

CHEM 1311A Syllabus

- Some descriptive chemistry of s- and p-block elements
 - Compounds of hydrogen
 - Compounds of oxygen and related elements
 - Compounds of the halogens (halides)
 - Acids and bases
- Redox chemistry of the elements

Third Exam – Friday, October 31

Hydrogen Compounds

- Classification
- Synthesis
 - Direct combination of the elements
 - Protonation of a Brønsted base
 - Metathesis (double replacement) of a halide with a hydride
- Reactions
 - Homolytic cleavage
 - Heterolytic cleavage by hydride transfer
 - Heterolytic cleavage by proton transfer
 - Oxidation (gives E_nO_m and H_2O except metallic and group 17)

Classification of Hydrogen Compounds

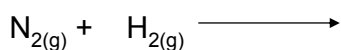
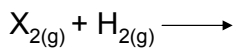
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn

	Salt-like
	Intermediate between salt-like and covalent
	Covalent
	Metallic
	Binary hydrides are unknown

Synthesis: direct combination of the elements

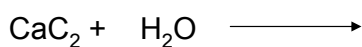
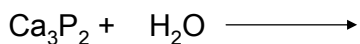
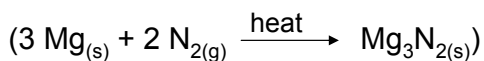
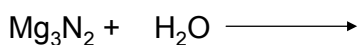


salt-like metal hydrides are among the strongest bases known



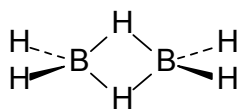
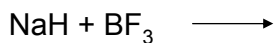
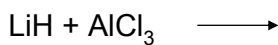
Synthesis: protonation of a Brønsted base

Brønsted base – proton acceptor



Other examples of Brønsted bases include Na_2O , Na_2S , CaH_2 , NaO_2CR

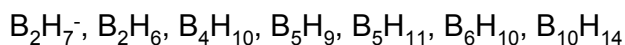
Synthesis: metathesis (double replacement) of a halide with a hydride



3-center-2-electron bonds

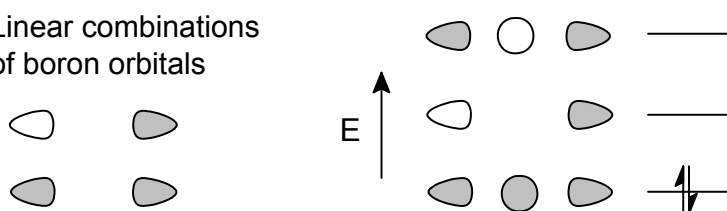
3-center-2-electron bonds

Many examples in boron and aluminum compounds; most often hydrogen is bridging but sometimes carbon groups, i.e., CH_3 in compounds such as $\text{Al}_2(\text{CH}_3)_6$ which is dimeric with bridging methyl groups



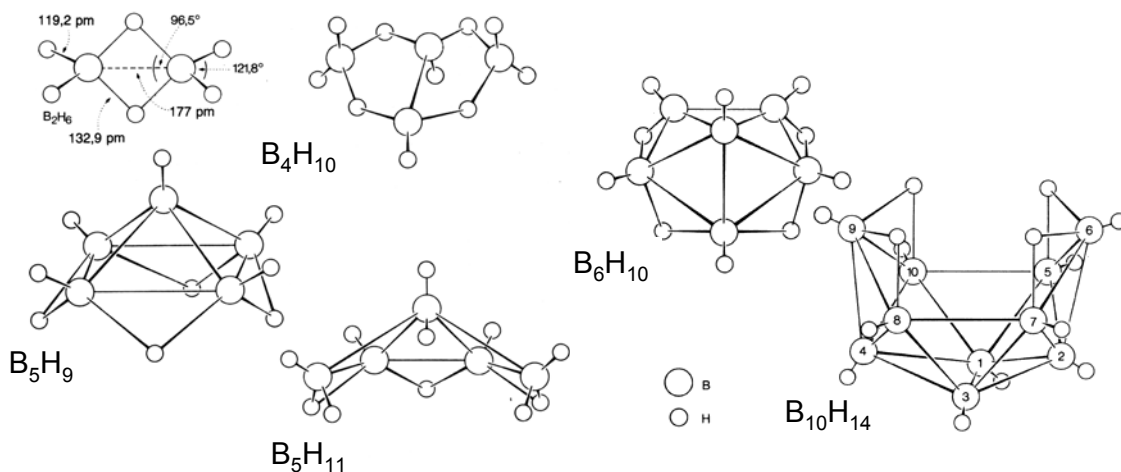
A MO description of the 3-center-2-electron bond in $\text{H}_3\text{B}-\text{H}-\text{BH}_3^-$ can be generated assuming that each boron uses an sp^3 hybrid orbital for combination with the hydrogen 1s orbital

Linear combinations of boron orbitals






Neutral Boranes

Besides diborane there is a large number of borane cluster compounds:



Structure and Bonding in Boranes

- To account for the structure and bonding in higher borane there are a total of five structurally different bonding elements present:

Bonding element	Bonding type	Symbol
Terminal boron-hydrogen bond	2c-2e	B—H
Hydrogen bridge bond	3c-2e	
Boron-boron bond	2c-2e	B—B
Open B—B—B bond	3c-2e	
Closed boron bond	3c-2e	

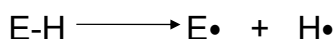
Definitions of acids and bases

- Arrhenius: H^+ is the acid and OH^- is the base.
- Bronsted: An acid is a proton donor and a base is a proton acceptor.
- Lewis: An acid is an electron pair acceptor and a base is an electron pair donor.

