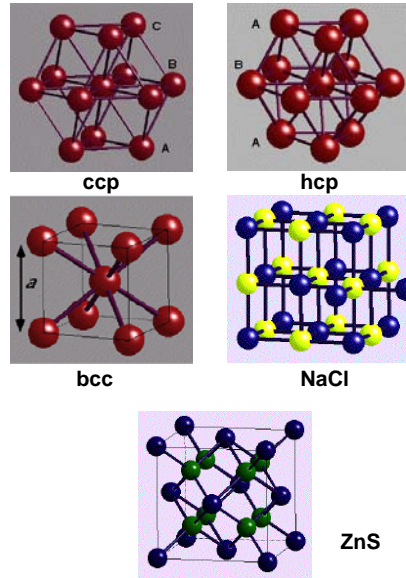


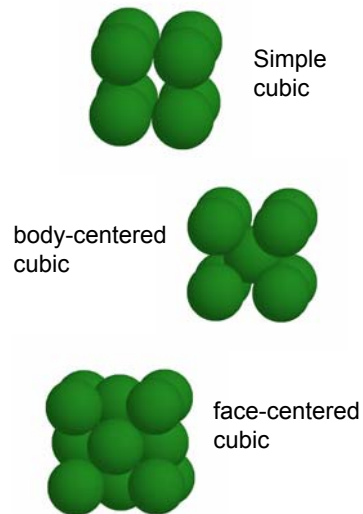
Metals and ionic compounds: structure, bonding and energetics

- Metals adopt three basic structures; cubic closest packed (ccp), hexagonal closest packed (hcp) or body centered cubic (bcc).
- Many simple salts can be viewed as having a structure in which one ion forms a closest packed array with the oppositely charged ion occupying voids (holes) in the array.
- Properties of metals, salts and non-metallic elements/molecular compounds differ greatly.

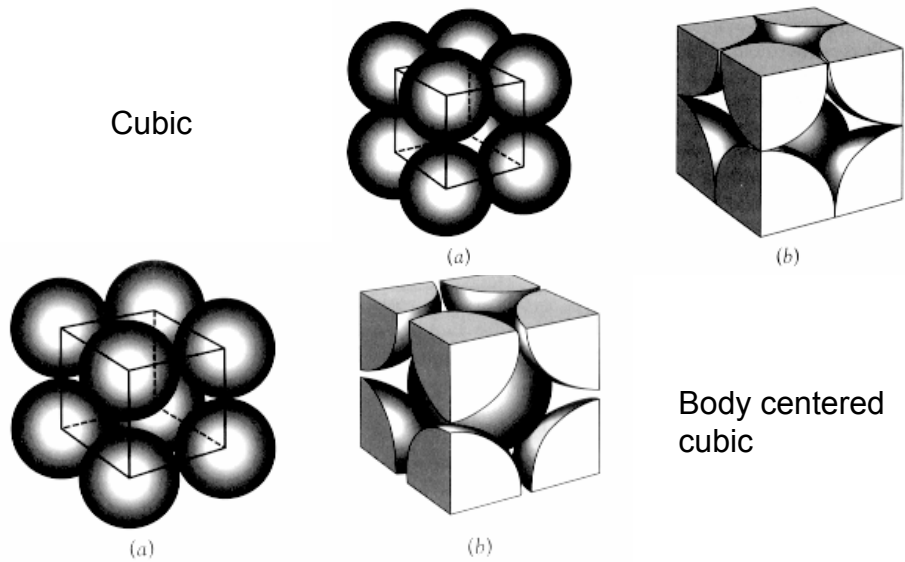


The unit cell

- The atoms in a crystal are in a regular repeating pattern called the *crystalline lattice*.
- The crystalline lattice can be reproduced by translation of the **unit cell** in three dimensions. The unit cell is that *unique part* of the crystal structure such that when translated along parallel lines, generates the entire crystal structure.
- For a substance containing more than one kind of atom, the ratio of atoms in the unit cell must be *exactly* the same as in the entire crystal.

