH(CH_3)_2 + HOH + H^+$$

75%

2-Propanol

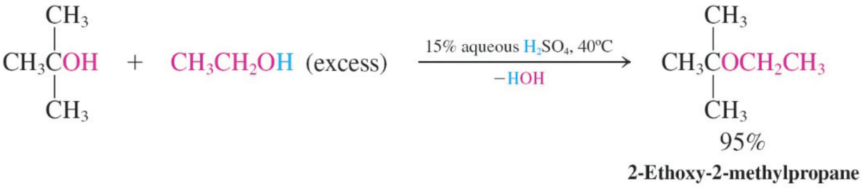
2-(1-Methylethoxy)propane
(Diisopropyl ether)

SN1 Mechanism for the Acid-Catalyzed Ether Formation from 2- Propanol



9.5.5 Synthesis of Ethers: Alcohols and Mineral Acids

Synthesis of a Mixed Ether from a Tertiary Alcohol



$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}OH + CH_3CH_2OH\ \text{(excess)} \xrightarrow[-HOH]{15\%\ \text{aqueous}\ H_2SO_4,\ 40°C} CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}OCH_2CH_3$$

95%

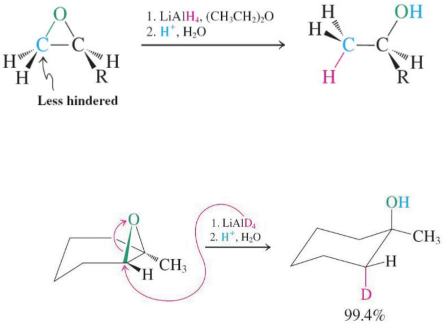
2-Ethoxy-2-methylpropane

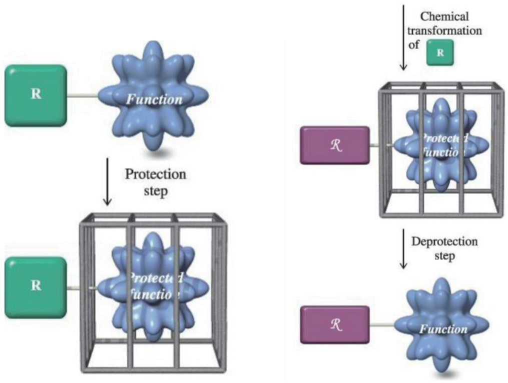
9.5 Summary & Practice

1. Concept

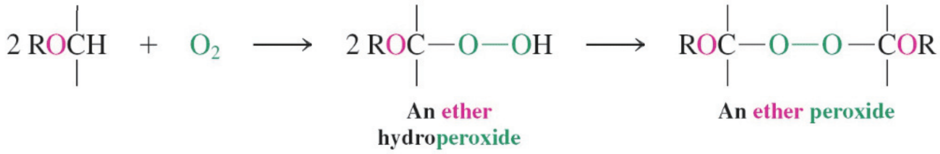
2. Example

9.6 Ether





9.6.1 Peroxides from Ethers



$$2\,\mathrm{ROCH} + O_2 \longrightarrow 2\,\mathrm{ROC{-}O{-}OH} \longrightarrow \mathrm{ROC{-}O{-}O{-}COR}$$

An ether hydroperoxide

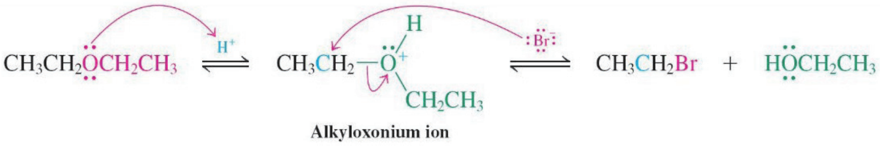
An ether peroxide

As mentioned earlier, ethers are normally rather inert. They do, however, react slowly with oxygen by radical mechanisms to form hydroperoxides and peroxides. Because peroxides can decompose explosively, extreme care should be taken with samples of ethers that have been exposed to air for several days.

9.6.2 Primary Ether Cleavage with HBr

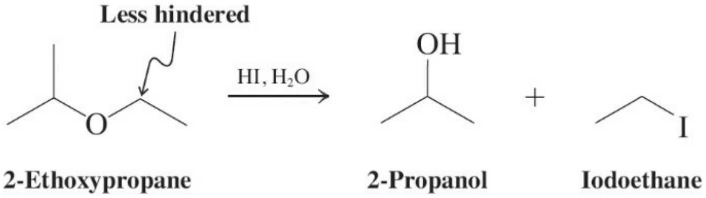

$$CH_3CH_2OCH_2CH_3 \xrightarrow{HBr} CH_3CH_2Br + CH_3CH_2OH$$

Mechanism of Primary Ether Cleavage: SN2S_N2



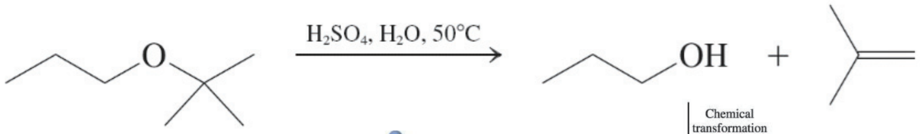
9.6.3 Primary-Secondary Ether Cleavage with HI

Primary-Secondary Ether Cleavage with HI: SN2 at Primary Center

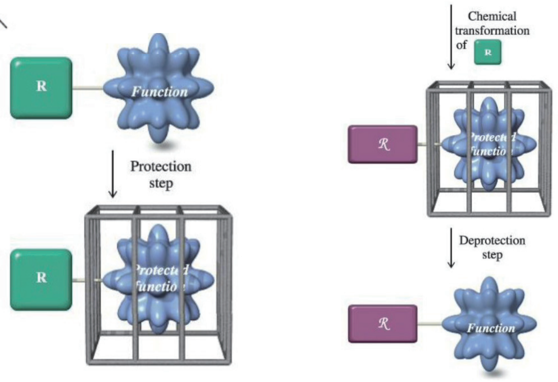


9.6.4 Tertiary butyl ethers function to protect alcohols

Primary-Tertiary Ether Cleavage with Dilute Acid: SN1 and E1 at Tertiary Center

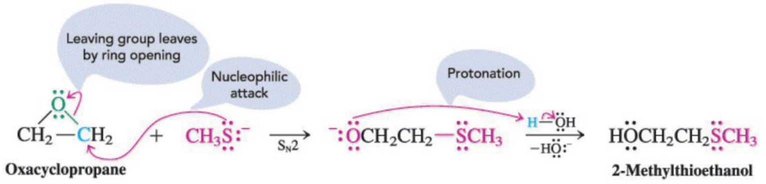


Protecting-Group Strategy



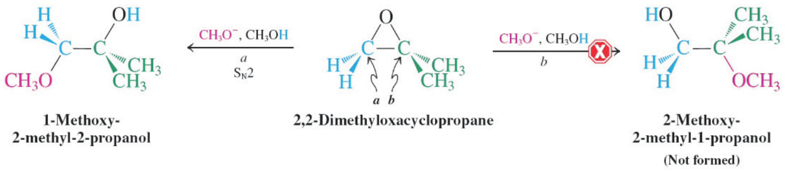
9.6.5 Reactions of Oxacyclopropane

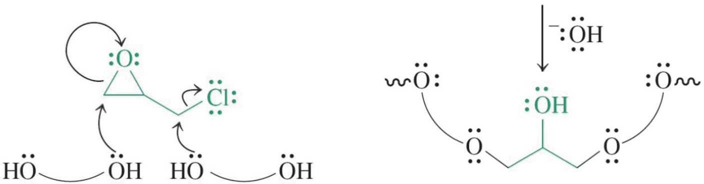
Nucleophilic ring opening of oxacyclopropanes by SN2 is regioselective and stereospecific



9.6.5 Reactions of Oxacyclopropane

Nucleophilic Ring Opening of an Unsymmetrically Substituted Oxacyclopropane

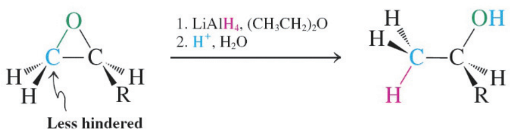




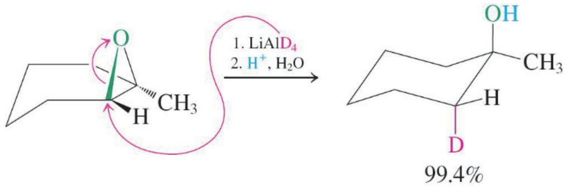
Epoxyresin

9.6.5 Reactions of Oxacyclopropane

Ring Opening of an Oxacyclopropane by Lithium Aluminum Hydride



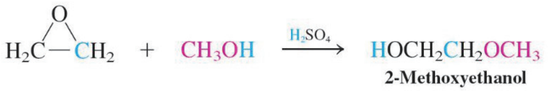
Inversion on Oxacyclopropane Opening



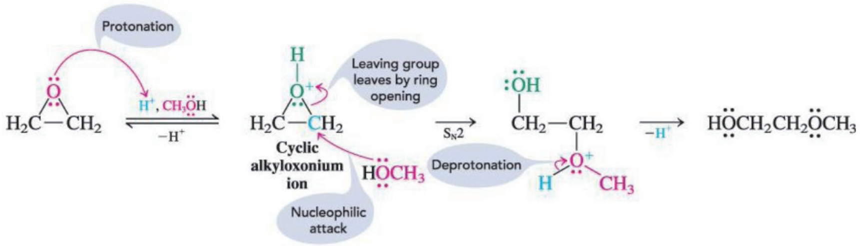
D and OH are trans, not cis

9.6.6 Acids catalyze oxacyclopropane ring opening

Acid-Catalyzed Ring Opening of Oxacyclopropane

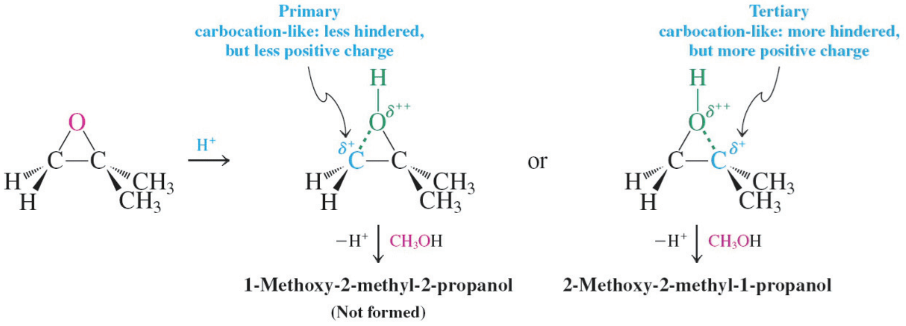


Mechanism of Acid-Catalyzed Ring Opening



9.6.6 Acids catalyze oxacyclopropane ring opening

Mechanism of Acid-Catalyzed Ring Opening of 2,2-Dimethyloxacyclopropane by Methanol



9.6 Summary & Practice

1. Concept

2. Example

UKChO

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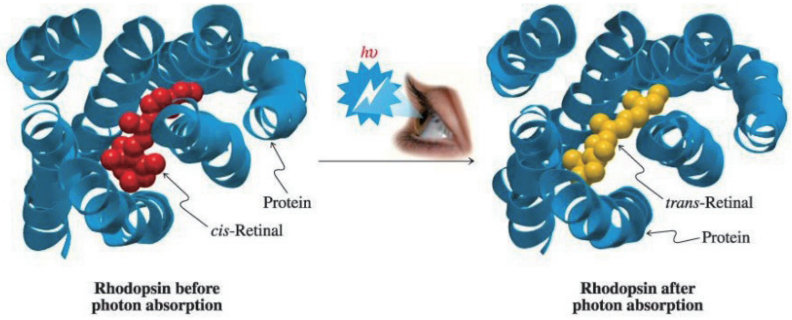
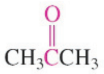
Unit 10 Organic Derivative

1. Aldehydes and ketone
2. Enol, enolate and aldol condensation
3. Carboxylic Acids
4. Carboxylic Acid Derivatives

10.1 Aldehydes and Ketone

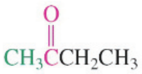


10.1.1 Naming the Aldehydes and Ketones



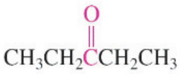
$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_3}$

Dimethyl ketone
(Acetone)



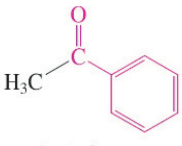
$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3}$