Solvent leveling effect on acid/base strengths

- The strongest acid and the strongest base that can exist in a given solvent are the acid/base (conjugate acid/conjugate base) generated by autoionization of the solvent.
 - $2 \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$
 - $2 \text{NH}_3 = \text{NH}_4^+ + \text{NH}_2^-$
 - $2 \text{CH}_3\text{CO}_2\text{H} = \text{CH}_3\text{C}(\text{OH})_3^+ + \text{CH}_3\text{CO}_3^-$
- Intrinsically stronger acids or bases will be “leveled” to the strength of the conjugate acid or conjugate base of the solvent.
 - $\text{NaNH}_2 + \text{H}_2\text{O}(\text{liq}) = \text{NH}_{3(\text{sol})} + \text{Na}^+_{(\text{sol})} + \text{OH}^-_{(\text{sol})}$
 - $\text{HCl} + \text{NH}_3(\text{liq}) = \text{NH}_{4(\text{sol})}^+ + \text{Cl}^-_{(\text{sol})}$

Reactions: homolytic cleavage

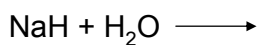


Thermal cleavage will occur at moderate temperatures only for very weak element (E) to hydrogen bonds.

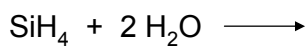
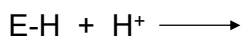
E-H bond energies (average), kJ mol⁻¹

B-H 389	C-H 411	N-H 386	O-H 459	F-H 565
Al-H 285	Si-H 318	P-H 322	S-H 363	Cl-H 428
Ga-H <274	Ge-H 288	As-H 247	Se-H 276	Br-H 362
In-H 243	Sn-H 264	Sb-H 257	Te-H 268	I-H 295

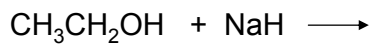
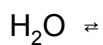
Heterolytic cleavage by hydride transfer



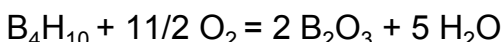
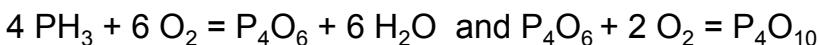
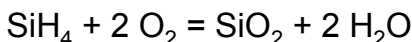
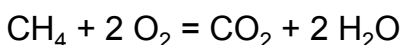
RXH is a Brønsted acid (X is an electronegative element)



Heterolytic cleavage by proton transfer

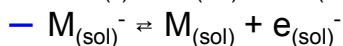
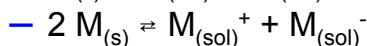
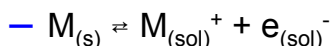


Oxidation of hydrogen compounds gives E_nO_m and H_2O (except metallic and group 17)



Dilute solutions of alkali metals in liquid NH_3

- Dilute solutions are deep blue with an absorption spectrum that is independent of the metal.
- Show conductivities that are comparable to those of electrolytes of equivalent concentration.
- Have magnetic susceptibilities consistent with ca. one unpaired electron per sodium.
- Exhibit electron spin resonance spectra that are consistent with those of free electrons and inconsistent with metal-based electrons

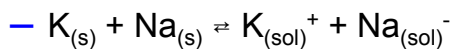


Conc. solutions of alkali metals in liquid NH₃

- Bronze colors with metallic luster.
- Metallic conductivities.
- Magnetic behavior comparable to that of pure metals.
- M_(sol)

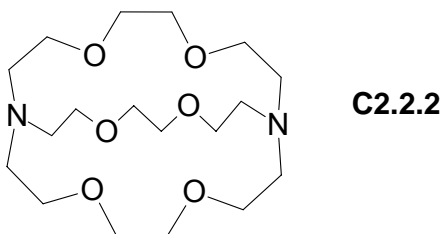
Solutions of alkali metals in other solvents

- Solubility varies with identity of solvent, but generally only dilute solutions can be made in absence of chelating agent.
- Metal independent spectral features are weak, when present, and are invariably dominated by metal dependent features. Only the latter are observed in the presence of chelating agents
- Sodium is insoluble in some solvents, but K-Na alloy dissolves.



Isolation of salts of the sodium anion

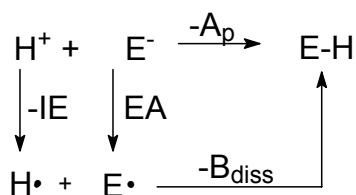
- Sodium is only slightly soluble in ethylamine (10^{-6} M) but gives 0.2 M solutions in the presence of C2.2.2.