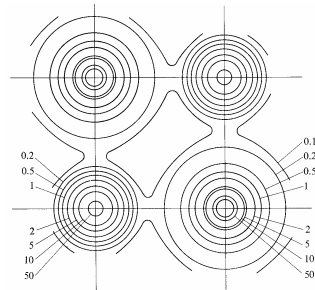


Contribution of atoms to unit cell



Evidence for presence of ions in solids

- Formed from elements with $\Delta X > 2$
- Exist as nonvolatile solid with poor conductance at RT
- Good conductance when molten
- Possess a 3-dimensional lattice with regular array of cations and anions where nearest neighbors are of opposite charge



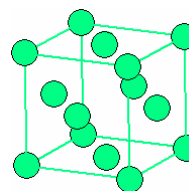
Electron density map of a portion of the face of NaCl unit cell

Comparison of properties of metals, simple salts and non-metallic elements

Metals	Salts	Non-metallic elements
Structures		
Close packed, C.N. = 8-12 Infinite structures	Close packed, C.N. = 4-8 Infinite structures	Loose packed, low connectivity Molecular, chain, layer or infinite structures
Properties		
Good conductors Malleable, ductile, elastic Lustrous, hard, high tensile strength Large range of densities and melting points	Insulators as solids, good conductors molten Brittle Non-reflective, low tensile strength Large range of densities; high melting points	Poor conductors Brittle (can be hard) Non-reflective, low tensile strength Large range of densities and melting points
Chemical Properties		
Tend to form cations Reducing agents More electropositive liberate H ₂ from water Form alloys with other metals Electropositive react with O ₂ to form (mostly ionic, basic) oxides	Combination of ions Simple salts are neither oxidizing or reducing Never liberate H ₂ from water Do not react with metals Do not react with oxygen	Tend to form anions Oxidizing agents Never liberate H ₂ from water Form salts with metals React with O ₂ to form covalent (mostly acidic) oxides

Determination of density from structural data

Aluminum has the face-centered cubic structure (to right) with a unit cell dimension of 4.041 Å.



$d = \text{mass of contents of cell} / \text{volume of cell}$

mass of atoms in the cell = 4 atoms \times 1 mol / 6.022×10^{23} atoms \times 26.98 g mol⁻¹
= 17.922×10^{-23} g

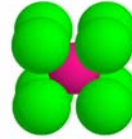
volume of unit cell = $(4.041 \times 10^{-8} \text{ cm})^3 = 6.599 \times 10^{-23} \text{ cm}^3$

$d = \text{mass} / \text{volume} = 17.922 \times 10^{-23} \text{ g} / 6.599 \times 10^{-23} \text{ cm}^3 = 2.715 \text{ g cm}^{-3}$

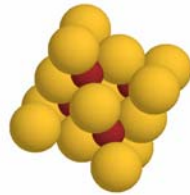
More unit cells



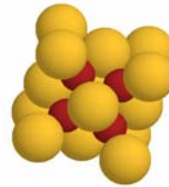
NaCl



CsCl

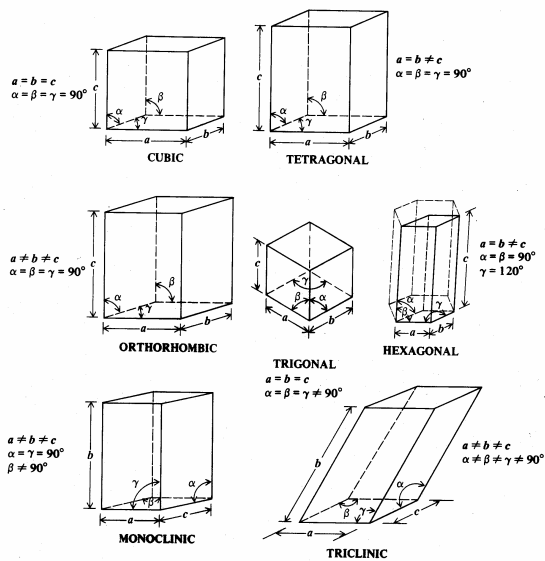


ZnS



Li₂Se

Not all unit cells are cubic!

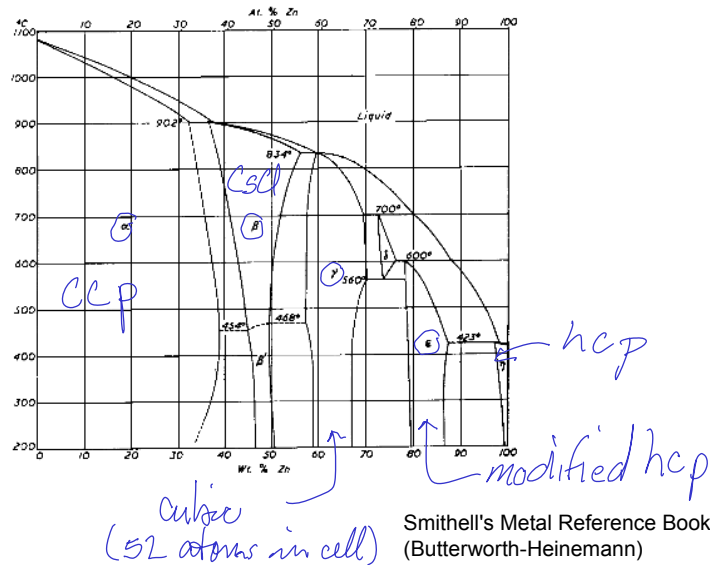


There are seven unique crystal systems; including the additional modifications of body and face centering result in a total of fourteen unique (Bravais) lattice systems