Ethyl methyl ketone

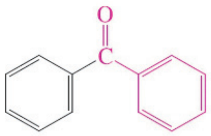


$\mathrm{CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3}$

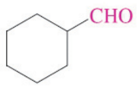
Diethyl ketone



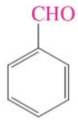
Acetophenone



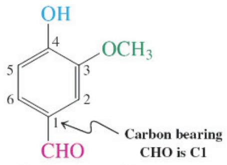
Benzophenone



Cyclohexanecarbaldehyde

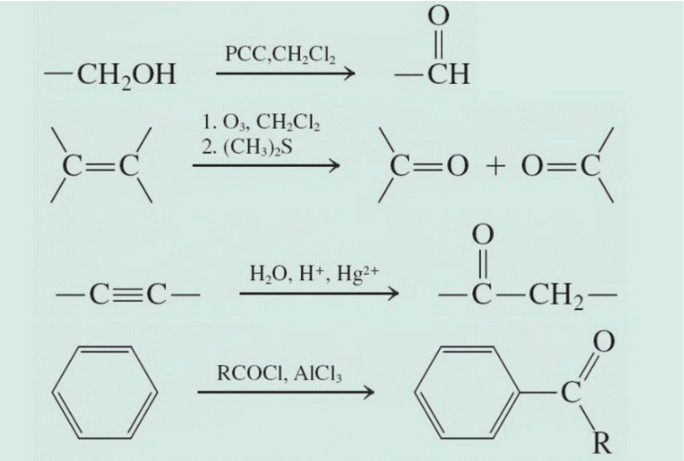


Benzenecarbaldehyde
(Benzaldehyde)



4-Hydroxy-3-methoxy-benzenecarbaldehyde
(4-Hydroxy-3-methoxy-benzaldehyde; vanillin)

10.1.2 Preparation of Aldehydes and Ketones



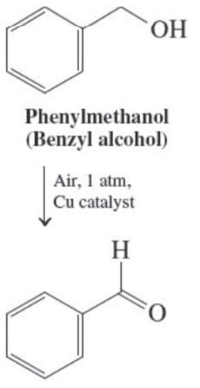
1.Oxidation of alcohols

2.Ozonolysis of alkenes

3.Hydration of alkynes

4.Friedel-Crafts acylation

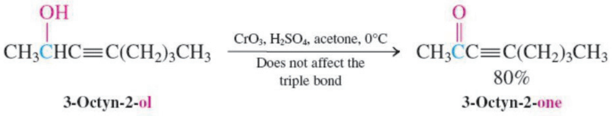
10.1.2 Preparation of Aldehydes and Ketones



Phenylmethanol (Benzyl alcohol)

100%
Benzaldehyde

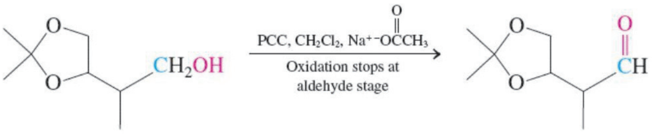
Selective Alcohol Oxidation



$\mathrm{CH_3\overset{OH}{\overset{|}{C}}HC{\equiv}C(CH_2)_3CH_3} \longrightarrow \mathrm{CH_3\overset{O}{\overset{\|}{C}}C{\equiv}C(CH_2)_3CH_3}$

3-Octyn-2-ol → **3-Octyn-2-one**

Use of PCC (CrO3+Pyridine+HCl)(CrO_3 + Pyridine + HCl) **to Oxidize a Primary Alcohol to an Aldehyde**

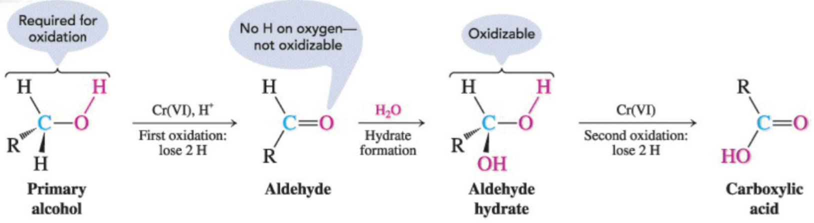


85%

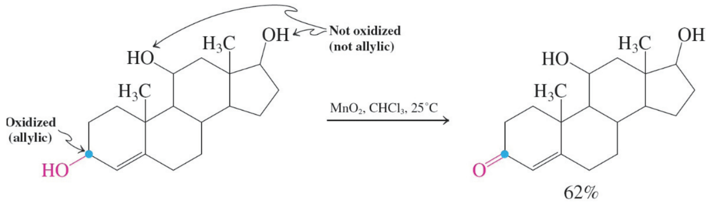
10.1.2

Preparation of Aldehydes and Ketones

Water Causes the Overoxidation of Primary Alcohols



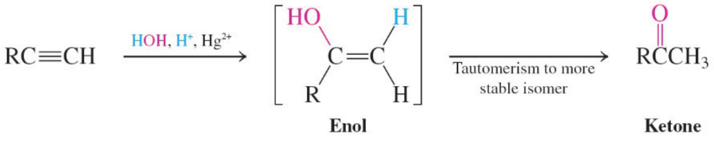
Selective Allylic Oxidations with Manganese Dioxide



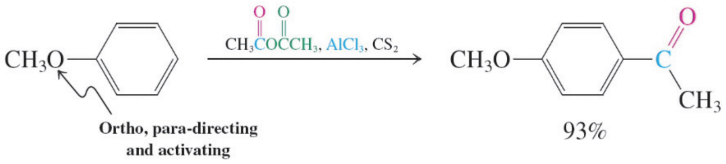
10.1.2

Preparation of Aldehydes and Ketones

Markovnikov Hydration of Alkynes



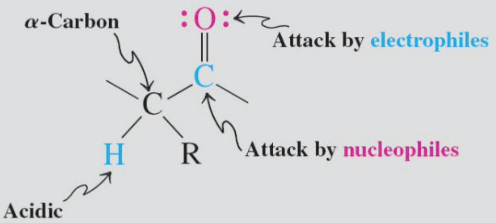
Friedel-Crafts Acylation



10.1.3

Reactivity of the Carbonyl Group

Regions of Reactivity in Aldehydes and Ketones



There are three regions of reactivity in aldehydes and ketones

10.1.3

Reactivity of the Carbonyl Group

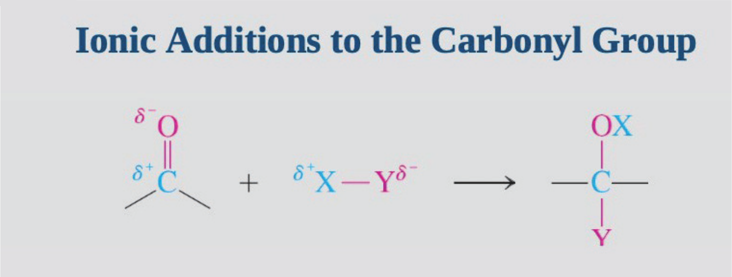
The carbonyl group undergoes ionic additions

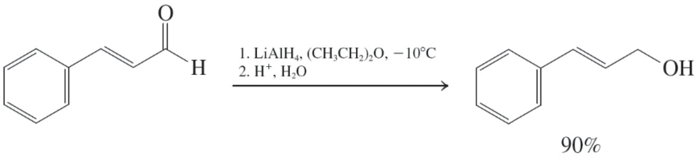
Reaction	Equation	
1. Aldehyde + hydride reagent	$RCHO \xrightarrow{NaBH_4,\ CH_3CH_2OH} RCH_2OH$	Primary alcohol
2. Ketone + hydride reagent	$R_2CO \xrightarrow{NaBH_4,\ CH_3CH_2OH} R_2CHOH$	Secondary alcohol
3. Formaldehyde + Grignard reagent	$H_2CO \xrightarrow{R'MgX,\ (CH_3CH_2)_2O} R'CH_2OH^a$	Primary alcohol
4. Aldehyde + Grignard reagent	$RCHO \xrightarrow{R'MgX,\ (CH_3CH_2)_2O} R'RCHOH^a$	Secondary alcohol
5. Ketone + Grignard reagent	$R_2CO \xrightarrow{R'MgX,\ (CH_3CH_2)_2O} R'R_2COH^a$	Tertiary alcohol

10.1.3

Reactivity of the Carbonyl Group

The carbonyl group undergoes ionic additions


Ionic Additions to the Carbonyl Group



10.1.3

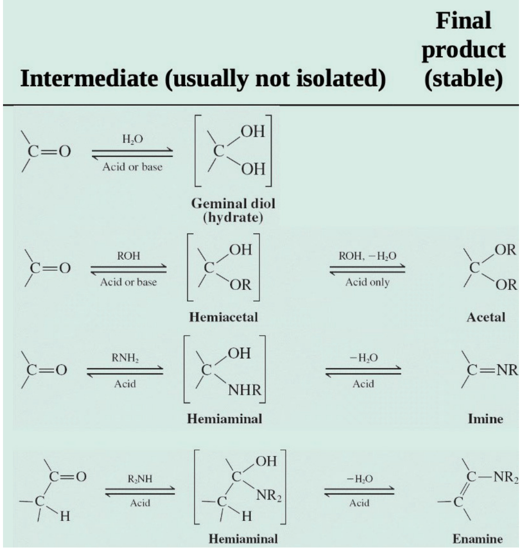
Reactivity of the Carbonyl Group

1. Water

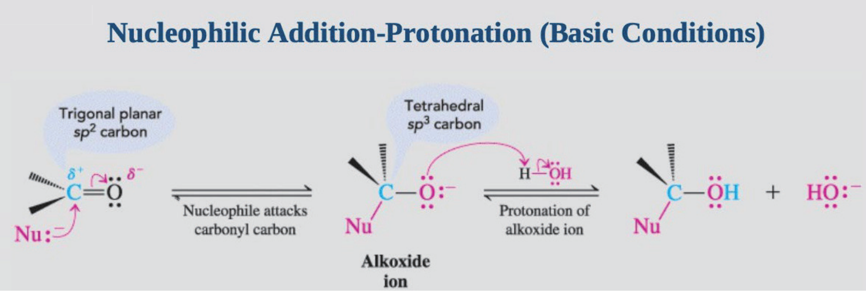
2. Alcohol

3. Ammonia (R=H) or primary amine (R = alkyl or aryl)

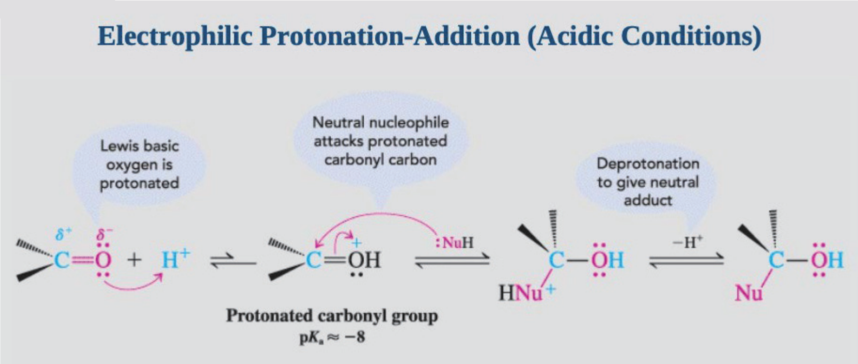
4. Secondary amine



10.1.3 Reactivity of the Carbonyl Group

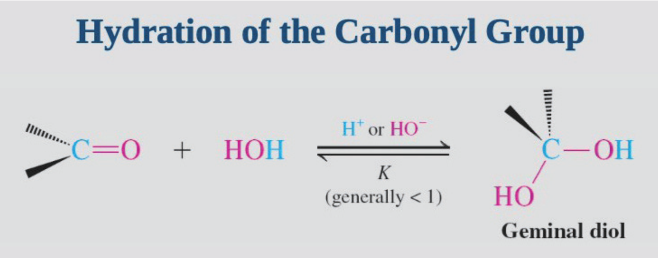

Nucleophilic Addition-Protonation (Basic Conditions)

10.1.3 Reactivity of the Carbonyl Group


Electrophilic Protonation-Addition (Acidic Conditions)

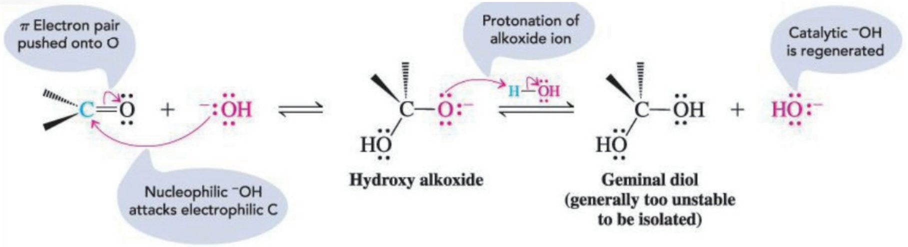
10.1.4 Addition of Water to Form Hydrates