- This occurs because of the equilibrium $2 \text{Na}_{(s)} + \text{C2.2.2} \rightleftharpoons [\text{Na}(\text{C2.2.2})]^+ + \text{Na}^-$
- Crystallization at low temperature gives $[\text{Na}(\text{C}2.2.2)]\text{Na}$ whose crystal structure is identical to that of $[\text{NaC}]\text{I}$ except that the radius of Na^- appears to be somewhat greater than that of iodide.
- ^{23}Na NMR measurements on $[\text{Na}(\text{C}2.2.2)]\text{Na}$ in solution indicate two types of sodium, one identical to that in $[\text{Na}(\text{C}2.2.2)]\text{X}$ and another consistent with predictions for Na^- .

Definition of proton affinity

Proton affinity, A_p , is defined as the energy associated with the heterolytic cleavage of the E-H bond in the gas phase



$$A_p = IE - EA + B_{\text{diss}}$$



Proton affinities for EH_n^{-*}

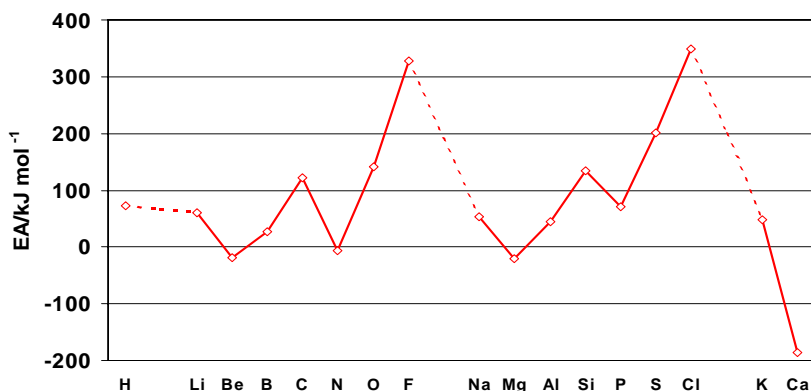
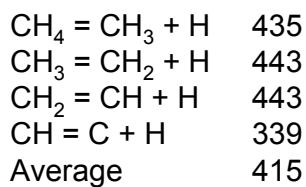
CH_3^- 1745	NH_2^- 1689	OH^- 1635	F^- 1554
SiH_3^- 1554	PH_2^- 1552	SH^- 1476	Cl^- 1395
GeH_3^- 1509	AsH_2^- 1502	SeH^- 1466	Br^- 1354
			I^- 1315

Proton affinity is for reaction $\text{H-EH}_n = \text{H}^+ + \text{EH}_n^-$

E-H bond energies (average), kJ mol^{-1}

B-H 389	C-H 411	N-H 386	O-H 459	F-H 565
Al-H 285	Si-H 318	P-H 322	S-H 363	Cl-H 428
Ga-H <274	Ge-H 288	As-H 247	Se-H 276	Br-H 362
In-H 243	Sn-H 264	Sb-H 257	Te-H 268	I-H 295

Step-wise dissociation energies for methane



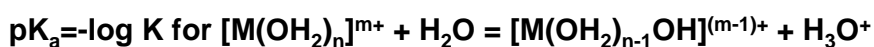
Inductive effects on acid strengths

	pK _a	
Cl-OH	7.5	
Br-OH	8.7	
I-OH	10.7	
HO-OH	11.8	
H-OH	15.7	
CH ₃ -OH	16.6	
F-CH ₂ C(O)OH	2.7	F-SO ₂ -OH > Cl-SO ₂ -OH > HO-SO ₂ -OH
Cl-CH ₂ C(O)OH	2.8	
Br-CH ₂ C(O)OH	2.9	F ₂ P(O)(OH) > FP(O)(OH) ₂ > HOP(O)(OH) ₂
I-CH ₂ C(O)OH	3.0	
H-CH ₂ C(O)OH	4.7	
CH ₃ -CH ₂ C(O)OH	4.9	

Similar effects exist for bases. For example base strengths vary in the order NH₃ > H₂NNH₂ > ClNH₂ > Cl₂NH > F₃N, etc.

pK_a values for hydrated metal ions, [M(OH₂)_n]^{m+}

	M ^{m+}	pK _a	M ^{m+}	pK _a
	Th ⁴⁺	3.2		
smaller pK _a = greater dissociation, <u>stronger acid</u>	Al ³⁺	5.0	Sc ³⁺	4.3
	Y ³⁺	7.7	Cr ³⁺	4.0
	La ³⁺	8.5	Fe ³⁺	2.2
	Mg ²⁺	11.4	Cr ²⁺	10.0
	Ca ²⁺	12.8	Mn ²⁺	10.6
	Sr ²⁺	13.3	Fe ²⁺	9.5
	Ba ²⁺	13.5	Co ²⁺	9.6
			Ni ²⁺	9.9
			Zn ²⁺	9.0
		Li ⁺	13.6	Ag ⁺
	Na ⁺	14.2	Tl ⁺	13.2
	K ⁺	14.5		



pK_a values for acids of type (HO)_mEO_n (oxidation state effects)