Alloys, intermetallic, and interstitial compounds

- Alloys are solid solutions of one metal in another; three rules apply to their formation
 - Atom radii differ by less than 15%
 - Crystal structures are identical
 - Chemically similar
- When only one or two of these rules apply then true solid solutions are generally formed only over limited compositions
- Intermetallic compounds of fixed stoichiometry may be formed in other composition ranges
 - Zn/Cu forms true alloys (solid solutions) in the range 0-35% Zn and >97% Zn. Brasses of approximate composition are formed in other ranges, i.e., CuZn (45-50%), Cu₅Zn₈ (60-65%), CuZn₃ (82-88%).
- Interstitial compounds such as hydrides, borides, carbides and nitrides generally have normal closest packed structures of metals with the non-metallic element in octahedral (common) or tetrahedral (rare) holes.
 - Interstitial compounds are often extremely hard and chemically inert because of the enhanced bonding interactions.

Copper-zinc phase diagram



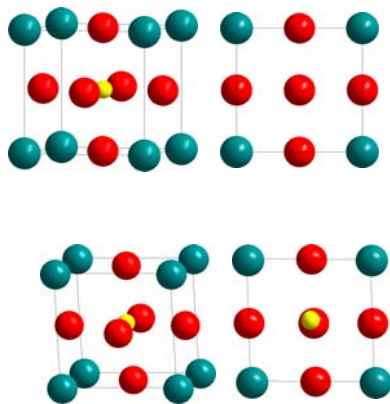
What do the following have in common?

- Push-button igniters (BBQ grills, cigarette lighters)
- Electronic beepers
- Tweeters in stereo speakers
- Sound-generating arrays for sonar, fish finders, etc.
- Crystal microphones
- Nanoscale positioners (Å precision)
- Functional element in time keepers (clocks, watches, etc.)

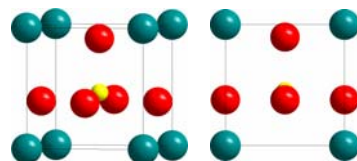
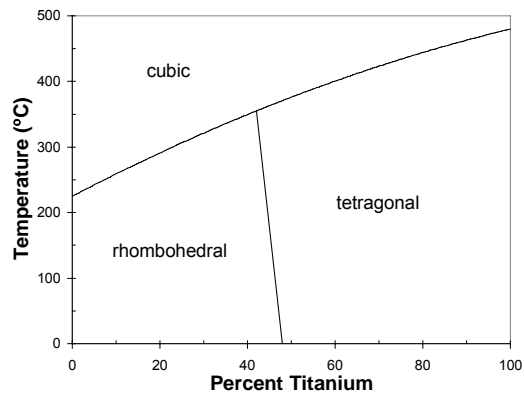
Crystals that are piezoelectric

- Piezo (Greek) means pressure; such crystals are pressure sensitive
- Piezoelectric crystals generate current when deformed and deform when a potential is applied
- Only materials whose crystal structures lack a center of symmetry can exhibit piezoelectric properties

Pb(Zr,Ti)O₃ (PZT) phase diagram

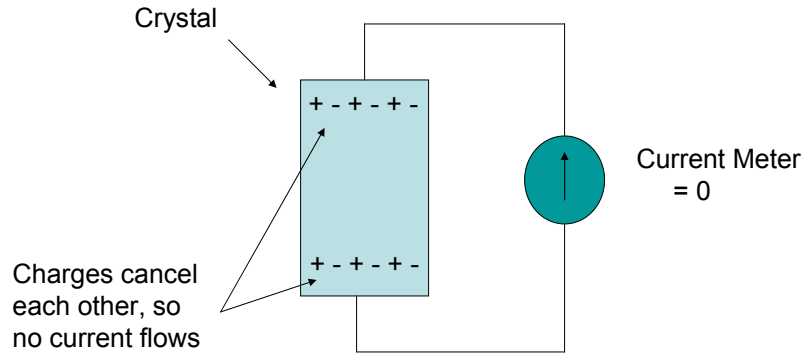


Only structures without a center of symmetry show piezoelectric properties



The Piezoelectric Effect

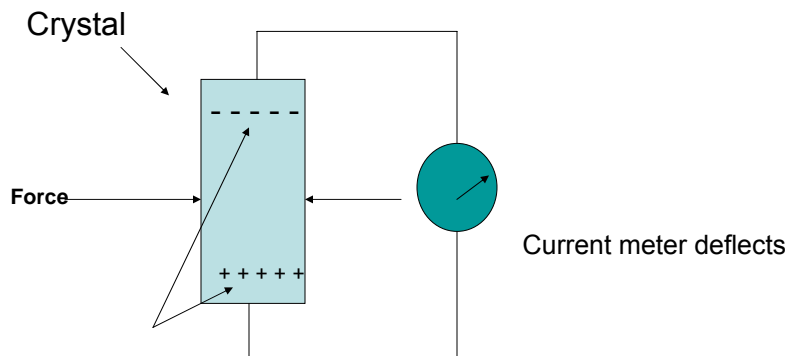
Crystal material at rest: No forces applied, so net current flow is 0