Water hydrates the carbonyl group

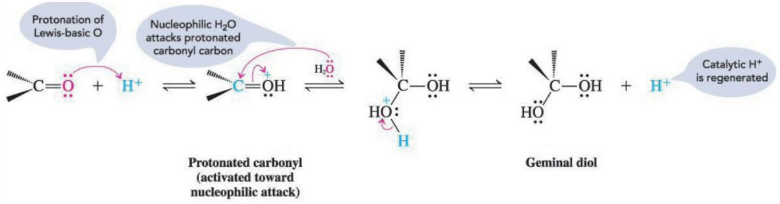

Hydration of the Carbonyl Group

10.1.4 Addition of Water to Form Hydrates

Mechanism of Base-Catalyzed Hydration



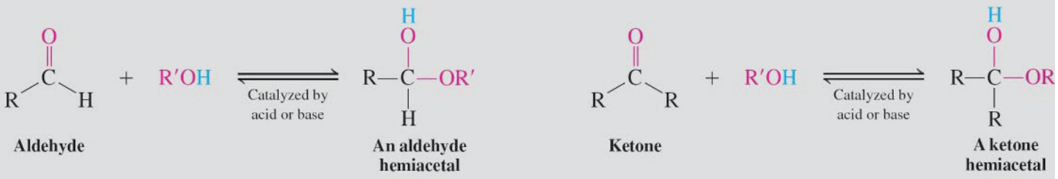
Mechanism of Acid-Catalyzed Hydration



10.1.5 Addition of Alcohols to Form Hemiacetals and Acetals

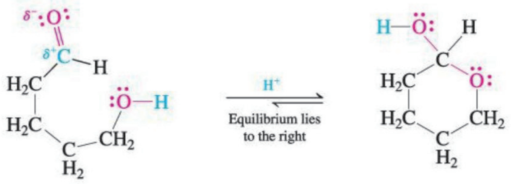
Aldehydes and ketones form hemiacetals reversibly

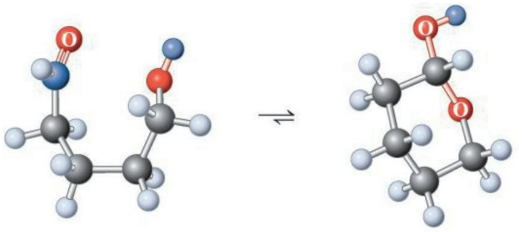
Hemiacetal Formation: Equilibria



10.1.5 Addition of Alcohols to Form Hemiacetals and Acetals

Intramolecular Hemiacetal Formation: Cyclic Hemiacetals Are More Stable than Acyclic Hemiacetals





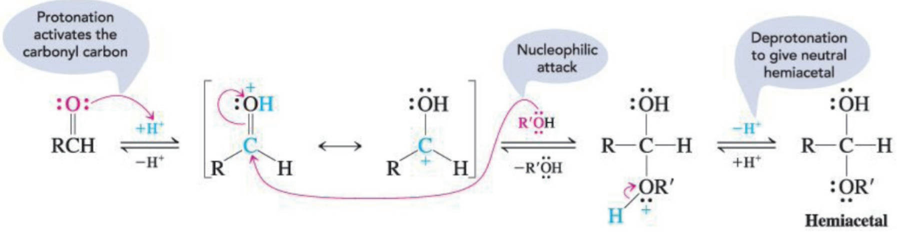
5-Hydroxypentanal

A cyclic hemiacetal, stable

10.1.5 Addition of Alcohols to Form Hemiacetals and Acetals

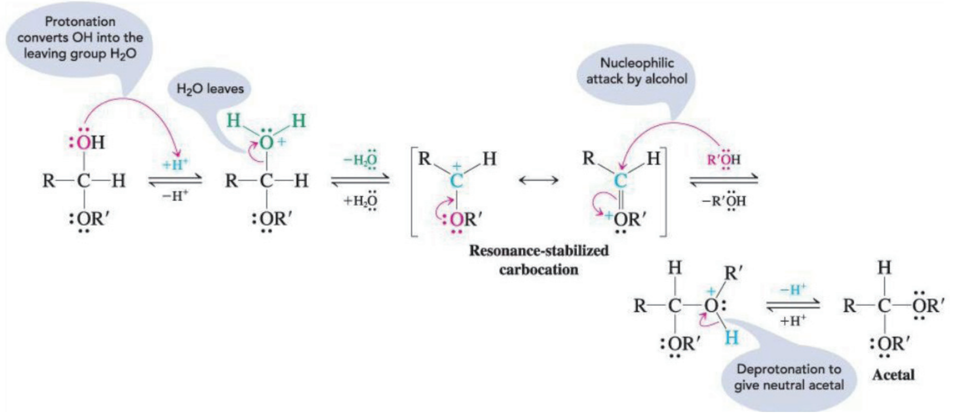
Mechanism of Acetal Formation

Step 1. Hemiacetal generation: acid-catalyzed addition of first molecule of alcohol



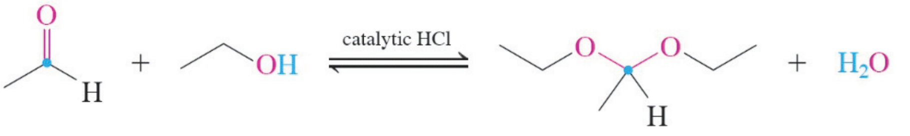
10.1.5 Addition of Alcohols to Form Hemiacetals and Acetals

Step 2. Acetal generation: acid-catalyzed SN1 displacement of water by second molecule of alcohol



10.1.5 Addition of Alcohols to Form Hemiacetals and Acetals

Acetal Formation and Hydrolysis



Acetaldehyde

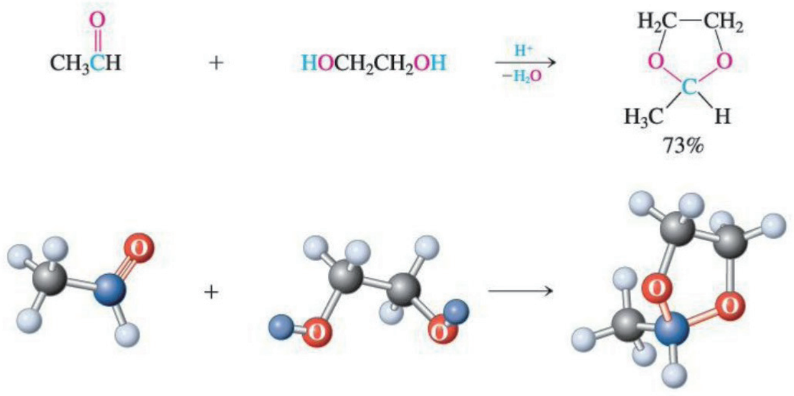
Ethanol
Excess alcohol
drives equilibrium
to the right

64%
1,1-Diethoxyethane
(from reaction with
excess alcohol)

Excess water
drives equilibrium
to the left

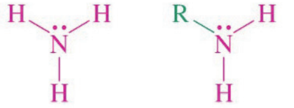
10.1.6 Acetals as Protecting Groups

Cyclic acetal formation protects carbonyl groups from attack by nucleophiles



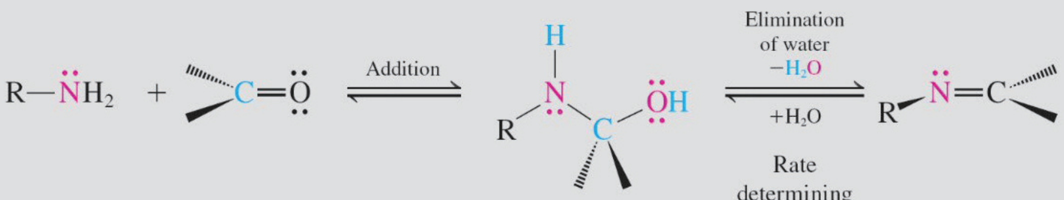
A cyclic acetal

10.1.6 Nucleophilic Addition of Ammonia and Its Derivatives



Ammonia **Primary amine**

Imine Formation from Amines and Aldehydes or Ketones

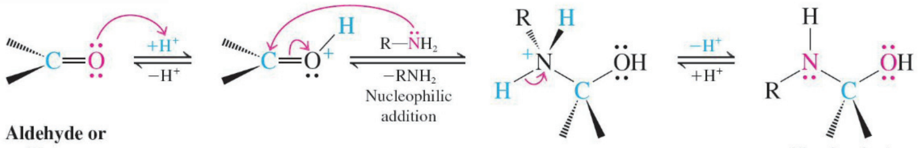


A hemiaminal

An imine

10.1.6 Nucleophilic Addition of Ammonia and Its Derivatives

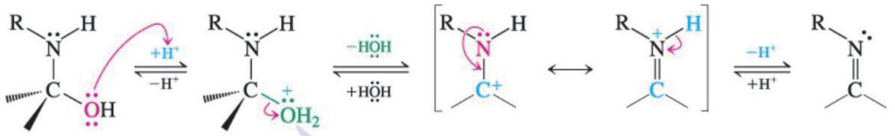
Mechanism of Hemiaminal Formation



Aldehyde or Ketone

Hemiaminal

Mechanism of Hemiaminal Dehydration



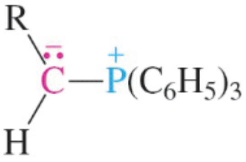
Hemiaminal

Iminium ion (resonance-stabilized)

Imine

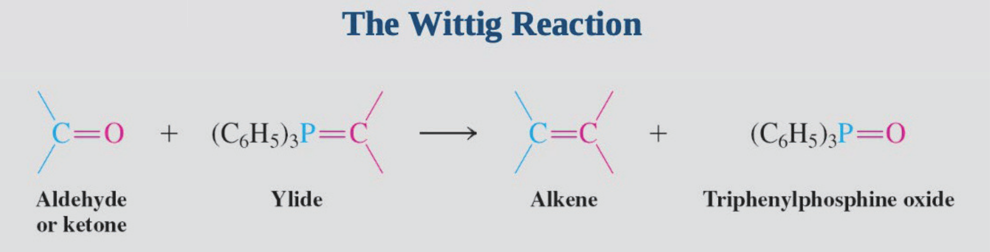
10.1.7 The Wittig Reaction (Addition of Phosphorus Ylides)

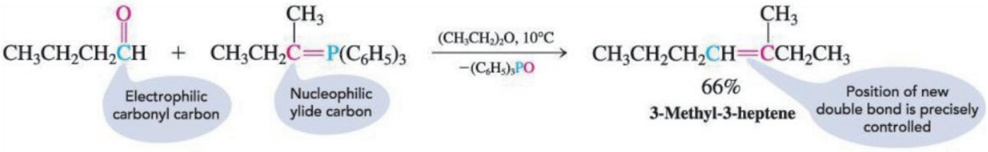
Another useful reagent in nucleophilic additions contains a carbanion that is stabilized by an adjacent, positively charged phosphorus group. Such a species is called a **phosphorus ylide,** and its attack on aldehydes and ketones is called the **Wittig reaction.**



Ylide

10.1.7 The Wittig Reaction (Addition of Phosphorus Ylides)





$$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H + CH_3CH_2\overset{CH_3}{\overset{|}{C}}{=}P(C_6H_5)_3 \xrightarrow[-(C_6H_5)_3PO]{(CH_3CH_2)_2O,\ 10°C} CH_3CH_2CH_2CH{=}\overset{CH_3}{\overset{|}{C}}CH_2CH_3$$

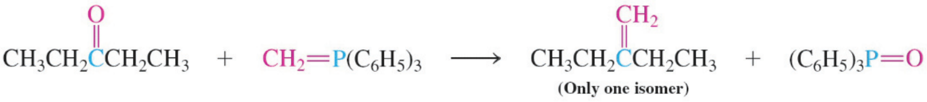
66%

3-Methyl-3-heptene

10.1.7 The Wittig Reaction (Addition of Phosphorus Ylides)

Comparison of Two Syntheses of 2-Ethyl-1-butene

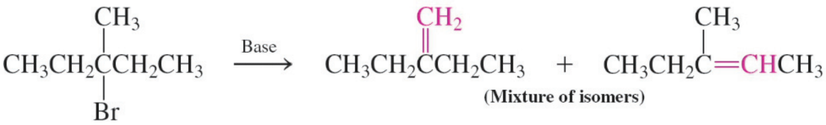
By Wittig reaction (a single product is formed cleanly)



$$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + CH_2{=}P(C_6H_5)_3 \longrightarrow CH_3CH_2\overset{CH_2}{\overset{\|}{C}}CH_2CH_3 + (C_6H_5)_3P{=}O$$

(Only one isomer)

By elimination (leads to a mixture of alkene isomers)



$$CH_3CH_2\overset{CH_3}{\overset{|}{\underset{\underset{Br}{|}}{C}}}CH_2CH_3 \xrightarrow{Base} CH_3CH_2\overset{CH_2}{\overset{\|}{C}}CH_2CH_3 + CH_3CH_2\overset{CH_3}{\overset{|}{C}}{=}CHCH_3$$