No. E=O	Acid	pK ₁	pK ₂	pK ₃
0	HOCl	7.4		
	HOBr	8.7		
	HOI	10.7		
1	HOCIO	1.94		
	HONO	3.3		
	(HO) ₃ PO	2.16	7.21	12.3
	(HO) ₃ AsO	2.25	6.77	11.6
2	HOCIO ₂	-1		
	HONO ₂	-1.4		
	(HO) ₂ SO ₂	-3	1.92	
3	HOCIO ₃	-10		

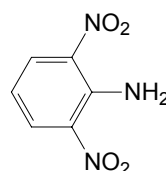
Solvent leveling (of acidities and basicities)

- The strongest acid and strongest base that can exist in a given solvent are the conjugate acid and base generated by autoionization
 - $2 \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$
 - $2 \text{NH}_3 = \text{NH}_4^+ + \text{NH}_2^-$
 - $2 \text{CH}_3\text{CO}_2\text{H} = \text{CH}_3\text{C}(\text{OH})_2^+ + \text{CH}_3\text{CO}_2^-$
 - $2 \text{HF} = \text{H}_2\text{F}^+ + \text{F}^-$
 - $2 \text{BrF}_3 = \text{BrF}_2^+ + \text{BrF}_4^-$
- An intrinsically stronger acid/base will be **leveled** (reduced) to the acidity/basicity of the conjugate acid or base for the solvent.
- To determine intrinsic acid/base strengths a solvent must be used that is sufficiently low in basicity/acidity such that the acid or base under investigation is not completely ionized.
- Solvation of ions affects ionization constant.

Acidities measured in CH₃CN

$$H_o = \text{pK}_{\text{BH}^+} - \log [\text{BH}^+]/[\text{B}]$$

H ₂ SO ₄	-2
HCl	-7
HBr	-9
HClO ₄	-10
HI	-11



$$\text{pK}_{\text{BH}^+} = -4.5$$



Superacids

Acids up to billions of times stronger than sulfuric acid have opened up fascinating new areas of chemistry.

George A. Olah, G. K. Surya Prakash, Jean Sommer

Olah awarded Nobel Prize in Chemistry in 1994

Until recently, chemists generally considered mineral acids, such as sulfuric, nitric, perchloric, and hydrofluoric acids, to be the strongest acid systems attainable. That view has changed considerably as extremely strong acid systems—hundreds of millions, even bil-

very closely to the degree of transformation of a base with its conjugate acid, keeping in mind that this will depend on the base itself and on medium effects. The advantage of this method was shown in the 1930's by Hammett and Deyrup (4), who investigated the proton donor

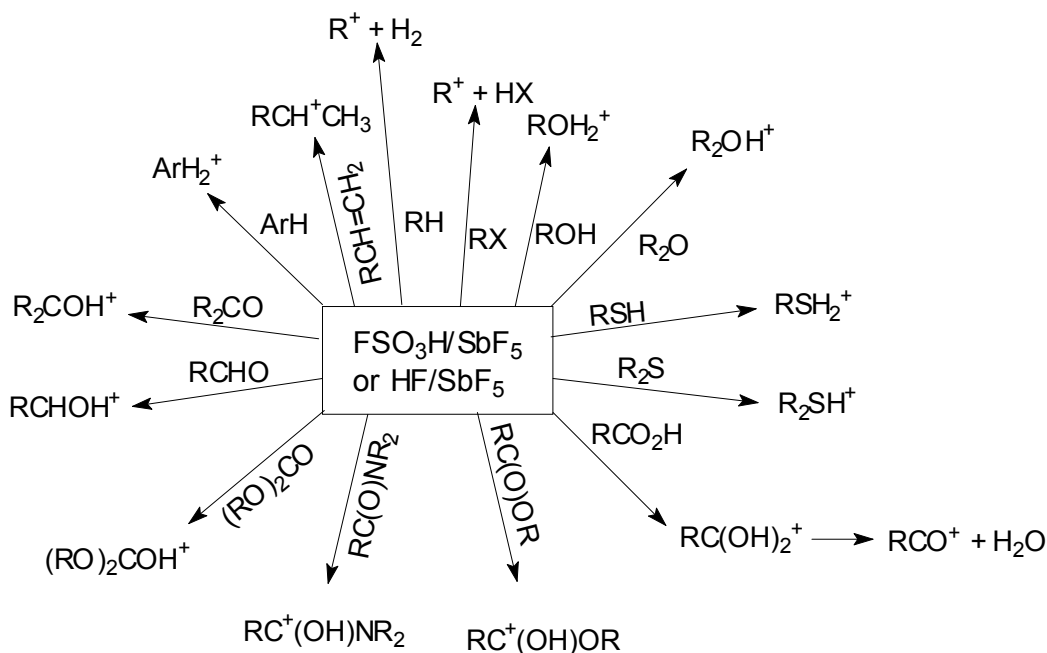
Summary. Superacids, although first referred to as early as 1927, were only extensively studied in the last decade. Acidities up to 10^{12} times that of sulfuric acid have now been obtained. The extremely low nucleophilicity of the counterions in superacidic systems is especially useful for the preparation of stable, electron-deficient cations, particularly carbocations. Many of these cations, which were formerly detectable only in the gas phase, can now be studied in solution. Novel organic syntheses that are not possible in ordinary acidic media can also be achieved in superacids, including syntheses of economically important hydrocarbons. The unique ability of superacids to bring about hydrocarbon transformations, even to activate methane to undergo electrophilic oligocondensation, can open up new fields in chemistry.