Adapted from copyrighted Valpey Fisher Corp. materials

The Piezoelectric Effect

Crystal material with forces applied in direction of arrows.....

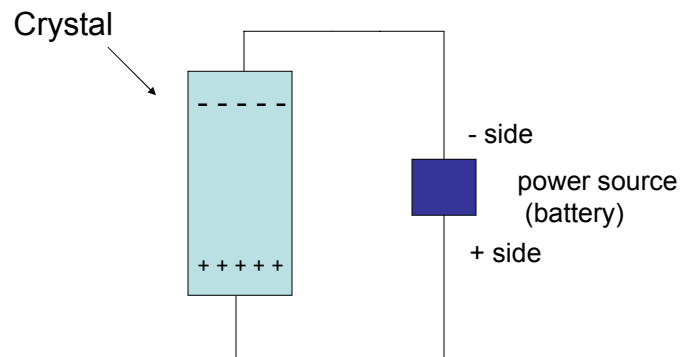


Charges are net + on one end and net - on the opposite end: crystal gets thinner and longer; changing direction of applied force will shorten and fatten crystal and reverse the charges (and current).

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The electromechanical effect

Now, replace the current meter with a power source capable of supplying a current meter....

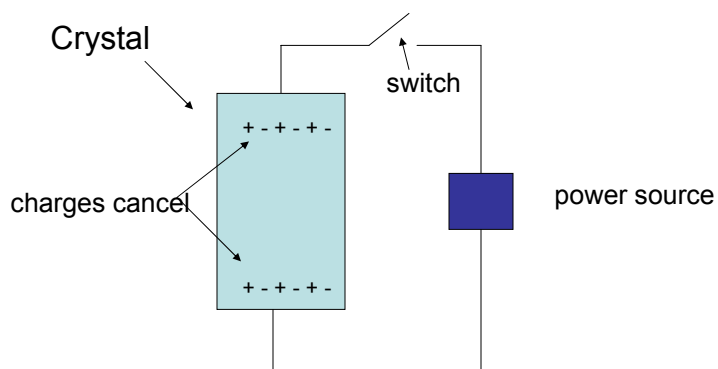


.... the crystal should get longer and skinnier (shown) or shorter and fatter depending upon polarity.

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The electromechanical effect

With the switch open, the crystal material is now at rest again: the positive charges cancel the negative charges.



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Summary of the Piezoelectric & Electromechanical Effect

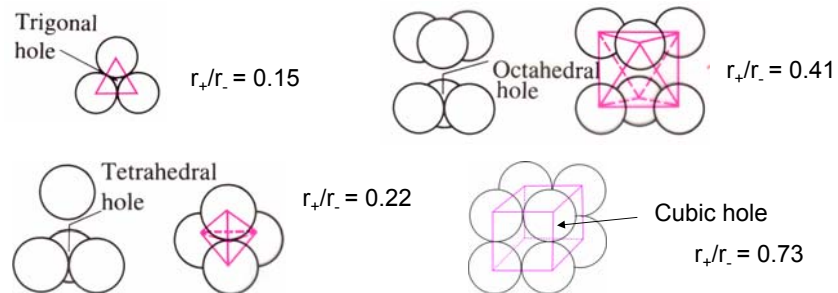
- A deformation of the crystal structure (eg: squeezing it) will result in an electrical current.
- Changing the direction of deformation (eg: pulling it) will reverse the direction of the current.
- If the crystal structure is placed into an electrical field, it will deform by an amount proportional to the strength of the field.
- If the same structure is placed into an electrical field with the direction of the field reversed, the deformation will be opposite.

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Structure prediction from ion radius ratios

The maximum electrostatic interaction between ions occurs when they are surrounded by the maximum number of ions of opposite charge separated by the shortest distance.

Assuming a model in which ions are considered as hard spheres with the smaller ion occupying holes in an array of larger ions allows calculation of the ideal size for a sphere in each type of hole.