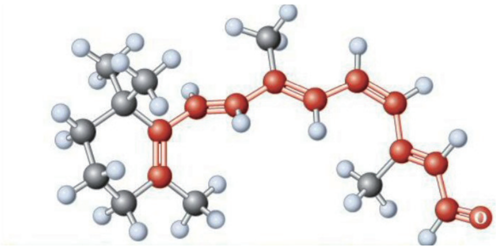
(Mixture of isomers)

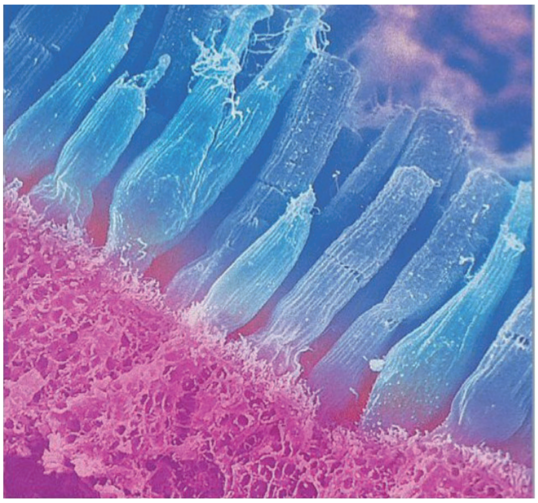
10.1 Summary & Practice

1. Concept

2. Example

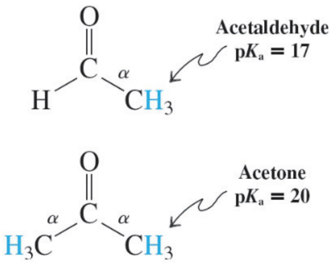
10.2 Enol, Enolate and Aldol Condensation



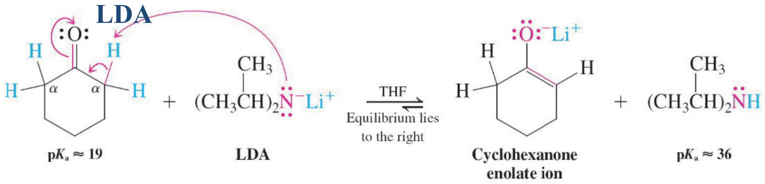


10.2.1 Enolate Ions

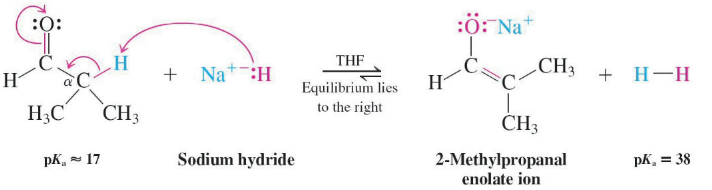
Acidity of α-Hydrogens



Quantitative Ketone Enolate Formation with LDA



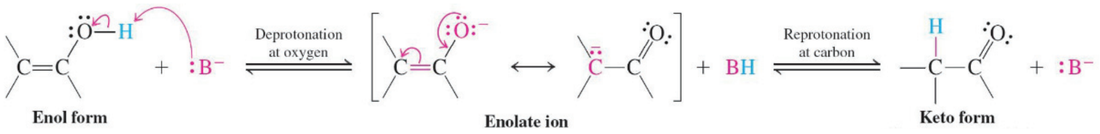
Quantitative Aldehyde Enolate Formation with NaH



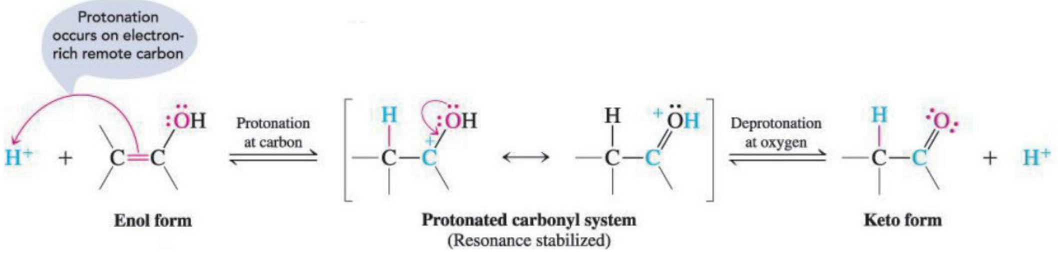
10.2.2

Keto–Enol Equilibria

Base-Catalyzed Enol–Keto Equilibration



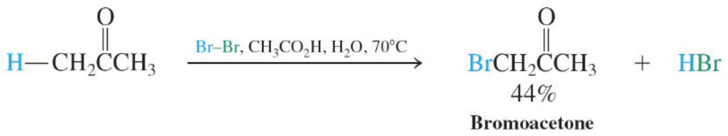
Acid-Catalyzed Enol–Keto Equilibration



10.2.3

Halogenation of Aldehydes and Ketones

Acid-Catalyzed αα-Halogenation of Ketones



$$H{-}CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{Br{-}Br,\ CH_3CO_2H,\ H_2O,\ 70°C} BrCH_2\overset{O}{\overset{\|}{C}}CH_3 + HBr$$

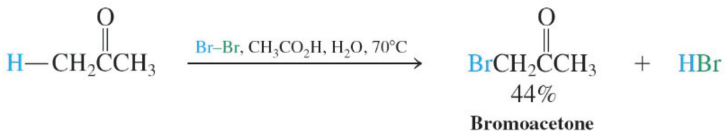
44%

Bromoacetone

10.2.3

Halogenation of Aldehydes and Ketones

Acid-Catalyzed αα-Halogenation of Ketones

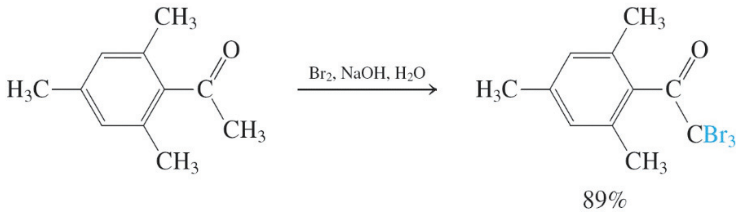


$$H{-}CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{Br{-}Br,\ CH_3CO_2H,\ H_2O,\ 70°C} BrCH_2\overset{O}{\overset{\|}{C}}CH_3 + HBr$$

44%

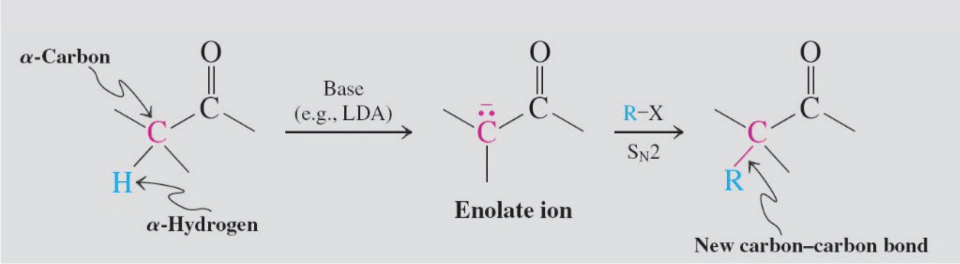
Bromoacetone

Base-Catalyzed αα-Halogenation of Ketones



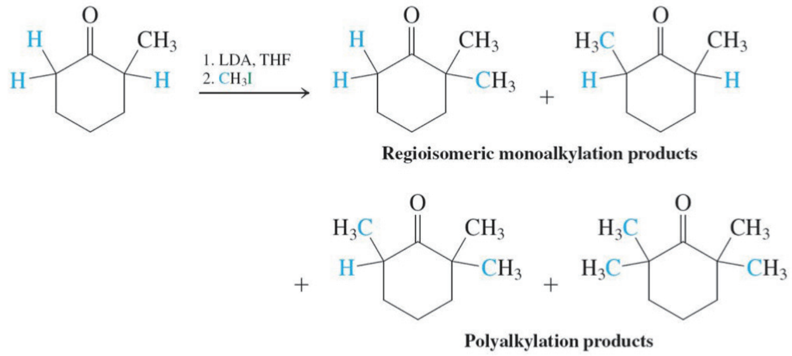
10.2.4 Alkylation of Aldehydes and Ketones

Alkylation of an Aldehyde or Ketone



10.2.4 Alkylation of Aldehydes and Ketones

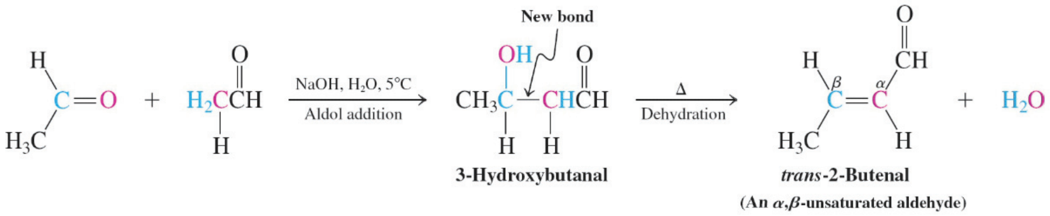
Products of Alkylation of 2-Methylcyclohexanone: An Uncontrollable Process



10.2.5 Aldol Condensation

Aldehydes undergo base-catalyzed condensations
Addition of a small amount of cold dilute aqueous sodium hydroxide to acetaldehyde initiates the conversion of the aldehyde into a dimer, 3- hydroxybutanal, with the common name *aldol* (from *ald*ehyde alcoh*ol*), a transformation called **aldol addition**.

Aldol Condensation Between Two Molecules of Acetaldehyde

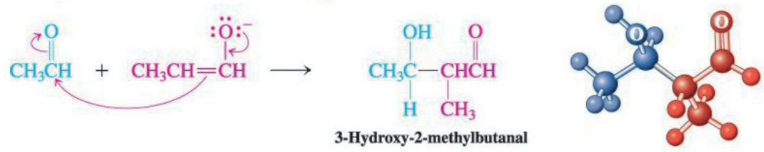


10.2.6 Crossed Aldol Condensation

Result of Nonselective Crossed Aldol Reaction Between Acetaldehyde and Propanal

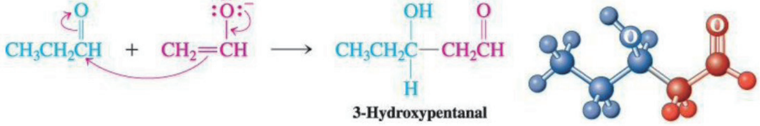
(All four reactions occur simultaneously)

1. Propanal enolate adds to acetaldehyde.



3-Hydroxy-2-methylbutanal

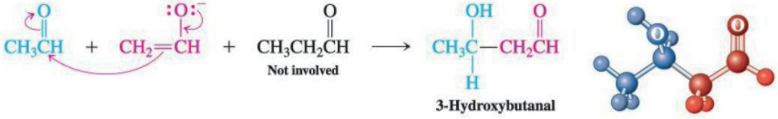
2. Acetaldehyde enolate adds to propanal.



3-Hydroxypentanal

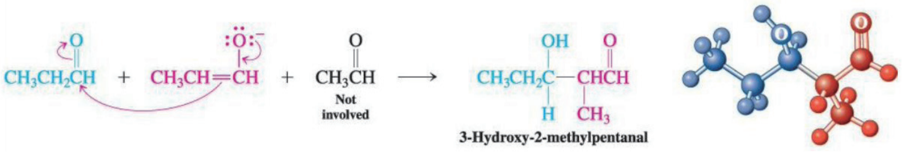
10.2.6 Crossed Aldol Condensation

3. Acetaldehyde enolate adds to acetaldehyde.



3-Hydroxybutanal

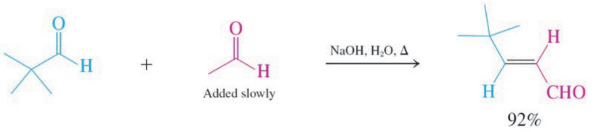
4. Propanal enolate adds to propanal.



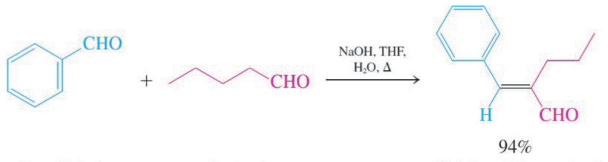
3-Hydroxy-2-methylpentanal

10.2.6

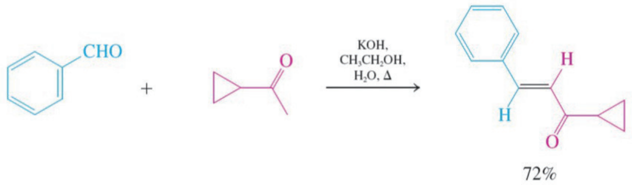
Successful Crossed Aldol Condensations



2,2-Dimethylpropanal (No α-hydrogen) | Acetaldehyde | (*E*)-4,4-Dimethyl-2-pentenal

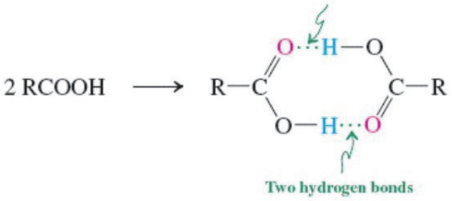


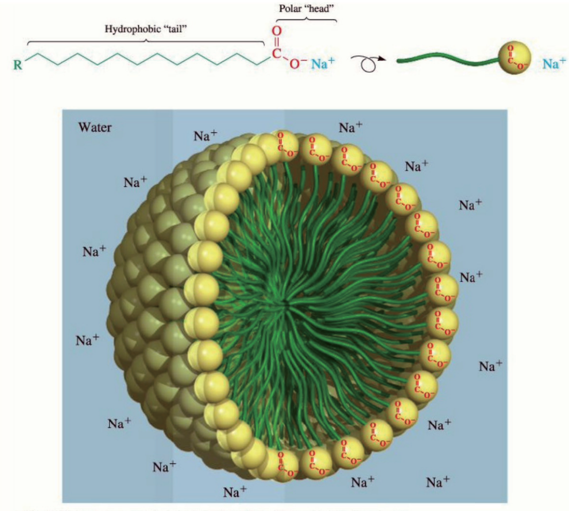
Benzaldehyde (No α-hydrogen) | Pentanal | (*E*)-2-Benzylidenepentanal



Benzaldehyde (No α-hydrogen) | Cyclopropylethanone | (*E*)-1-Cyclopropyl-3-phenyl-2-propen-1-one

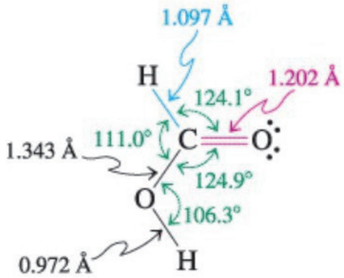
10.3 Carboxylic Acids



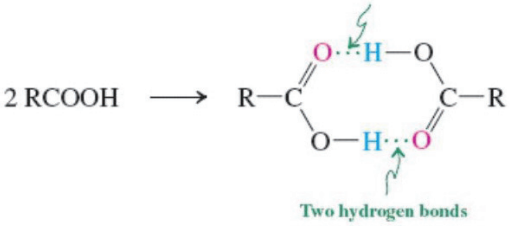


10.3.1 Structural and Physical Properties

Formic acid is planar

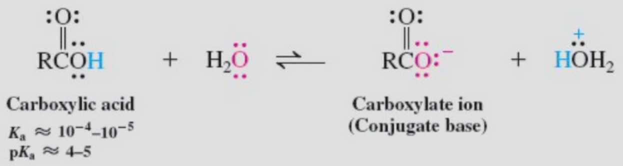


Carboxylic Acids Form Dimers Readily

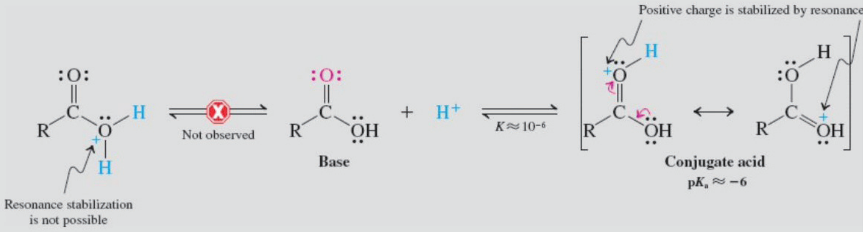


10.3.2 Acidic and Basic Character

Carboxylic Acids Dissociate Readily

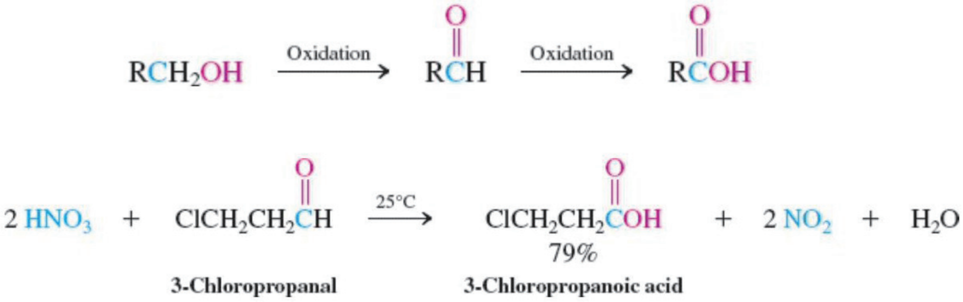


Protonation of a Carboxylic Acid



10.3.3 Introducing the Carboxy Functional Group

Carboxylic Acids by Oxidation

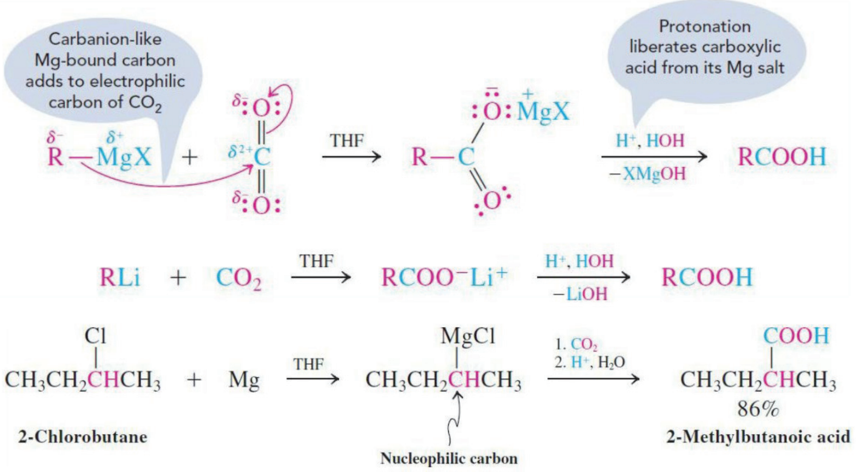


$$RCH_2OH \xrightarrow{\text{Oxidation}} R\overset{\overset{O}{\|}}{C}H \xrightarrow{\text{Oxidation}} R\overset{\overset{O}{\|}}{C}OH$$

$$2\,HNO_3 + ClCH_2CH_2\overset{\overset{O}{\|}}{C}H \xrightarrow{25^\circ C} ClCH_2CH_2\overset{\overset{O}{\|}}{C}OH + 2\,NO_2 + H_2O$$

10.3.3 Introducing the Carboxy Functional Group

Carbonation of Organometallics



Carbanion-like Mg-bound carbon adds to electrophilic carbon of CO_2

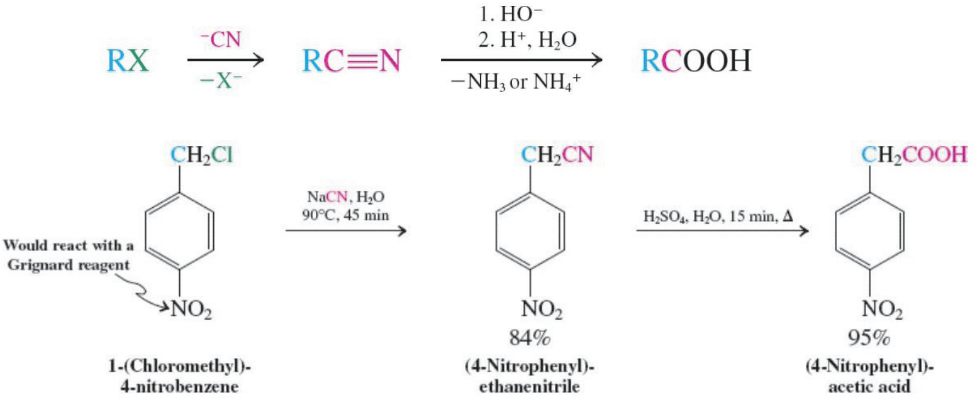
Protonation liberates carboxylic acid from its Mg salt

$$RLi + CO_2 \xrightarrow{THF} RCOO^-Li^+ \xrightarrow[-LiOH]{H^+,\ HOH} RCOOH$$

$$CH_3CH_2\overset{\overset{Cl}{|}}{C}HCH_3 + Mg \xrightarrow{THF} CH_3CH_2\overset{\overset{MgCl}{|}}{C}HCH_3 \xrightarrow{1.\ CO_2 \quad 2.\ H^+,\ H_2O} CH_3CH_2\overset{\overset{COOH}{|}}{C}HCH_3$$

10.3.3 Introducing the Carboxy Functional Group

Carboxylic Acids from Haloalkanes Through Nitriles

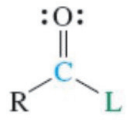


$$RX \xrightarrow[-X^-]{^-CN} RC{\equiv}N \xrightarrow[-NH_3 \text{ or } NH_4^+]{1.\ HO^- \quad 2.\ H^+,\ H_2O} RCOOH$$

10.3.4

Substitution at the Carboxy Carbon

The carbonyl carbon is attacked by nucleophiles



Carboxylic acid derivative

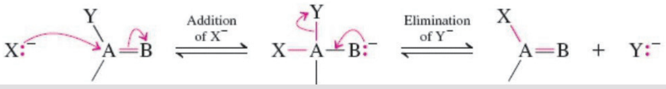
Carboxylic Acid Derivatives

$\overset{O}{\|}\mathrm{RCX}$ **Acyl halide** $\overset{O}{\|}\mathrm{RC}\overset{O}{\|}\mathrm{OCR}$ **Anhydride** $\overset{O}{\|}\mathrm{RCOR'}$ **Ester** $\overset{O}{\|}\mathrm{RCNR'_2}$ **Amide**

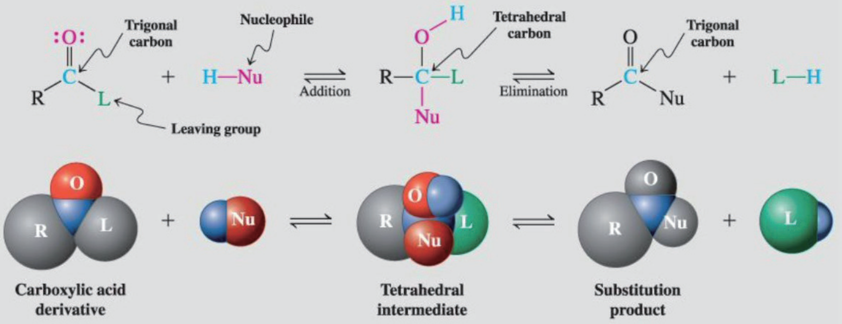
10.3.4

Substitution at the Carboxy Carbon

General Mechanistic Pattern for an Addition–Elimination Sequence



Nucleophilic Substitution by Addition–Elimination



10.3.5

Acyl Halides and Anhydrides

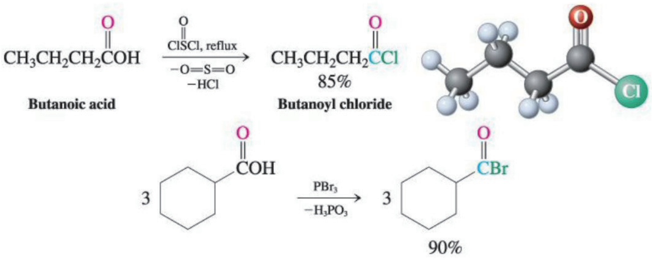
Replacement of the hydroxy group in RCOOH by halide gives rise to **acyl halides;** substitution by alkanoate (RCOO−)furnishes **carboxylic anhydrides**

Acyl halides are formed by using inorganic derivatives of carboxylic acids

$\overset{O}{\|}\mathrm{RCX}$

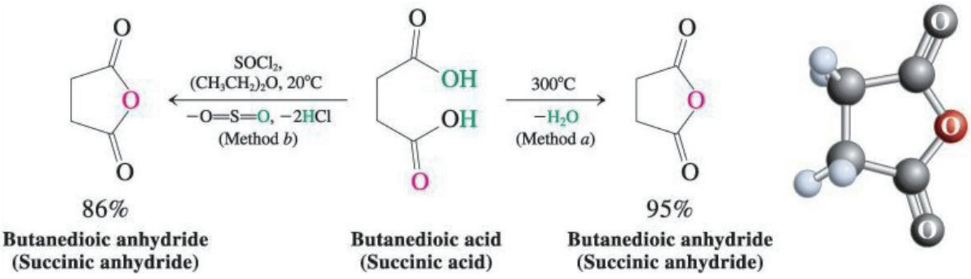
Acyl halide

Acyl Halide Synthesis



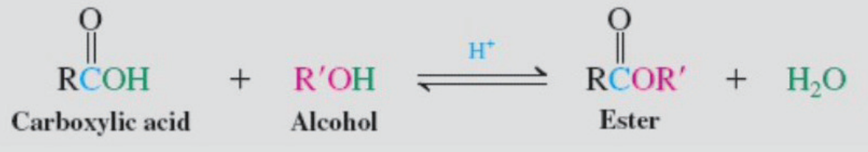
10.3.5 Acyl Halides and Anhydrides

Two Methods for Cyclic Anhydride Formation

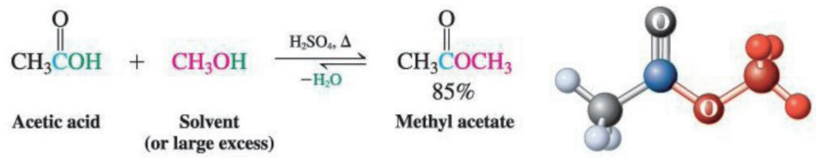


10.3.6 Esters

Acid-Catalyzed (Fischer) Esterification



$$R\overset{O}{\overset{\|}{C}}OH + R'OH \xrightleftharpoons{H^+} R\overset{O}{\overset{\|}{C}}OR' + H_2O$$

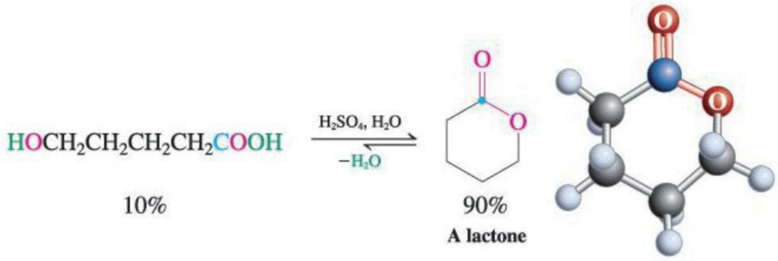


$$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3OH \underset{-H_2O}{\overset{H_2SO_4,\ \Delta}{\rightleftharpoons}} CH_3\overset{O}{\overset{\|}{C}}OCH_3$$

10.3.6 Esters

When hydroxy carboxylic acids are treated with catalytic amounts of mineral acid, cyclic esters—or **lactones**—may form. This process is called **intramolecular esterification** and is favorable for formation of five- and six- membered rings.

Formation of a Lactone

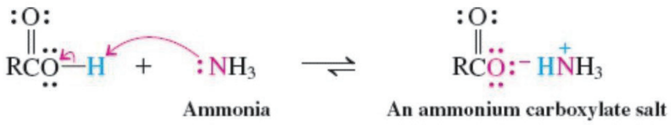


10.3.7 Amides

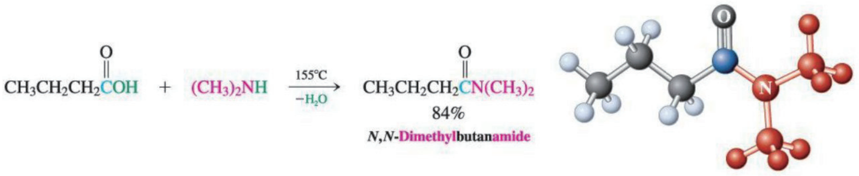
$$\overset{O}{\overset{\|}{R C N R'_2}}$$

Carboxylic amide

Ammonium Salts from Carboxylic Acids: An Acid-Base Reaction



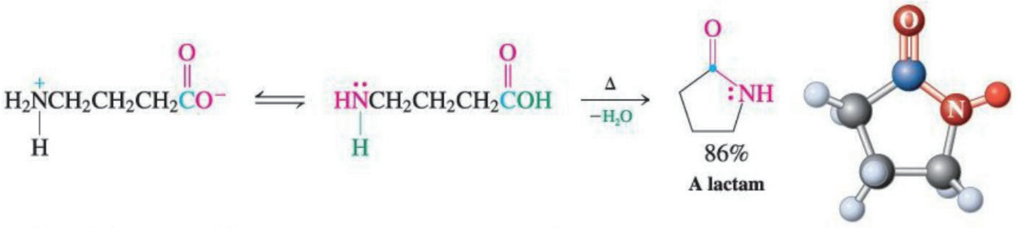
Formation of an Amide from an Amine and a Carboxylic Acid



10.3.7 Amides

Amino acids cyclize to lactams

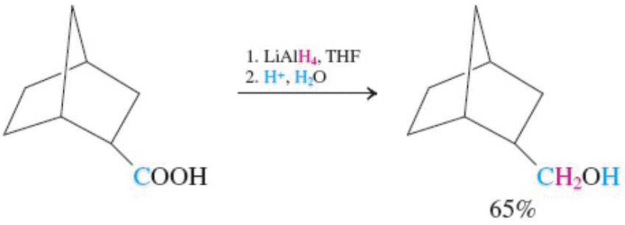
In analogy to hydroxycarboxylic acids, which form lactones, some amino acids undergo cyclization to the corresponding cyclic amides, called **lactams**



10.3.8 Reduction of Carboxylic Acids

Reduction of a Carboxylic Acid

$$RCOOH \xrightarrow{\substack{1.\ LiAlH_4,\ THF \\ 2.\ H^+,\ H_2O}} RCH_2OH$$

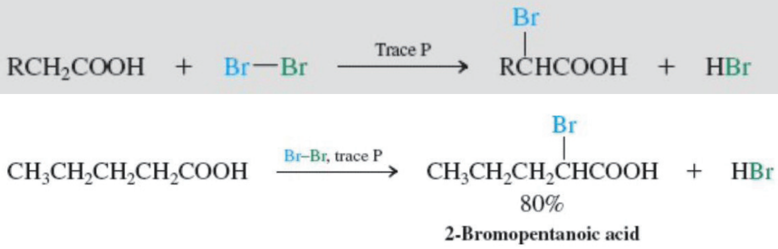


10.3.8

The Hell-Volhard-Zelinsky Reaction

Bromination Next to the Carboxy Group

Hell-Volhard-Zelinsky Reaction



$$RCH_2COOH + Br{-}Br \xrightarrow{\text{Trace P}} R\overset{Br}{C}HCOOH + HBr$$

$$CH_3CH_2CH_2CH_2COOH \xrightarrow{\text{Br–Br, trace P}} CH_3CH_2CH_2\overset{Br}{C}HCOOH + HBr$$

80%

2-Bromopentanoic acid

10.3

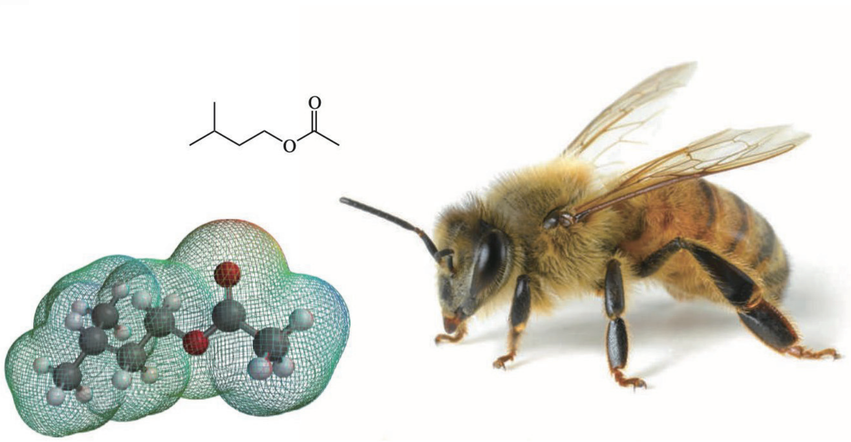
Summary & Practice

1. Concept

2. Example

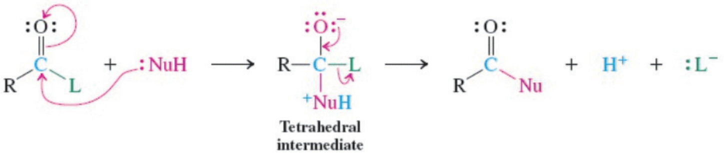
10.4

Carboxylic Acid Derivatives

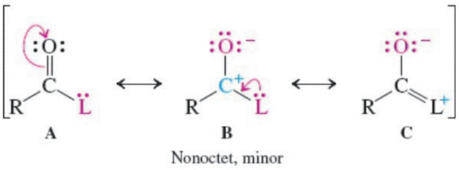


10.4.1 Relative Reactivities, Structures,

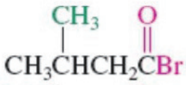
Addition–Elimination in Carboxylic Acid Derivatives



Resonance in Carboxylic Acid Derivatives

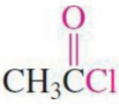


10.4.2 Acyl Halides

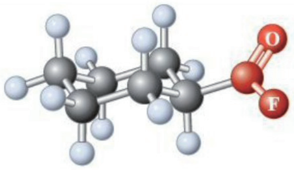


$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}Br$

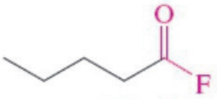
3-Methylbutanoyl bromide



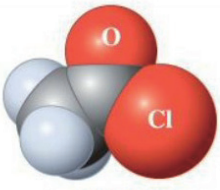
$CH_3\overset{O}{\overset{\|}{C}}Cl$



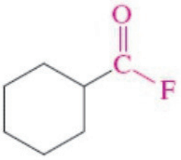
Cyclohexanecarbonyl fluoride



Pentanoyl fluoride

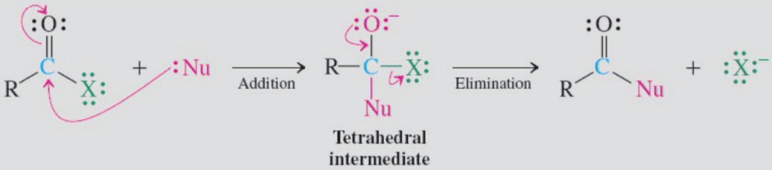


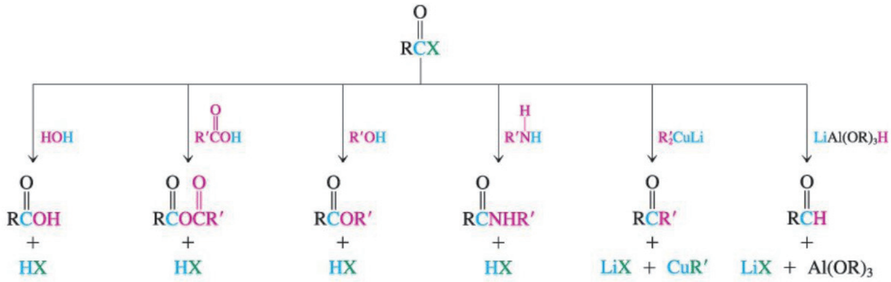
Acetyl chloride



10.4.2 Acyl Halides

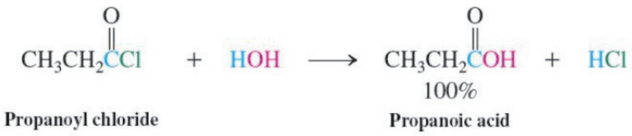
Addition–Elimination Reactions of Acyl Halides





10.4.2 Acyl Halides

Acyl Chloride Hydrolysis



$$CH_3CH_2\overset{\overset{\Large O}{\|}}{C}Cl + HOH \longrightarrow CH_3CH_2\overset{\overset{\Large O}{\|}}{C}OH + HCl$$

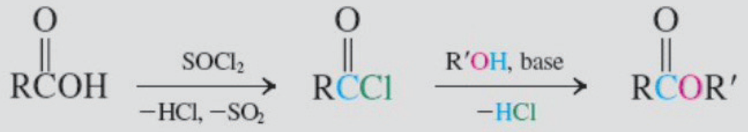
Propanoyl chloride

100%

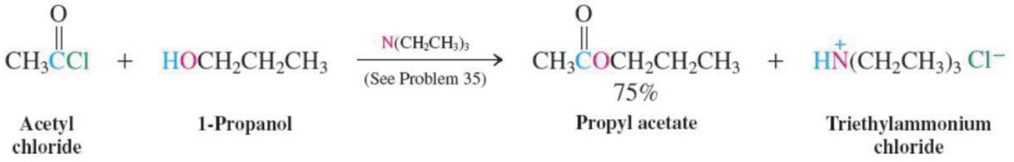
Propanoic acid

10.4.2 Acyl Halides

Ester Synthesis from Carboxylic Acids Through Acyl Chlorides



$$R\overset{\overset{\Large O}{\|}}{C}OH \xrightarrow[-HCl,\ -SO_2]{SOCl_2} R\overset{\overset{\Large O}{\|}}{C}Cl \xrightarrow[-HCl]{R'OH,\ base} R\overset{\overset{\Large O}{\|}}{C}OR'$$



$$CH_3\overset{\overset{\Large O}{\|}}{C}Cl + HOCH_2CH_2CH_3 \xrightarrow[\text{(See Problem 35)}]{N(CH_2CH_3)_3} CH_3\overset{\overset{\Large O}{\|}}{C}OCH_2CH_2CH_3 + H\overset{+}{N}(CH_2CH_3)_3\ Cl^-$$

Acetyl chloride

1-Propanol

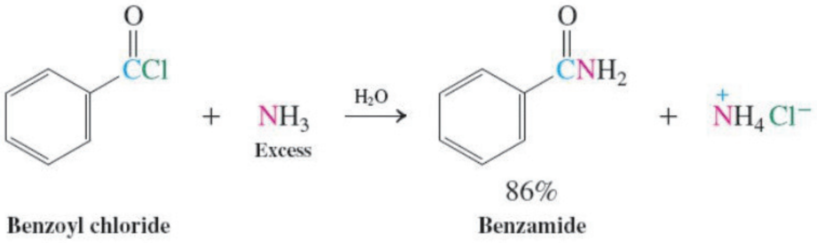
75%

Propyl acetate

Triethylammonium chloride

10.4.2 Acyl Halides

Amides from Acyl Halides

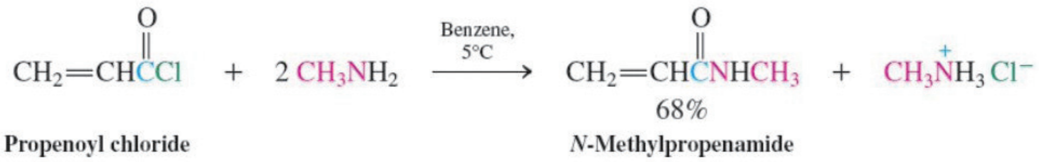


Benzoyl chloride + NH_3 (Excess) $\xrightarrow{H_2O}$ Benzamide + $\overset{+}{N}H_4\ Cl^-$

86%

Benzoyl chloride

Benzamide



$$CH_2{=}CH\overset{\overset{\Large O}{\|}}{C}Cl + 2\ CH_3NH_2 \xrightarrow{\text{Benzene, } 5°C} CH_2{=}CH\overset{\overset{\Large O}{\|}}{C}NHCH_3 + CH_3\overset{+}{N}H_3\ Cl^-$$

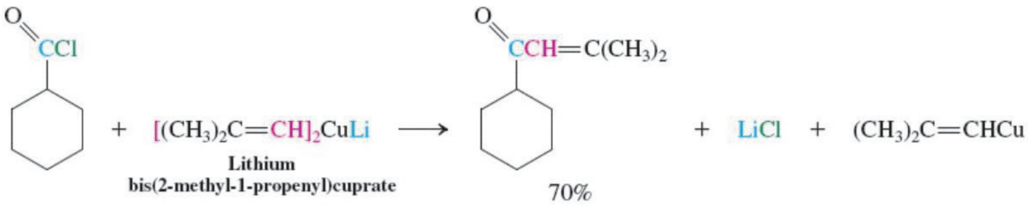
68%

Propenoyl chloride

N-Methylpropenamide

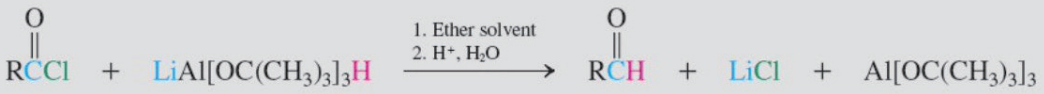
10.4.2 Acyl Halides

Formation of a Ketone from an Acyl Halide and an Organocuprate Reagent



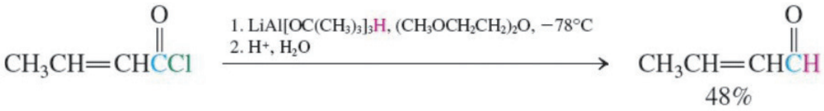
10.4.2 Acyl Halides

Reductions by Modified Lithium Aluminum Hydride



$$R\overset{O}{\overset{\|}{C}}Cl + LiAl[OC(CH_3)_3]_3H \xrightarrow{\substack{1.\ \text{Ether solvent} \\ 2.\ H^+,\ H_2O}} R\overset{O}{\overset{\|}{C}}H + LiCl + Al[OC(CH_3)_3]_3$$

Reduction of an Acyl Halide to an Aldehyde

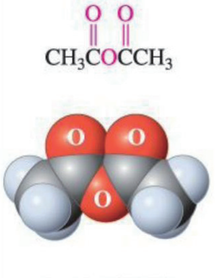


$$CH_3CH{=}CH\overset{O}{\overset{\|}{C}}Cl \xrightarrow{\substack{1.\ LiAl[OC(CH_3)_3]_3H,\ (CH_3OCH_2CH_2)_2O,\ -78°C \\ 2.\ H^+,\ H_2O}} CH_3CH{=}CH\overset{O}{\overset{\|}{C}}H$$

48%

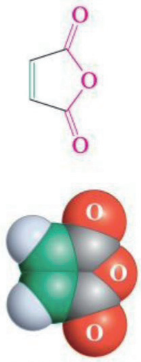
2-Butenoyl chloride **2-Butenal**

10.4.3 Carboxylic Anhydrides

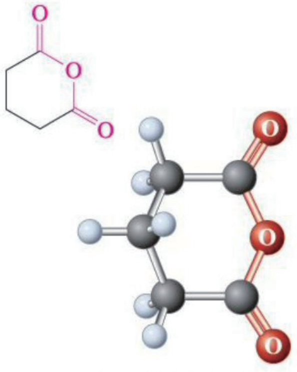


$$CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3$$

Acetic anhydride



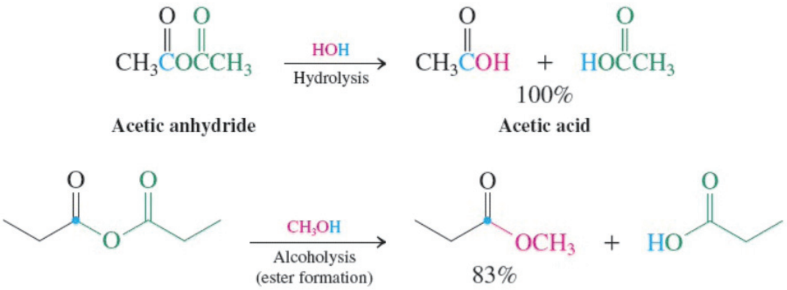
2-Butenedioic anhydride
(Maleic anhydride)



Pentanedioic anhydride
(Glutaric anhydride)

10.4.3 Carboxylic Anhydrides

Typical Reactions of Anhydrides



Acetic anhydride

Acetic acid

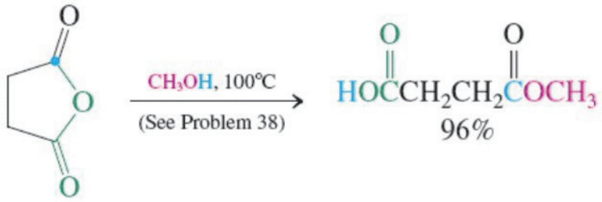
Propanoic anhydride

Methyl propanoate

Propanoic acid

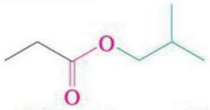
10.4.3 Carboxylic Anhydrides

Nucleophilic Ring Opening of Cyclic Anhydrides

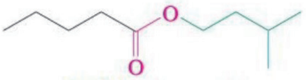


Butanedioic (succinic) anhydride

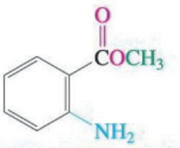
10.4.4 Esters



2-Methylpropyl propanoate
(Isobutyl propionate)
(A component of rum flavor)

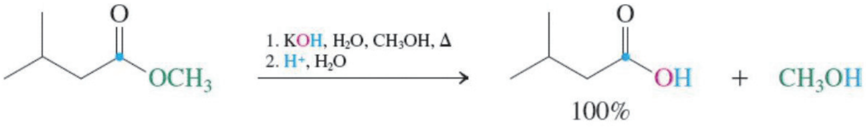


3-Methylbutyl pentanoate
(Isopentyl valerate)
(A component of apple flavor)



Methyl 2-aminobenzoate
(Methyl anthranilate)
(A component of grape flavor)

Example of Ester Hydrolysis Using Aqueous Base

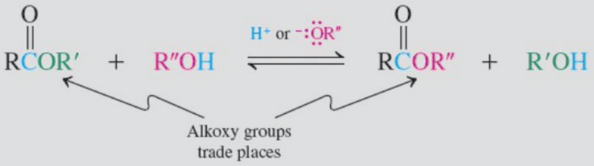


Methyl 3-methylbutanoate

3-Methylbutanoic acid

10.4.4 Esters

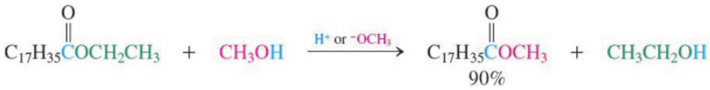
Transesterification



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR'} + \mathrm{R''OH} \overset{\mathrm{H^+}\text{ or }{}^-\!:\ddot{\mathrm{O}}\mathrm{R''}}{\rightleftharpoons} \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OR''} + \mathrm{R'OH}$$

Alkoxy groups
trade places

Conversion of an Ethyl Ester into a Methyl Ester

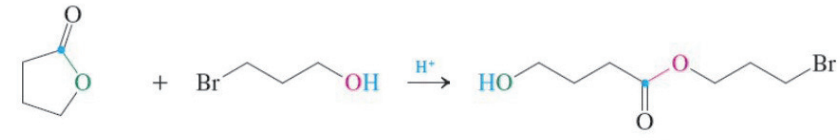


$$\mathrm{C_{17}H_{35}\overset{O}{\overset{\|}{C}}OCH_2CH_3} + \mathrm{CH_3OH} \xrightarrow{\mathrm{H^+}\text{ or }{}^-\mathrm{OCH_3}} \mathrm{C_{17}H_{35}\overset{O}{\overset{\|}{C}}OCH_3} + \mathrm{CH_3CH_2OH}$$

90%

Ethyl octadecanoate | **Methanol (Solvent)** | **Methyl octadecanoate**

10.4.4 Esters



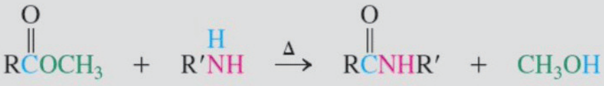
80%

γ-Butyrolactone | **3-Bromopropanol** | **3-Bromopropyl 4-hydroxybutanoate**

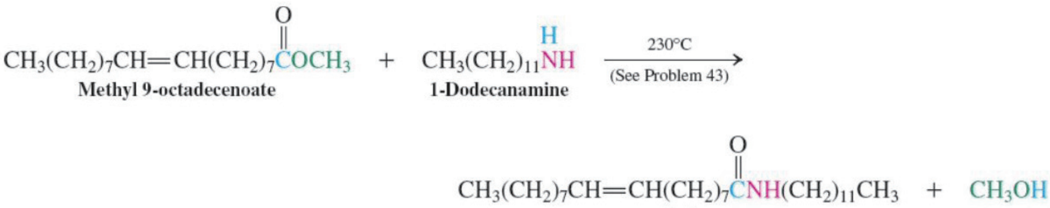
10.4.4 Esters

Amines convert esters into amides

Amide Formation from Methyl Esters



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_3} + \mathrm{R'}\overset{\mathrm{H}}{\mathrm{N}}\mathrm{H} \xrightarrow{\Delta} \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHR'} + \mathrm{CH_3OH}$$



$$\mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}OCH_3} + \mathrm{CH_3(CH_2)_{11}\overset{H}{N}H} \xrightarrow[\text{(See Problem 43)}]{230°\mathrm{C}} \mathrm{CH_3(CH_2)_7CH{=}CH(CH_2)_7\overset{O}{\overset{\|}{C}}NH(CH_2)_{11}CH_3} + \mathrm{CH_3OH}$$

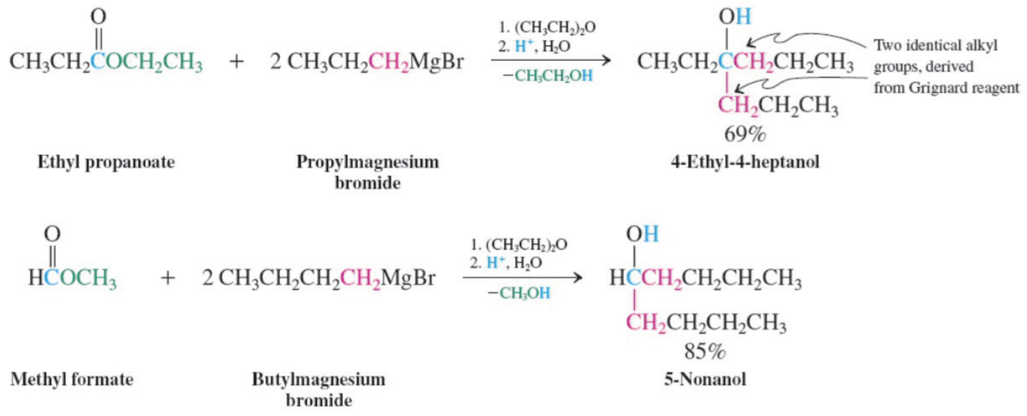
Methyl 9-octadecenoate | **1-Dodecanamine**

69%

***N*-Dodecyl-9-octadecenamide**

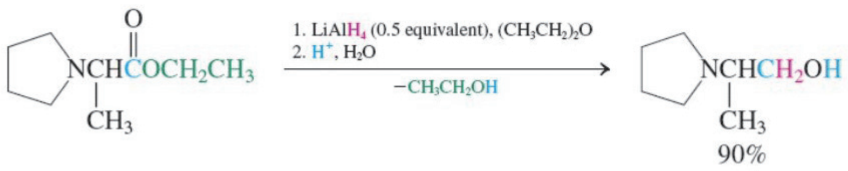
10.4.4 Esters

Alcohols from Esters and Grignard Reagents

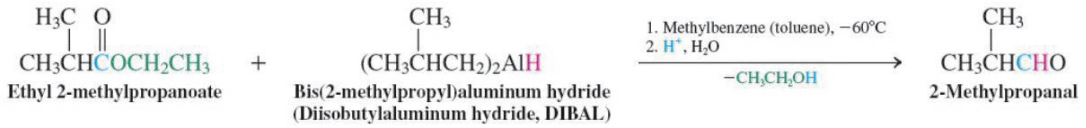


10.4.4 Esters

Reduction of an Ester to an Alcohol

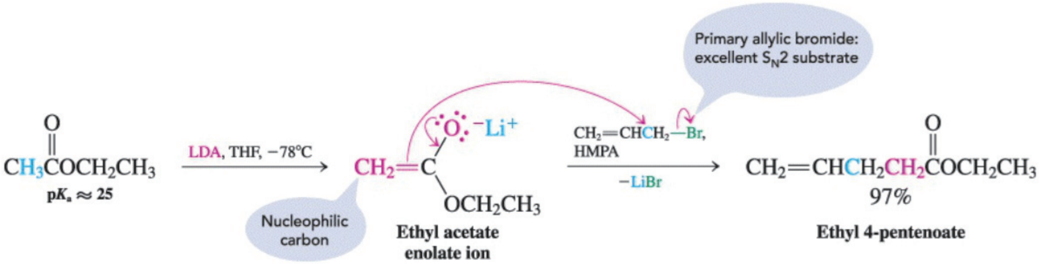


Reduction of an Ester to an Aldehyde



10.4.4 Esters

Alkylation of an Ester Enolate



10.4 Summary & Practice

1. Concept

2. Example

UKChO

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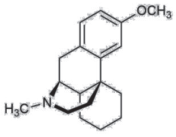
Unit 11

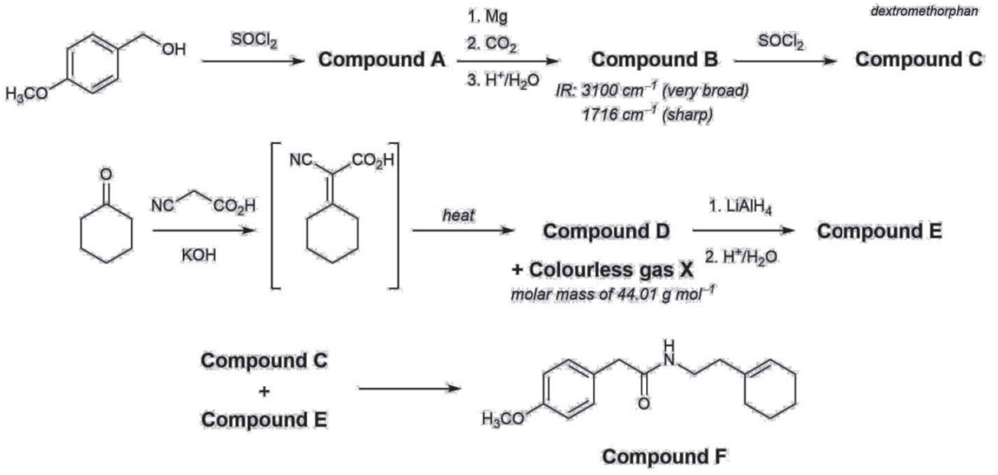
Organic Synthesis

2018-4

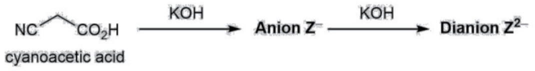
The synthesis of dextromethorphan begins with the synthesis of compound **F**.



dextromethorphan



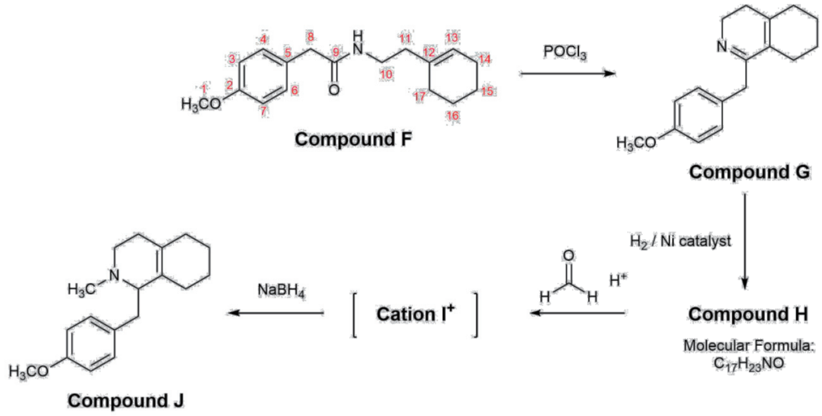
In the reaction to make compound **D**, the cyanoacetic acid can be deprotonated twice by the potassium hydroxide.



(d) **(i)** Draw a structure for anion Z^-.

(ii) Draw a structure for dianion Z^{2-}.

The synthesis continues with the conversion of compound **F** to compound **J**.



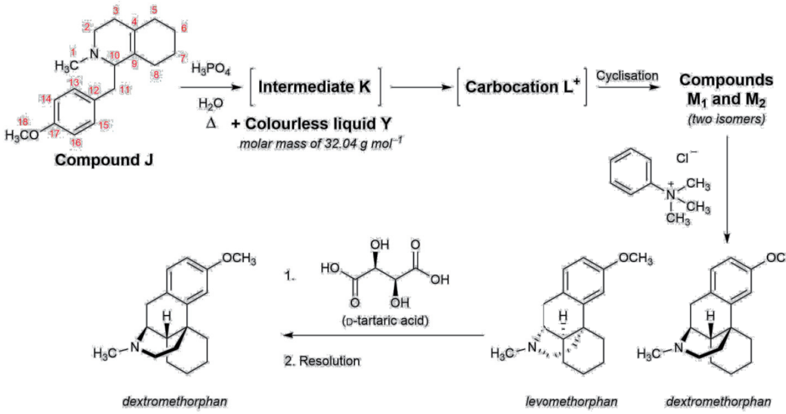
(e) Write down the numbers of the two carbon atoms in compound **F** that are connected in the reaction to synthesise compound **G**.

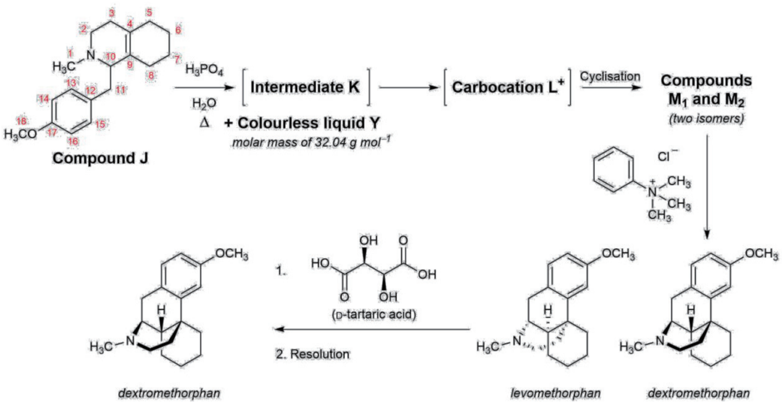
(f) Draw the structures of compound **H** and cation I^+.

The synthesis continues with the conversion of compound **J** to compounds **M₁ and M₂** in one step. Upon heating with aqueous phosphoric acid, compound **J** is first converted into intermediate **K** and a colourless liquid **Y**. Intermediate **K** is then converted to carbocation L^+, which undergoes cyclisation to give the mixture of the two isomers M_1 and M_2.

Treatment of the mixture of M_1 and M_2 with trimethylphenylammonium chloride (a methylating agent) gives a mixture of levomethorphan and dextromethorphan.

The addition of D-tartaric acid to this mixture allows the desired dextromethorphan to be separated from the undesired levomethorphan. This process is called resolution.





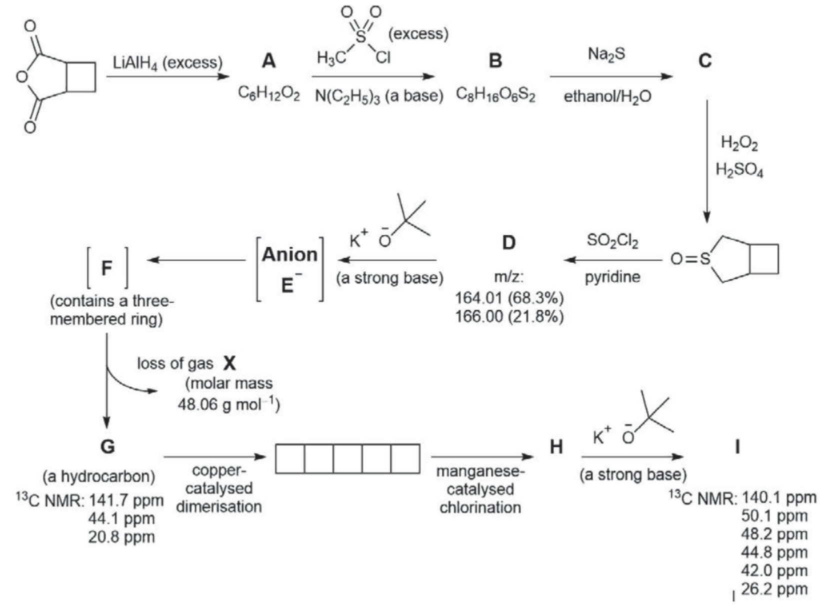
(g) Indicate all pairs of carbon atoms that can be connected in this reaction.

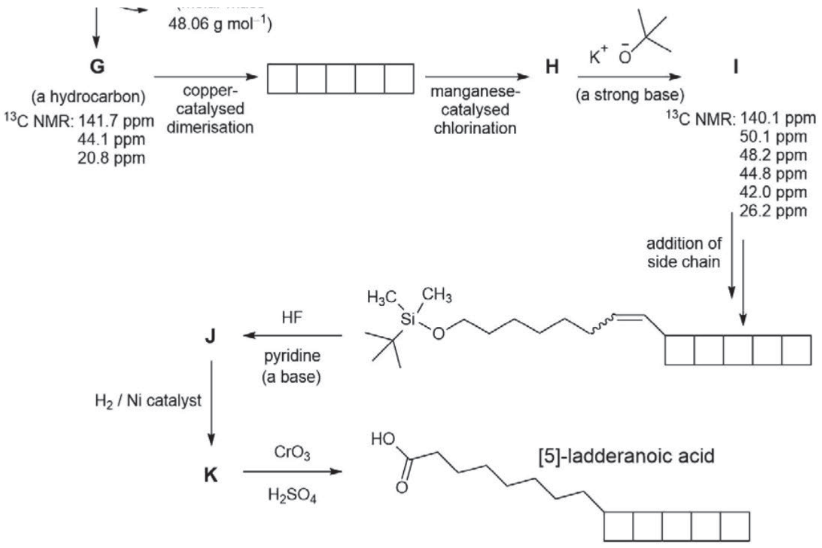
(h) Draw the structures of intermediate **K**, carbocation **L⁺** and liquid **Y**.

(i) Complete the structures of the two isomers **M₁** and **M₂** indicating clearly any atoms other than hydrogen that come out of the plane of the paper (with wedged lines) and go into the plane of the paper (with dashed lines).

State what type of isomers **M₁** and **M₂** are.

2020-6





11

Summary & Practice

1. Concept

2. Example

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Unit 12

General Review of Organic Chemistry