Superacids (no solvent)

$$(H_o = pK_{BH^+} - \log [BH^+]/[B])$$

HF	-11
H ₂ SO ₄	-11.9
HClO ₄	-13
CF ₃ SO ₃ H	-14.6
FSO ₃ H	-15.6
FSO ₃ H/SbF ₅ (25%)	-21 (Magic Acid)
HF/SbF ₅ (1:1)	-28 (est.)

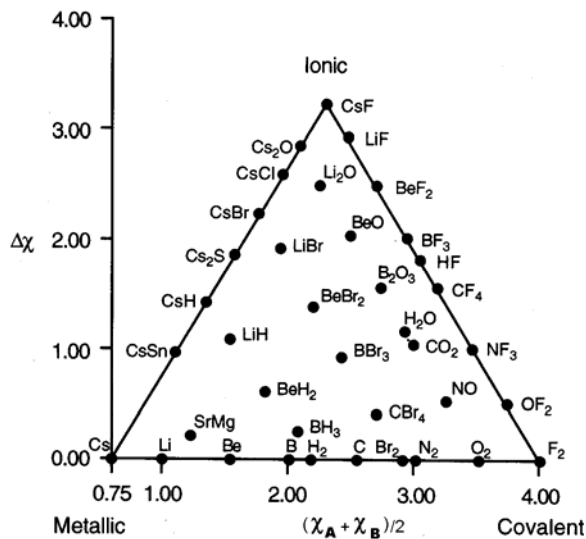
Applications of superacids



Oxides: structural classification

Li ₂ O LiO ₂ Li ₂ O ₂	BeO	B ₂ O ₃	CO CO ₂	NO N ₂ O N ₂ O ₃ N ₂ O ₄ N ₂ O ₅	O ₂ O ₃	F ₂ O F ₂ O ₂	
Na ₂ O NaO ₂ Na ₂ O ₂	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₆ P ₄ O ₁₀	SO ₂ SO ₃	Cl ₂ O ClO ₂ Cl ₂ O ₇	
K ₂ O KO ₂ K ₂ O ₂	CaO	Ga ₂ O ₃	GeO ₂	As ₄ O ₆ As ₂ O ₅	SeO ₂ SeO ₃	Br ₂ O BrO ₂	
Rb ₂ O	SrO	In ₂ O ₃	SnO SnO ₂	Sb ₄ O ₆ Sb ₂ O ₅	TeO ₂ TeO ₃	I ₂ O ₄ I ₂ O ₅ I ₂ O ₉	XeO ₃ XeO ₄
Cs ₂ O	BaO	Tl ₂ O Tl ₂ O ₃	PbO PbO ₂	Bi ₂ O ₃ Bi ₂ O ₅	PoO ₂		
Ionic		Polymeric					Molecular Covalent

Ionic vs covalent character and electronegativity



Acid-base properties of s- and p-block oxides

H	
Li	Be
Na	Mg
K	Ca
Rb	Sr
Cs	Ba

B	C	N		
Al	Si	P	S	Cl
Ga	Ge	As	Se	Br
In	Sn	Sb	Te	I
Tl	Pb	Bi	Po	

acidic

basic

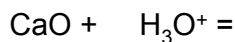
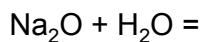
circle – amphoteric

octagon - amphoteric in

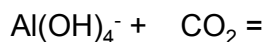
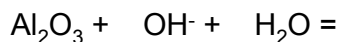
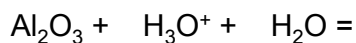
lower oxidation state,

acidic in higher

Ionic oxides: bases

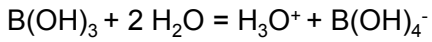
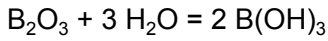


Amphoteric oxides

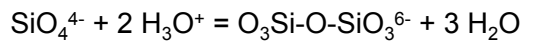
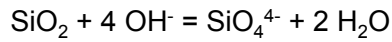
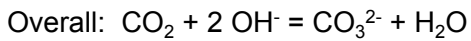
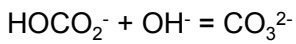
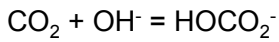
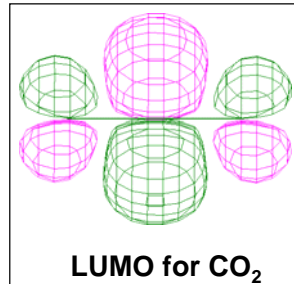
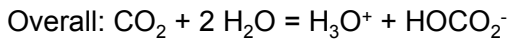
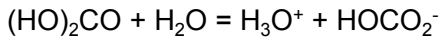
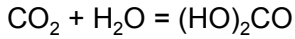


Acidic oxides

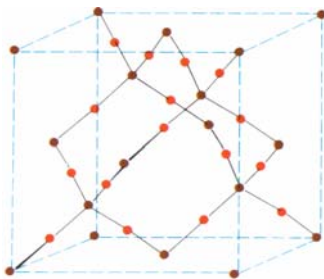
Group 13



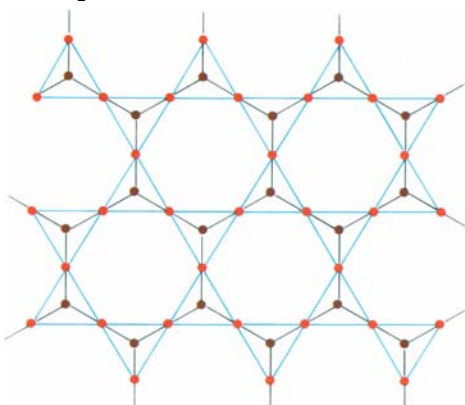
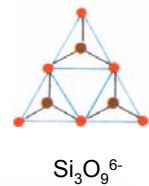
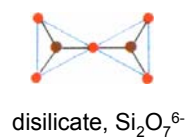
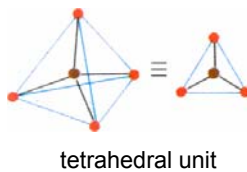
Group 14



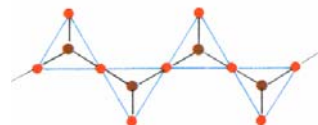
Silicates



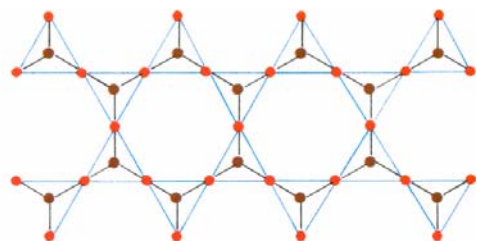
SiO₂ (cristobalite)



infinite sheet, Si₂O₅²⁻
micas

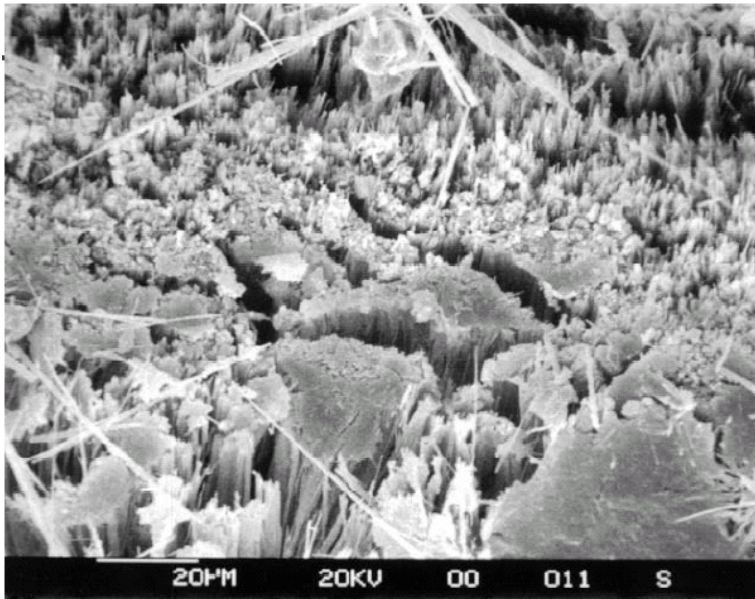


infinite chain, SiO₃²⁻
pyroxenes



infinite double chain,
Si₄O₁₁⁶⁻, amphiboles

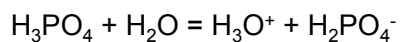
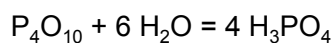
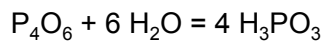
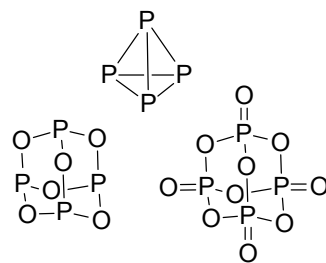
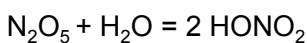
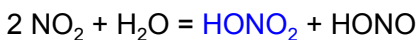
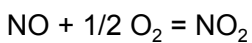
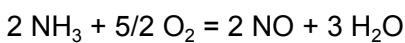
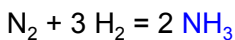
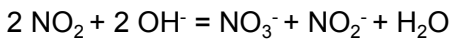
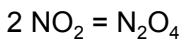
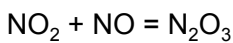
Tremolite asbestos from Jamestown, CA



<http://www.epa.gov/swerrims/ahec/summary/presentations/day1/addison1.pdf>

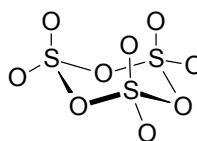
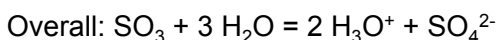
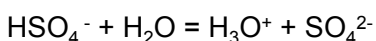
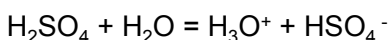
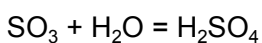
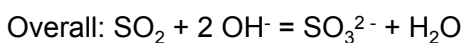
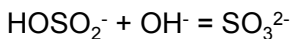
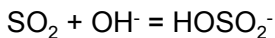
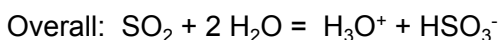
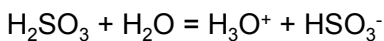
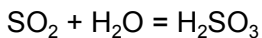
Acidic oxides, con't

Group 15



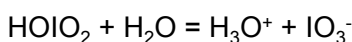
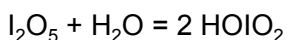
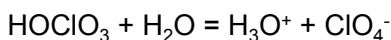
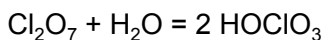
Acidic oxides, con't

Group 16



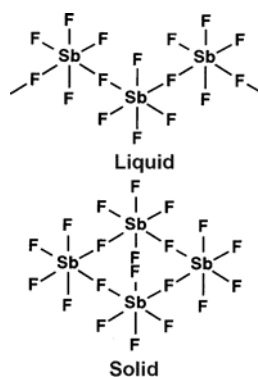
solid SO_3

Group 17



Structural classification of fluorides

1	2	13	14	15	16	17
LiF	BeF ₂	BF ₃	CF ₄	NF ₃	OF ₂	F ₂
NaF	MgF ₂	AlF ₃	SiF ₄	PF ₃	SF ₂	ClF
				PF ₅	SF ₄	ClF ₃
					SF ₆	ClF ₅
KF	CaF ₂	GaF ₃	GeF ₂	AsF ₃	SeF ₄	BrF
			GeF ₄	AsF ₅	SeF ₆	BrF ₃
						BrF ₅
RbF	SrF ₂	InF	SnF ₂	SbF ₃	TeF ₄	IF
		InF ₃	SnF ₄	SbF ₅	TeF ₆	IF ₃
						IF ₅
						IF ₇
CsF	BaF ₂	TlF	PbF ₂	BiF ₃		
		TlF ₃	PbF ₄	BiF ₅		

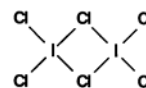
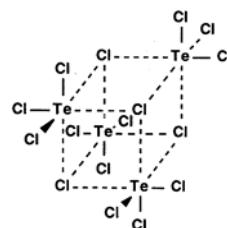
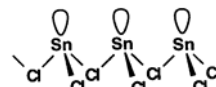
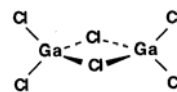
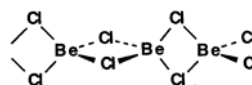


ionic, polymeric, molecular

Structural classification of chlorides

1	2	13	14	15	16	17
LiCl	BeCl ₂	BCl ₃	CCl ₄	NCl ₃	OCl ₂	FCl
NaCl	MgCl ₂	AlCl ₃	SiCl ₄	PCl ₃ PCl ₅	SCl ₂ SCl ₄	Cl ₂
KCl	CaCl ₂	GaCl ₃	GeCl ₂ GeCl ₄	AsCl ₃ AsCl ₅	SeCl ₄	BrCl BrCl ₃
RbCl	SrCl ₂	InCl InCl ₃	SnCl ₂ SnCl ₄	SbCl ₃ SbCl ₅	TeCl ₄	ICl ICl ₃ ICl ₅
CsCl	BaCl ₂	TlCl TlCl ₃	PbCl ₂	BiCl ₃		

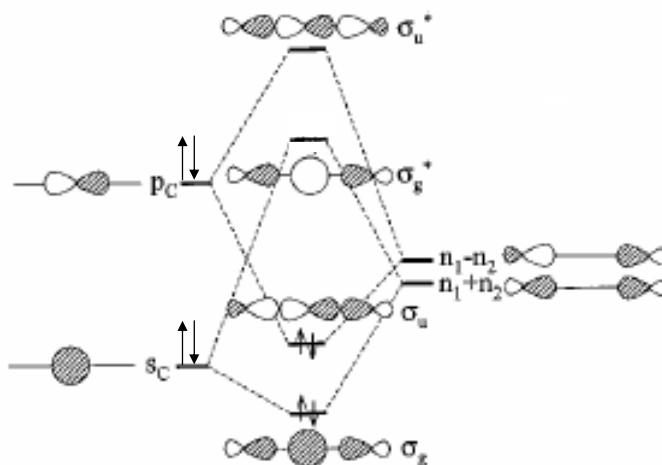
ionic, polymeric, molecular



Bonding in Bridged Halides

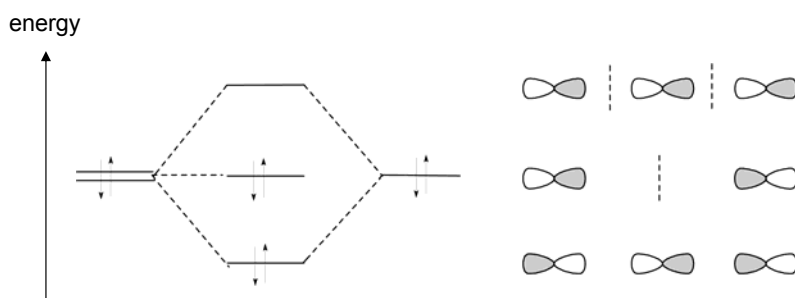
- The bonding in bridged halides appears similar to that in boranes; however,
- In group 13 compounds there are actually plenty of electrons and orbitals and the bonding is not electron deficient

2 BF₃ + F⁻
same as
BF₃ + BF₄⁻



Description of bonding in I_3^-

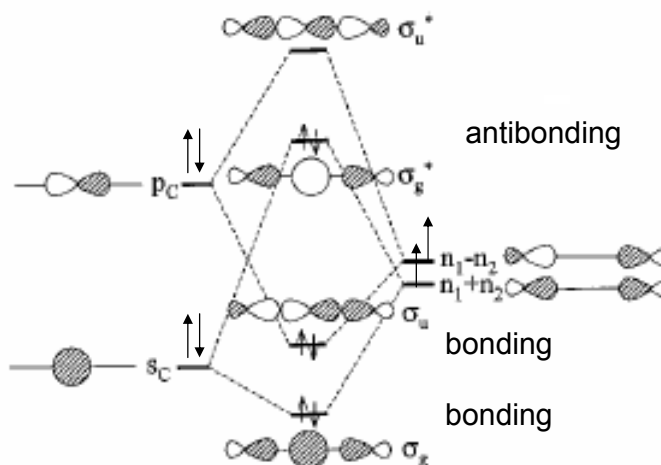
- When there is an expansion of valence shells the situation is different
 - The linear structure of I_3^- can be described via a sp^3d hybridized central atom and a total of five electron pairs (two BPs, 3 LPs)
 - Alternatively, the central atom can be looked at as sp^2+p hybridized with only the p orbital used to bond to the terminal iodine atoms
 - the resulting bond order is 0.5, which readily accounts for the weaker axial bond found in molecules such as PX_5 , BrF_3 , etc.
- Note: I-I bond length in I_3^- 290 pm, in I_2 267 pm!



Description of bonding in I_3^- , cont'd

- Note that the situation is not improved by invoking a model that employs the s orbital on the central atom.

$2 I \cdot + I^-$
 same as
 $I_2 + I^-$

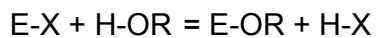
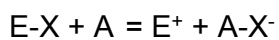
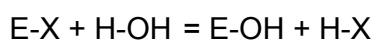
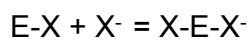


Common reactions of covalent halides

As Lewis acid $EX_n + :B = B-EX_n$

B = electron pair donor; may be neutral or anionic

Common reactions of covalent halides



Hard and soft acids and bases

- First recognized for halide bases; acid behavior was referred to as class *a* and class *b*
 - K_f for adduct with hard acids (class *a*) increases in order $I^- < Br^- < Cl^- < F^-$
 - Hard acids include Al(III), Sc(III), Cu(II), Zn(II)
 - K_f for adduct with soft acids (class *b*) increases in order $F^- < Cl^- < Br^- < I^-$
 - Soft acids include Ag(I), Cd(II), Hg(II), Pb(II), Pd(II)
- Later extended to many other bases
 - Hard acids bond in order: $R_3P \ll R_3N, R_2S \ll R_2O$
 - Soft acids bond in order: $R_3N \ll R_3P, R_2O \ll R_2S$
- It follows that hard acids prefer hard bases and soft acids prefer soft bases
 - Hard-hard interactions are substantially electrostatic in nature; hard acids are generally species with high energy LUMO's and hard bases generally have low energy HOMO's
 - Soft-soft interactions are substantially more covalent in nature; soft acids and bases are generally larger and are significantly more polarizable. Soft acids generally have low energy LUMO's and soft bases have high energy HOMO's

More examples of hard and soft acids and bases

	Hard	Borderline	Soft
Acids	H ⁺ , Li ⁺ , Na ⁺ , Be ²⁺ , Mg ²⁺ , Cr ²⁺ , Cr ³⁺ , Al ³⁺ , SO ₃ , BF ₃ , Al(CH ₃) ₃	Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Pb ²⁺ , SO ₂ , BBr ₃	Tl ⁺ , Ag ⁺ , BH ₃ , Hg ⁺ , Hg ²⁺ , Ga(CH ₃) ₃ , I ₂
Bases	F ⁻ , OH ⁻ , H ₂ O, NH ₃ , CO ₃ ²⁻ , NO ₃ ⁻ , O ²⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ , ClO ₄ ⁻	<u>N</u> O ₂ ⁻ , SO ₃ ²⁻ , Br ⁻ , N ₃ ⁻ , N ₂ , C ₆ H ₅ N, <u>S</u> CN ⁻	H ₂ S, R ₂ S, I ⁻ , <u>S</u> CN ⁻ , R ₃ P, CN ⁻ , CO, H ⁻ , R ⁻

Spectral changes when I₂ reacts with bases