MX: radius ratios predicted/actual structures

	Li	Na	K	Rb	Cs
F	0.51	0.74	1.0	0.90	0.80
Cl	0.38	0.54	0.73	0.82	0.92
Br	0.35	0.50	0.68	0.75	0.85
I	0.31	0.45	0.61	0.67	0.76

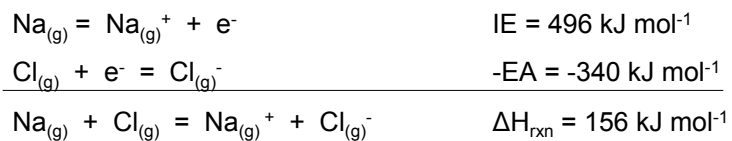
Green - CsCl structure

Pink - predicted to have CsCl based upon radius ratios but actually have NaCl structures

Red - have NaCl structure, but radius ratio is between ideal tetrahedral and octahedral values.

Energetics of reaction of sodium and chlorine

Gaseous Na and Cl atoms to give non-interacting ions



Reaction of sodium and chlorine, cont'd

Gaseous sodium and chlorine atoms to give ion pairs

If the $\text{Na}_{(g)}^+$ and $\text{Cl}_{(g)}^-$ ions are allowed to combine to give ion pairs $(\text{Na}^+, \text{Cl}^-)_{\text{IP}}$ the stabilization can be calculated on the basis of electrostatics using the expression

$$E = N_A Z_+ Z_- e^2 / 4\pi\epsilon_0 r_0 = -589 \text{ kJ mol}^{-1}$$

$$N_A = \text{Avogadro's number} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$Z_+ = \text{charge of the cation} = +1$$

$$Z_- = \text{charge of the anion} = -1$$

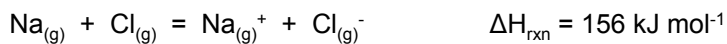
$$e = \text{electron charge} = 1.6022 \times 10^{-19} \text{ C}$$

$$4\pi\epsilon_0 = 1.113 \times 10^{-10} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$$

$$r_0 = \text{internuclear separation, experimentally determined as } 236 \text{ pm (} 2.36 \text{ \AA)}$$

Reaction of sodium and chlorine, cont'd

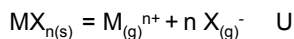
Now the energy balance is



The lattice energy for NaCl is 770 kJ mol^{-1} or about 31% greater than the 589 kJ mol^{-1} generated by the formation of one mole of ion pairs. The larger value results from the extended interactions between ions in the solid state. Note that $r_0 = 281 \text{ pm}$ in the crystal.

Lattice energy: definition, calculation

- Lattice energy is defined as the energy required (U) to vaporize a mole of salt to non-interacting constituent ions.



- Lattice energies vary in a predictable way with ion charge, ion size (internuclear distance), and lattice type.
- Lattice energies are determined from experimental data (Born-Haber cycle) and calculated based upon an electrostatic model.

Salt	mp/K	d	r _o	Unit cell/Å	U, kJ/mol
NaF	1268	2.56	2.31	4.63	928
NaCl	1073	2.16	2.76	5.64	770
NaBr	1020	3.20	2.94	5.94	736
MgO	3073	3.58	2.05	4.21	3791
MgCl ₂	981	2.32	2.46		2526

Experimental lattice energies: Born-Haber cycle

The lattice energy of a salt MX(s) can be calculated using experimental thermochemical data (Born-Haber cycle):

$\text{M}_{(s)} \rightarrow \text{M}_{(g)}$	Heat of sublimation (ΔH_{sub})
$\text{M}_{(g)} \rightarrow \text{M}_{(g)}^{+}$	Ionization energy (IE)
$\frac{1}{2} \text{X}_{2(g)} \rightarrow \text{X}_{(g)}$	$\frac{1}{2}$ Bond Dissociation energy (Diss)
$\text{X}_{(g)} \rightarrow \text{X}_{(g)}^{-}$	-Electron affinity (Ea)
$\text{M}_{(g)}^{+} + \text{X}_{(g)}^{-} \rightarrow \text{MX}_{(s)}$	-Lattice Energy (U)
$\text{M}_{(s)} + \frac{1}{2} \text{X}_{2(g)} \rightarrow \text{MX}_{(s)}$	Heat of formation (ΔH_f)

Adding the first five reactions produces the reaction of solid metal with gaseous X₂; therefore must be equal to the sum of the energies for the five reactions, $\Delta H_f = \Delta H_{\text{sub}} + \text{IE} + \frac{1}{2} \text{Diss} - \text{Ea} - U$. Rearranging this equation gives

$$U = \Delta H_{\text{sub}} + \text{IE} + \frac{1}{2} \text{Diss} - \text{Ea} - \Delta H_f$$

Lattice energies from an electrostatic model

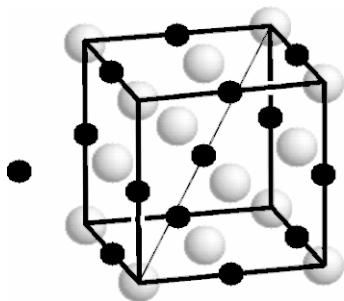
Lattice energies can be approximated using an electrostatic model that includes ion charges, structure constant, internuclear distance.

$$U \propto N_A Z_+ Z_- e^2 M / 4\pi\epsilon_0 r_0$$

Z_+ , Z_- are cation and anion charges

M is the structure (Madelung) constant

r_0 is the internuclear distance ($r_+ + r_-$)



Coordination numbers and Madelung (structure) constants for common structures

Salt	Cation	Anion	M
NaCl	6	6	1.74756
CsCl	8	8	1.76267
ZnS	4	4	1.63805
CaF ₂	8	4	2.519
Antifluorite	4	8	2.519

Total coulombic potential energy V

= sum of coulombic interactions of individual ions

$$= \sum \frac{(Z_a)(Z_b)}{4\pi\epsilon_0 r}$$

For a given Na⁺ ion V

$$= \frac{1}{4\pi\epsilon_0} (-6e^2/r_0 + 12e^2/\sqrt{2}r_0 - 8e^2/\sqrt{3}r_0 + 6e^2/2r_0 \dots)$$

Lattice Energies (kJ/mol) of Some Alkali and Alkaline Earth Halides

Salt	U	r_0
LiF	1021	2.01
NaF	928	2.31
KF	813	2.67
RbF	776	2.82
CsF	732	3.01
NaF	928	2.31
NaCl	770	2.81
NaBr	736	2.97
NaI	703	3.23
MgF ₂	2908	1.98
CaF ₂	2590	2.27
BaF ₂	2314	2.62

Not all ionic compounds are high melting solids; some are liquids!

- Salts of multi-atom ions often have relatively low melting points (large radii → low lattice energy)
- An increasing number of compounds that consist of oppositely charged ions have been discovered/designed to be liquid at or slightly above room temperature – Ionic Liquids.
- Ionic liquids have very low vapor pressures and are often excellent solvents for polar compounds. Because they are immiscible with many solvents, frequently including water, products from reactions done in ionic liquids can often be recovered by extraction with environmentally friendly solvents (Green Chemistry).

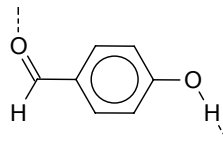
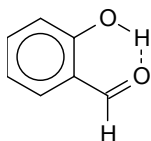
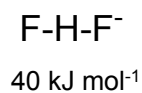


Davis, J.H., Jr.; Fox, P.A. "From curiosities to commodities: ionic liquids begin to transition" *Chem. Commun.* **2003**, 1209-1212

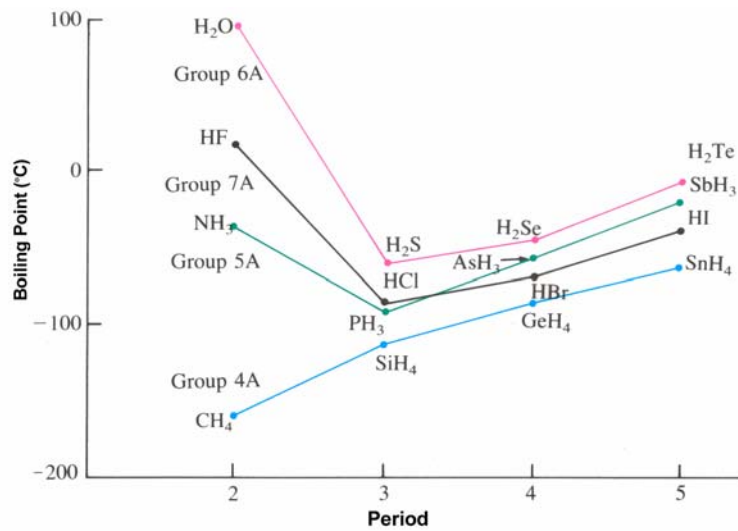
Intermolecular forces

In addition to the interatomic forces that characterize covalent bonding and the electrostatic interactions between ions that characterize the interactions in ion pairs and in ionic solids, there are a variety of other types of forces that are very important in determining the behavior of gases, liquids and solutions, including solubilities.

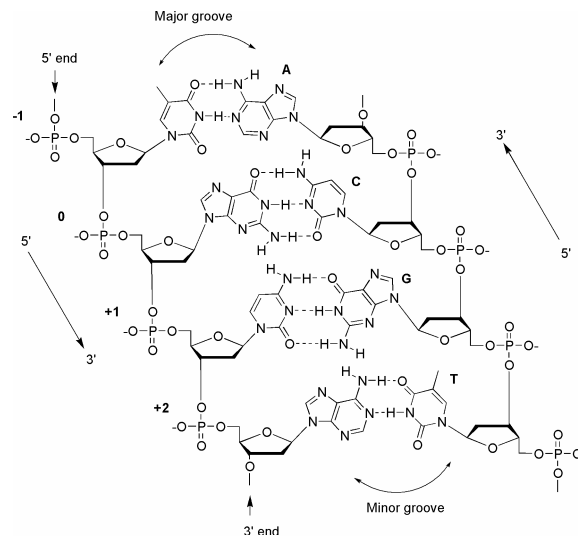
- **Hydrogen bonding.** An interaction between a lone pair of electrons on an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It may be considered as an electrostatic interaction between the partial positive charge on the small hydrogen and the partial negative charge on the electronegative atom. The strongest bonds involve electronegative atoms from the second row of the periodic table, i.e. N, O or F. Energies are generally less than 20–25 kJ mol⁻¹ (5–6 kcal mol⁻¹).



Boiling points of covalent hydrides

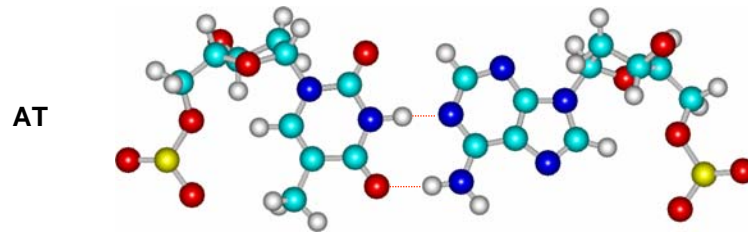
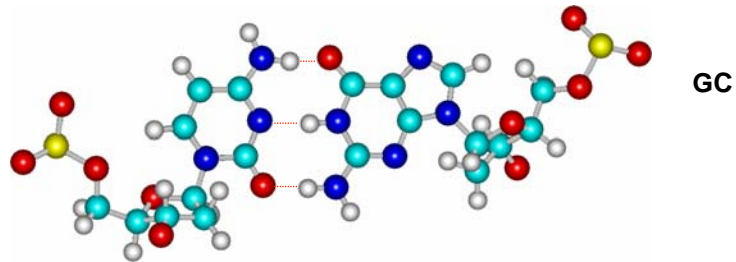


Schematic DNA structure

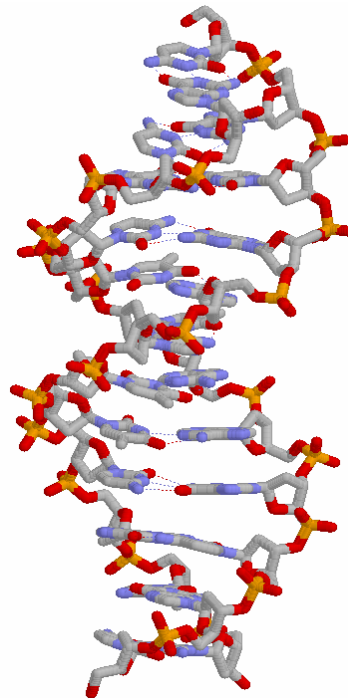


Watson, J. D.; Crick, F. H. C. *Nature* **1953**, *171*, 964-967.

Hydrogen bonding in GC and AT base pairs



Duplex DNA



Intermolecular forces, cont'd

- **Ion-dipole forces.** These are highly directional interactions between ions and polar molecules. $E = -Z_{\pm} \mu / \alpha r^2$
- **Dipole-dipole forces.** Polar molecules (those that have dipole moments) tend to align with the positive and negative ends of the dipole toward one another. $E = -2 \mu_1 \mu_2 / \alpha r^3$
- **Induced dipole forces.** Close approach of an ion or polar molecule to a nonpolar molecule (no permanent dipole moment) can result in inducement of a dipole in the nonpolar molecule and an instantaneous attraction between the species. Ions, $E = -Z^2 P / 2 \alpha r^4$; dipoles, $E = -\mu^2 P / 2 \alpha r^6$
- **Instantaneous dipole-dipole forces** (also known as Van der Waals interactions or London dispersion forces). Result from instantaneous nonuniform distribution of electron density. $E = -3 I P^2 / \alpha r^6$

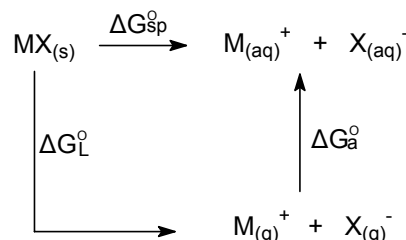
Dipole moment

- $\mu = qr$ where q is the charge and r is the length of the vector from the origin to the charge. 1 Debye = 1×10^{-18} esu cm; $e^- = 4.8 \times 10^{-10}$ esu
- For a heteronuclear diatomic molecule q is the partial charge on each atom and r is the internuclear distance
- For polyatomic molecules μ is the sum of the vector components of the individual bond dipoles.
- Highly symmetric molecules have zero dipole moment regardless of the magnitudes of the individual bond dipoles. These include the following when the terminal atoms are identical:
 - Linear triatomic
 - trigonal planar
 - tetrahedral
 - trigonal bipyramidal
 - octahedral

Dissolution of ionic solids

- Dissolution of an ionic solid requires disruption of the electrostatic (coulombic) interactions between the oppositely charged ions in the lattice, which is unfavorable. The increase in entropy resulting from the increase in disorder favors the process.

- $K_{sp} = [M^+][X^-]$
- $\Delta G_{sp} = -RT \ln K_{sp}$
- $-RT \ln K_{sp} = \Delta H - T\Delta S$
- $\ln K_{sp} = -\Delta H/RT + \Delta S/R$



- ΔG_{sp} is generally rather small, between -80 and +80 kJ mol⁻¹, whereas ΔG_L and ΔG_a are both very large and of opposite sign.
- Prediction of absolute magnitude of ΔG_L and ΔG_a is hard!

More on dissolution

- Dissolution means solvating the ions, i.e., surrounding both the cation and the anion with solvent molecules so that the negative end of the dipole is orientated toward the cation, and the positive end of the dipole toward the anion. In the case of protic solvents the interaction with the anion may involve hydrogen bonding.
- Binding of the solvent molecules to the cation and anion results in interactions between the bound solvent molecules those in a second (and third) coordination sphere. This is especially true for water, which hydrogen bonds both to anions and to itself.
- For small and/or highly charged ions this results in a significant decrease in entropy due to the loss of mobility of large numbers of solvent molecules.
- Never-the-less solubilities of salts frequently parallel the dielectric constant of the solvent.
 - Dielectric constant of a solvent (ϵ) is a quantitative measure of its ability to decrease the force with which two oppositely charged ions attract each other.

ΔH and $T\Delta S$ (at 298 K) for hydration of M^{n+} *

Ion	radius/Å	$\Delta H/\text{kJ mol}^{-1}$	$T\Delta S/\text{kJ mol}^{-1}$
Cs ⁺	1.81	-263	-11
Rb ⁺	1.66	-296	-13
K ⁺	1.52	-321	-16
Na ⁺	1.16	-405	-27
Li ⁺	0.90	-515	-36
Mg ²⁺	0.86	-1922	-86
Ca ²⁺	1.14	-1592	-62
Sr ²⁺	1.32	-1445	-59
Ba ²⁺	1.49	-1304	-48
Sc ³⁺	0.88	-3960	-123
Y ³⁺	1.04	-3620	-124
Fe ³⁺	0.78	-4376	-146

*Quantities refer to transfer of the ion from the ideal gas phase to the aqueous phase at infinite dilution.

ΔH and $T\Delta S$ (at 298 K) for hydration of anions*

Ion	radius/Å	$\Delta H/\text{kJ mol}^{-1}$	$T\Delta S/\text{kJ mol}^{-1}$
F ⁻	1.19	-497	-48
Cl ⁻	1.67	-355	-29
Br ⁻	1.82	-328	-24
I ⁻	2.06	-287	-17
OH ⁻	1.19	-453	-55
S ²⁻	1.70	-1356	-50
ClO ₄ ⁻	2.26	-227	-24
NO ₃ ⁻	1.89		-29
CO ₃ ²⁻	1.85		-86
PO ₄ ³⁻	2.38		-145

*Quantities refer to transfer of the ion from the ideal gas phase to the aqueous phase at infinite dilution.

Solubilities of salts: - practical knowledge

- Salts in which both the cation and anion are multiply charged are generally insoluble. Important exceptions are sulfate salts where many involving multiply charged cations are soluble and the alkaline earth sulfides which are soluble.
- Salts in which both the anion and cation are singly charged are generally soluble; important exceptions include the silver halides.
- Many salts in which the anion or cation is singly charged are soluble; hydroxides and fluorides of most polyvalent cations are exceptions.
- Solubilities of salts that involve basic anions will be greatly increased in acidic media, where protonation of the basic anion will drive the equilibrium as shown in the following example:

