

Welcome to  
APS104S – Introduction to Materials &  
Chemistry

Lecture 3  
January 8, 2016

# Subjects we will study today

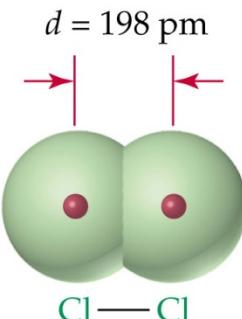
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- Atomic and ionic radii
- Bond formation
- Primary interatomic bonding
- Secondary bonding

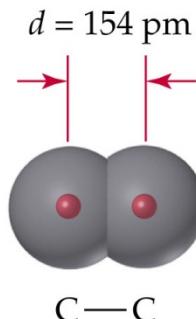
# Atomic and ionic radii

## Atomic Radii

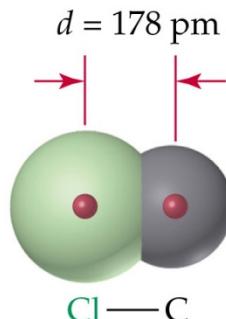
Atomic radius is half the distance between the nuclei of two identical atoms when they are bonded together.



$$\frac{d}{2} = 99 \text{ pm}$$



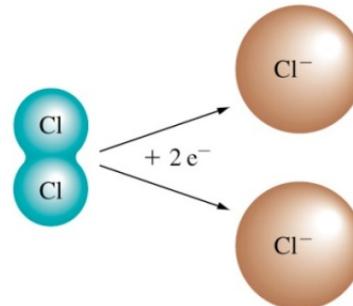
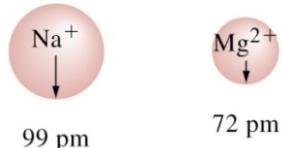
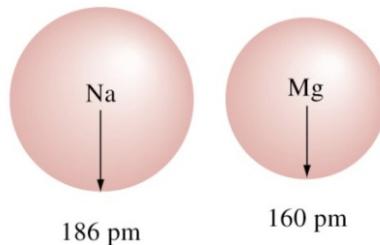
$$\frac{d}{2} = 77 \text{ pm}$$



$$(99 \text{ pm} + 77 \text{ pm} = 176 \text{ pm})$$

predicted

## A comparison of atomic and ionic sizes



Covalent radius  
99 pm

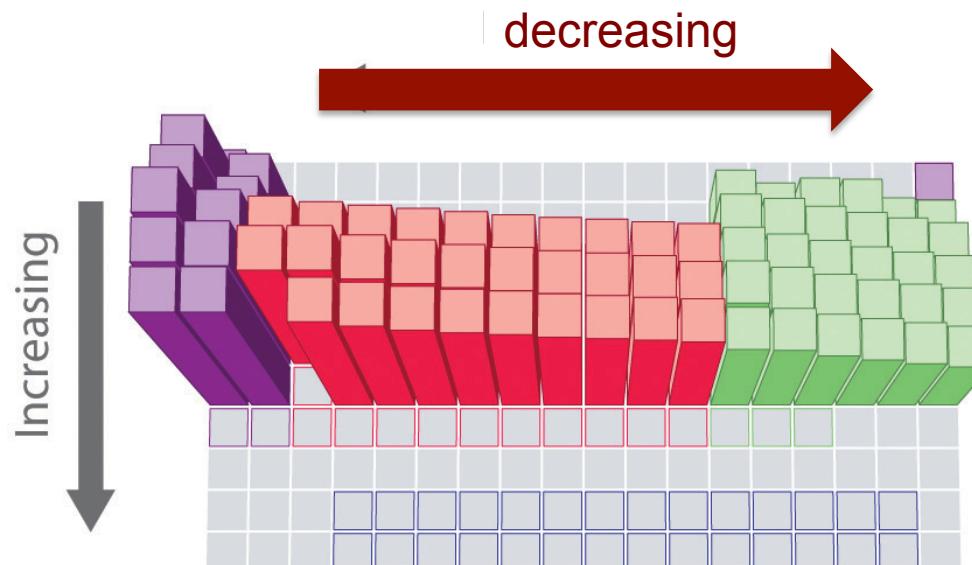
Ionic radius  
181 pm

In general all **cations** are smaller than their **parent atoms**.

In general all **anions** are larger than their **parent atoms**.

# Periodic trend in atomic radii

Because it is impossible to measure the sizes of both metallic and nonmetallic elements using any one method, *chemists have developed a self-consistent way of calculating atomic radii using the quantum mechanical functions*. These values provide a way to compare the intrinsic sizes of all elements.



Because the number of shell are increasing

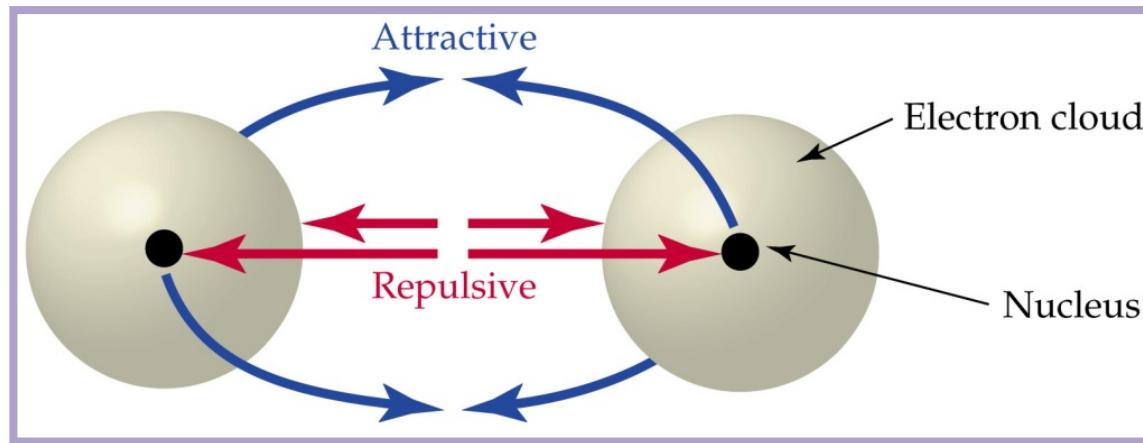
Calculated atomic radius (pm),  
s-, p-, and d-block elements

Because in a row, the number of shell is constant, but the numbers of protons is increasing from left to right → the effective nuclear charge ( $Z_{\text{eff}}$ ) increases and the outer most electrons are more attracted to the nucleus → smaller atomic radii

# Bond formation

# Bond formation

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attractive  
forces

=

repulsive  
forces



bond formation

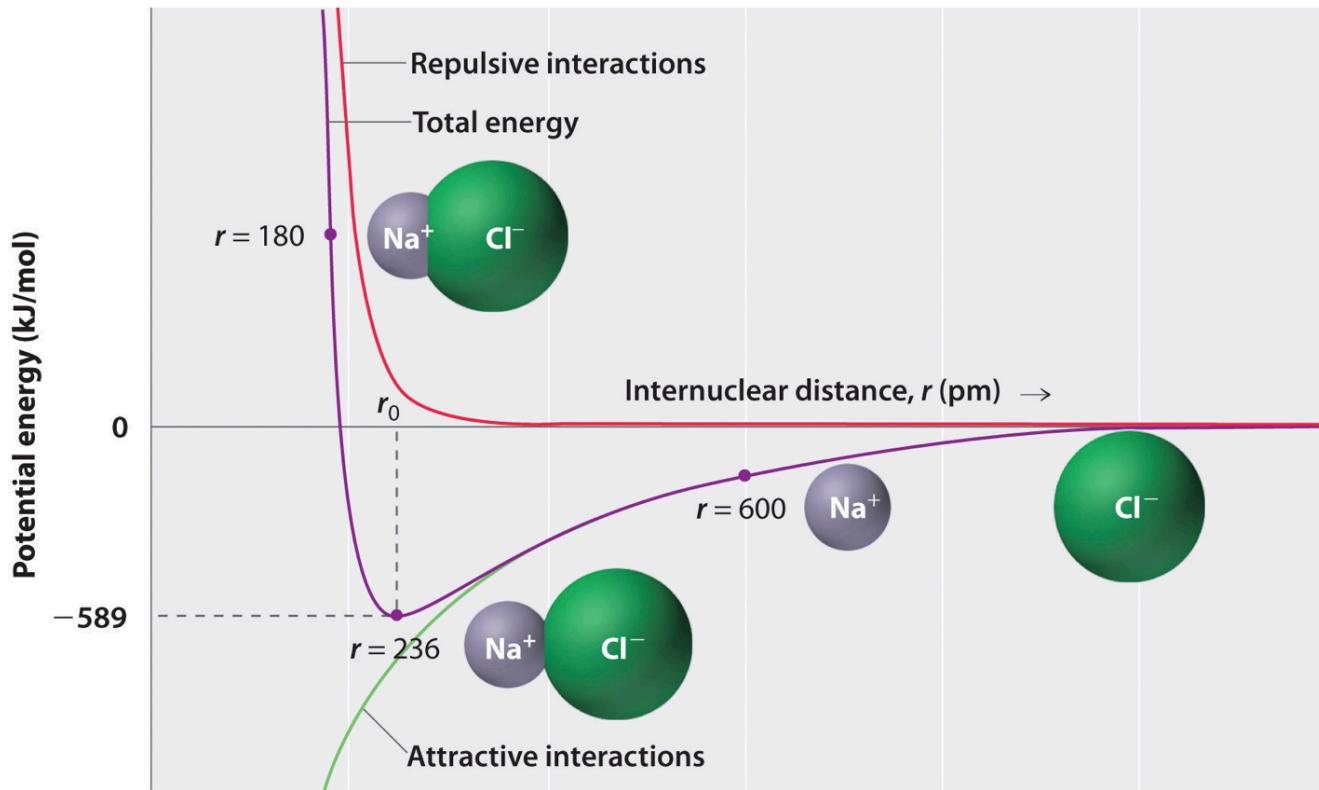
If the atoms are **too far apart**, attraction are weak and no bonding occurs.

If the atoms are **too close**, strong repulsions occur.

When atoms are **optimally separated**, net force is zero, and the energy is at a minimum → that's when bond forms.

# Generic bonding curve

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- At  $r_0$ , the ions are more stable (have a lower potential energy) than they are at an infinite internuclear distance. When oppositely charged ions are brought together from  $r = \infty$  to  $r = r_0$ , the energy of the system is lowered (energy is released).

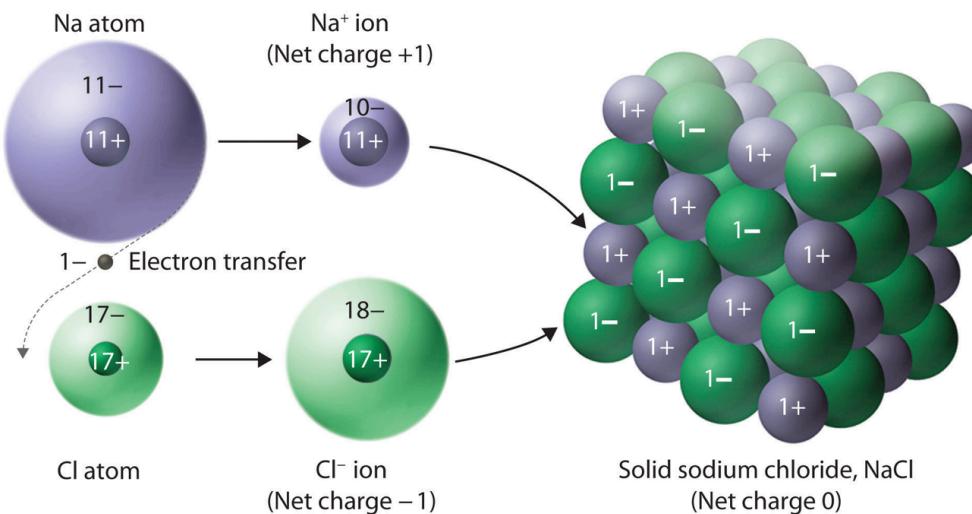
Primary interatomic bonding  
(between atoms)

# Primary interatomic bonds

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**1 - Ionic bonds** – between metals and non-metals – the metal gives up its valence electron (cation) & the non-metal receives the electron (anion) – columbic interaction between positive and negative ions

Ionic bonds are **non-directional** – anions and cations pack closely together in mineral structures.

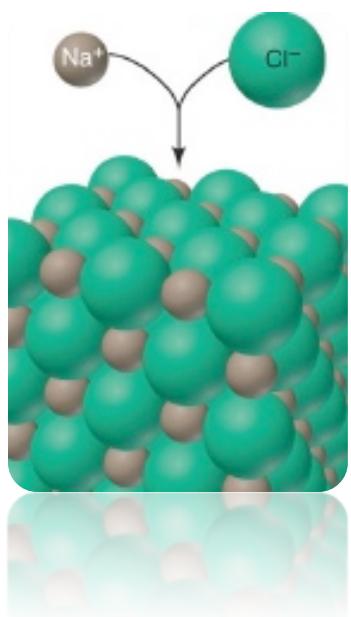


# Ionic bonds

Properties (nature of ionic bonding in solids):

- Exchange of electron between the metal and non-metal
- Bonding energy high → high melting T
- Hard
- Brittle
- Electrically and thermally insulative (no free electrons)

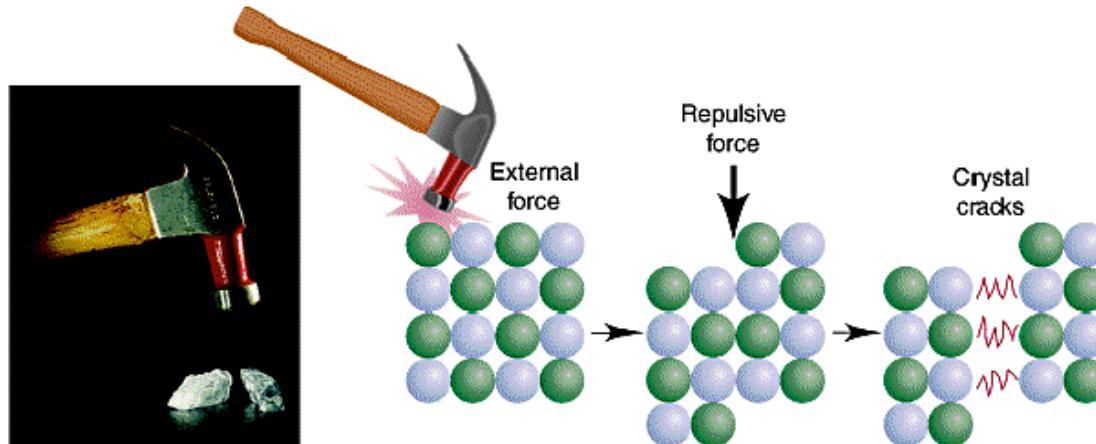
*electrostatic  
attraction*



**high melting points**

**low electrical conductivity**

**in solid state, brittle, hard**



# Ionic bonds

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 <b>H</b> Hydrogen 1.008	2 <b>Be</b> Beryllium 9.0121...	30 <b>Zn</b> Zinc 65.38	2 <b>He</b> Helium 4.002602															
2 <b>Li</b> Lithium 6.94	4 <b>Be</b> Beryllium 9.0121...	3 <b>Zn</b> Zinc 65.38	5 <b>Al</b> Aluminum 26.981...	6 <b>Si</b> Silicon 28.085	7 <b>N</b> Nitrogen 14.007	8 <b>O</b> Oxygen 15.999	9 <b>F</b> Fluorine 18.998...	10 <b>Ne</b> Neon 20.1797	11 <b>P</b> Phosphorus 30.973...	12 <b>S</b> Sulfur 32.06	13 <b>Cl</b> Chlorine 35.45	14 <b>Ar</b> Argon 39.948	15 <b>Br</b> Bromine 79.904	16 <b>Kr</b> Krypton 31.798	17 <b>Xe</b> Xenon 131.293	18 <b>Rn</b> Radon (222)		
3 <b>Na</b> Sodium 22.989...	4 <b>Mg</b> Magnesium 24.305	5 <b>Sc</b> Scandium 44.955...	6 <b>Ti</b> Titanium 47.867	7 <b>V</b> Vanadium 50.9415	8 <b>Cr</b> Chromium 51.9961	9 <b>Mn</b> Manganese 54.938...	10 <b>Fe</b> Iron 55.845	11 <b>Co</b> Cobalt 58.933...	12 <b>Ni</b> Nickel 58.6934	13 <b>Cu</b> Copper 63.546	14 <b>Zn</b> Zinc 65.38	15 <b>Ga</b> Gallium 69.723	16 <b>Ge</b> Germanium 72.63	17 <b>As</b> Arsenic 74.921...	18 <b>Se</b> Selenium 78.971			
4 <b>K</b> Potassium 39.0983	5 <b>Ca</b> Calcium 40.078	6 <b>V</b> Yttrium 88.90584	7 <b>Ti</b> Zirconium 91.224	8 <b>Sc</b> Zirconium 92.90637	9 <b>Mn</b> Niobium 95.95	10 <b>Cr</b> Molybdenum 95.95	11 <b>Fe</b> Technetium (98)	12 <b>Co</b> Ruthenium 101.07	13 <b>Ni</b> Rhodium 106.42	14 <b>Cu</b> Palladium 107.6862	15 <b>Zn</b> Cadmium 112.414	16 <b>Ga</b> Indium 118.818	17 <b>Ge</b> Antimony 121.760	18 <b>As</b> Tellurium 127.80				
5 <b>Rb</b> Rubidium 85.4678	6 <b>Sr</b> Strontium 87.62	7 <b>Y</b> Yttrium 88.90584	8 <b>Zr</b> Zirconium 91.224	9 <b>Nb</b> Zirconium 92.90637	10 <b>Mo</b> Niobium 95.95	11 <b>Tc</b> Molybdenum 95.95	12 <b>Ru</b> Technetium (98)	13 <b>Fe</b> Ruthenium 101.07	14 <b>Co</b> Rhodium 106.42	15 <b>Ni</b> Palladium 107.6862	16 <b>Cu</b> Cadmium 112.414	17 <b>Zn</b> Indium 118.818	18 <b>Ga</b> Antimony 121.760					
6 <b>Cs</b> Caesium 132.90...	7 <b>Ba</b> Barium 137.327	8 <b>Hf</b> Hafnium 178.49	9 <b>Ta</b> Tantalum 180.94...	10 <b>W</b> Tungsten 183.84	11 <b>Re</b> Rhenium 186.207	12 <b>Os</b> Osmium 190.23	13 <b>Ir</b> Iridium 192.217	14 <b>Pt</b> Platinum 195.084	15 <b>Au</b> Gold 196.96...	16 <b>Hg</b> Mercury 200.59	17 <b>Tl</b> Thallium 204.38	18 <b>Pb</b> Lead 207.2						
7 <b>Fr</b> Francium (223)	8 <b>Ra</b> Radium (226)	9 <b>Rf</b> Rutherfordium (267)	10 <b>Db</b> Dubnium (268)	11 <b>Sg</b> Seaborgium (271)	12 <b>Bh</b> Bohrium (272)	13 <b>Hs</b> Hassium (270)	14 <b>Mt</b> Meitnerium (276)	15 <b>Ds</b> Damstadtium (281)	16 <b>Rg</b> Roentgenium (280)	17 <b>Cn</b> Copernicium (285)	18 <b>Uut</b> Ununtrium (284)							
		57–71	89–103															

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Periodic Table Design & Interface Copyright © 1997 Michael Dayah. Ptable.com Last updated Sep 20, 2014

57 <b>La</b> Lanthanum 138.90...	58 <b>Ce</b> Cerium 140.116	59 <b>Pr</b> Praseodymium 140.90...	60 <b>Nd</b> Neodymium 144.242	61 <b>Pm</b> Promethium (145)	62 <b>Sm</b> Samarium 150.36	63 <b>Eu</b> Europium 151.964	64 <b>Gd</b> Gadolinium 157.25	65 <b>Tb</b> Terbium 158.92...	66 <b>Dy</b> Dysprosium 162.500	67 <b>Ho</b> Holmium 164.93...	68 <b>Er</b> Erbium 167.259	69 <b>Tm</b> Thulium 168.93...	70 <b>Yb</b> Ytterbium 173.054	71 <b>Lu</b> Lutetium 174.9668			
89 <b>Ac</b> Actinium (227)	90 <b>Th</b> Thorium 232.0377	91 <b>Pa</b> Protactinium 231.03...	92 <b>U</b> Uranium 238.02...	93 <b>Np</b> Neptunium (237)	94 <b>Pu</b> Plutonium (244)	95 <b>Am</b> Americium (243)	96 <b>Cm</b> Curium (247)	97 <b>Bk</b> Berkelium (247)	98 <b>Cf</b> Californium (251)	99 <b>Es</b> Einsteinium (252)	100 <b>Fm</b> Fermium (257)	101 <b>Md</b> Mendelevium (258)	102 <b>No</b> Nobelium (259)	103 <b>Lr</b> Lawrencium (262)			

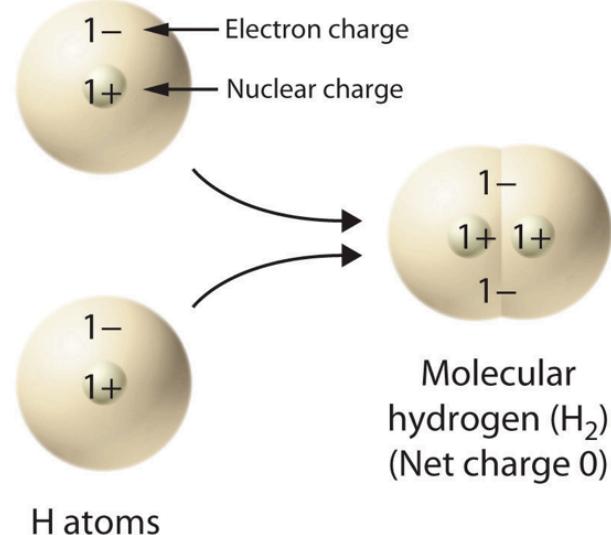
Usually between metals from column IA and IIA and non metals from VIA and VIIA  
Examples: KCl, LiCl, LiBr, NaBr, BaS, CaO, CaF<sub>2</sub>, Na<sub>2</sub>S, CsF, MgS, ...

# Primary interatomic bonds

**2 - Covalent bonds** – due to sharing of valence electrons (usually between non metals)

$\text{Cl}_2$ ,  $\text{H}_2$ ,  $\text{F}_2$ ,  $\text{N}_2$   
 $\text{CH}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$   
Diamond  
SiC

Most polymers (along carbon chains)



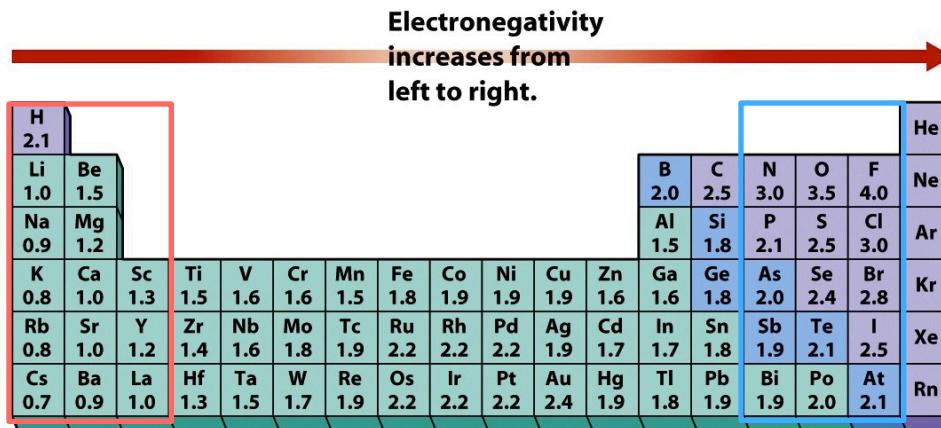
(a) Covalent bonding

These materials can be very hard (like diamond) and can have very high melting T  
They can also be weak and have low melting T

# Polar covalent bonds: electronegativity

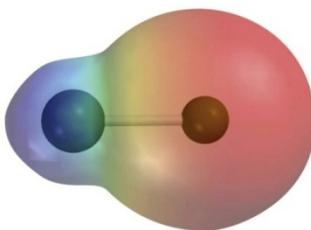
**ELECTRONEGATIVITY:** The ability of an atom in a molecule to attract the shared electrons in a covalent bond.

Electropositive elements:  
Readily give up electrons  
to become + ions.



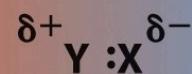
Electronegative elements:  
Readily acquire electrons  
to become - ions.

Electronegativity decreases from top to bottom.



NaCl

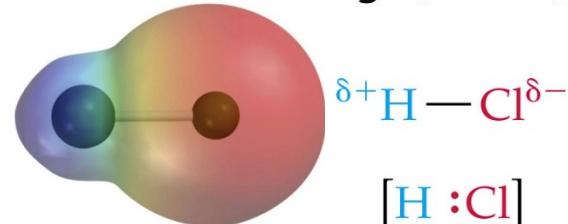
$\text{M}^+ \text{X}^-$   
Ionic  
(full charges)



Polar covalent  
(partial charges)



Nonpolar covalent  
(electronically symmetrical)

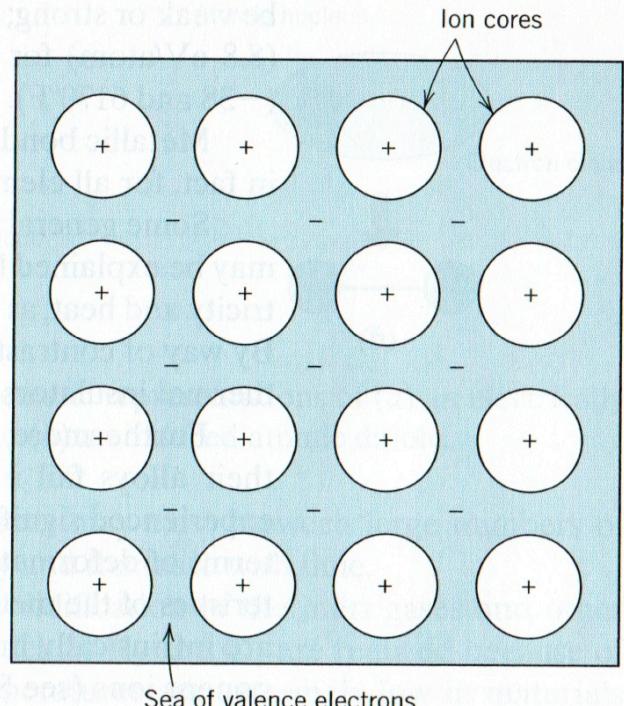


# Primary interatomic bonds

**3 - Metallic bonds** – consists of metal cores (net positive charge) in a sea of free electrons – this bond is non-directional

Properties (nature of metallic bonding in solids):

- Electrically and thermally conductive (because of free electrons)
- They exist between all metals in the P-table
- Ductile (can deform significantly before fracturing (but ionic bonds are brittle))



**Figure 2.11** Schematic illustration of metallic bonding.

# Summary: Primary interatomic bonding (between atoms)

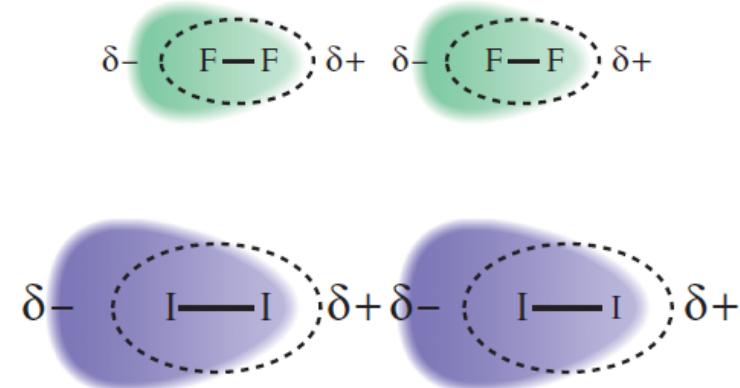
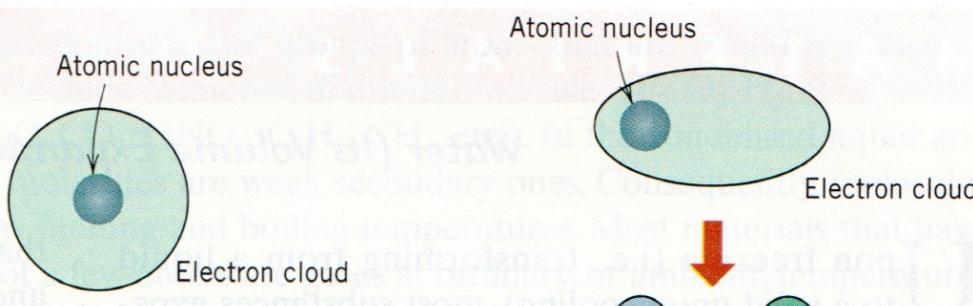
1. Ionic (electrostatic between cation & anion)
2. Covalent (electron sharing, stable electronic structure)
3. Metallic (positively charged ions, shielded from each other, kept together by a sea of  $e^-$ )

Secondary bonding  
(between molecules)

# Secondary bonding

**1. Van der Waals bonds: Fluctuating induced dipole bonds** – an electrically symmetric molecule (non-polar) may lose its symmetry instantaneously and becomes dipole and induces this to its neighbor – then there will be attraction between these molecules (like noble gases,  $\text{Cl}_2$ ,  $\text{H}_2$ )

Melting T and boiling T are very low; the weakest type of bonding

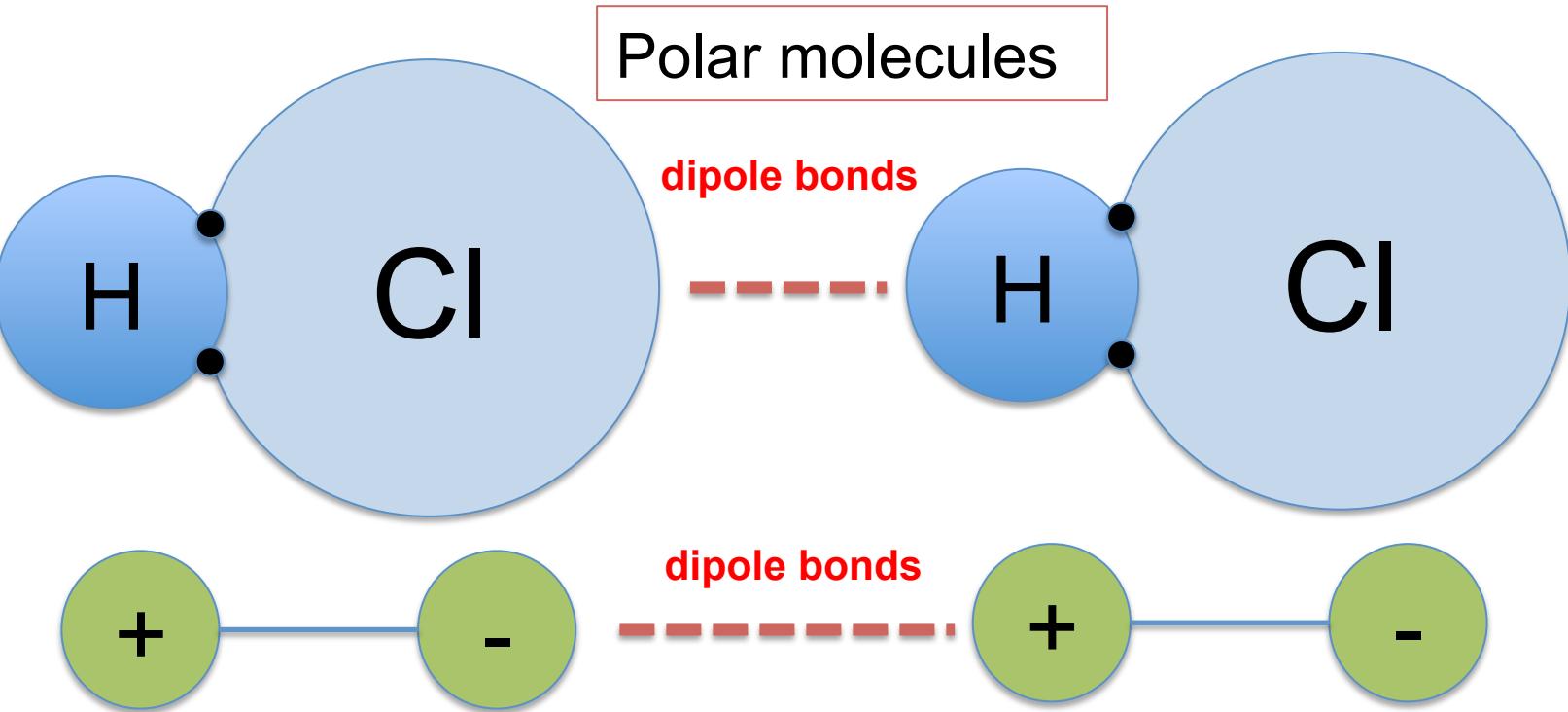


# Secondary bonding

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**2. Polar molecules – dipole bonds** – between molecules that are polar (have negative and positive poles due to electronegativity difference)

Polar molecules consist of atoms with different electronegativity like HCl, H<sub>2</sub>S, SO<sub>2</sub>

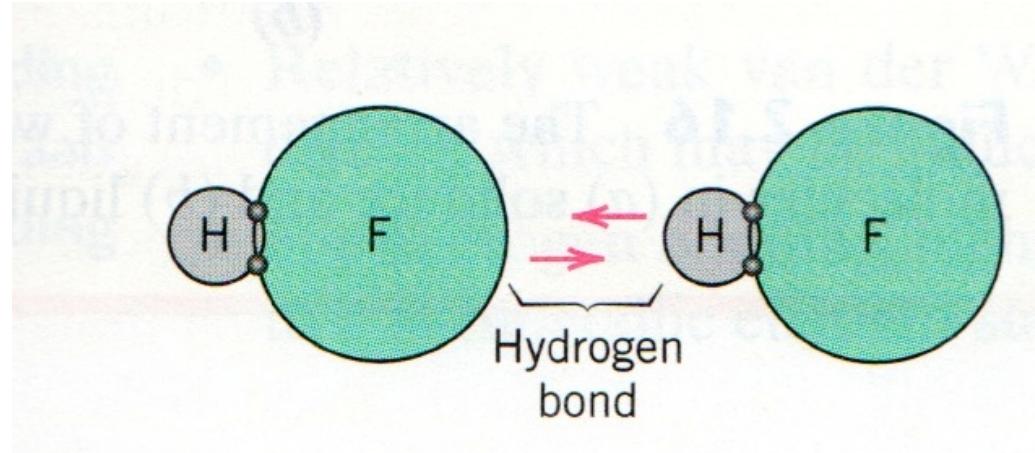
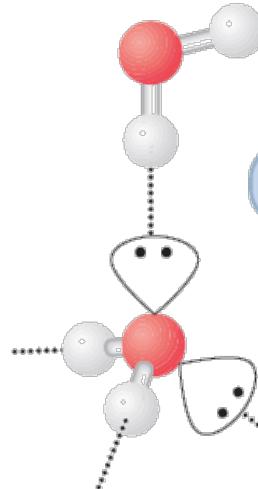


# Secondary bonding

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**3. Hydrogen bonding**— between molecules in which hydrogen is bonded with F, O, or N (H – F) (H – O) (H – N)  
(Example: HF, H<sub>2</sub>O, NH<sub>3</sub>)

Hydrogen is highly positively charged in these molecules and it can accept an electron pair from the negative end of an adjacent molecule → each proton is like a bridge between two negatively charged atoms.

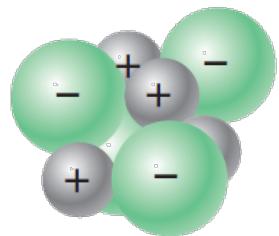


# Summary: Secondary bonding (between molecules)

1. Van der Waals bonds (Fluctuating induced dipole bonds) (**weakest**)
2. Dipole bonds (between polar molecules) (**intermediate**)
3. Hydrogen bonds (**strongest**)

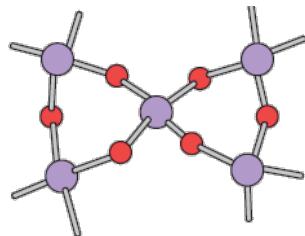
# Various types of solids

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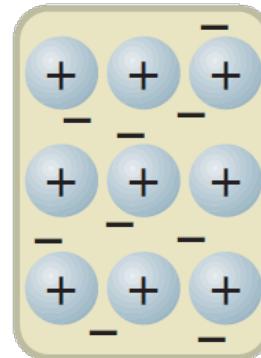
Ionic solid

KCl, NaI



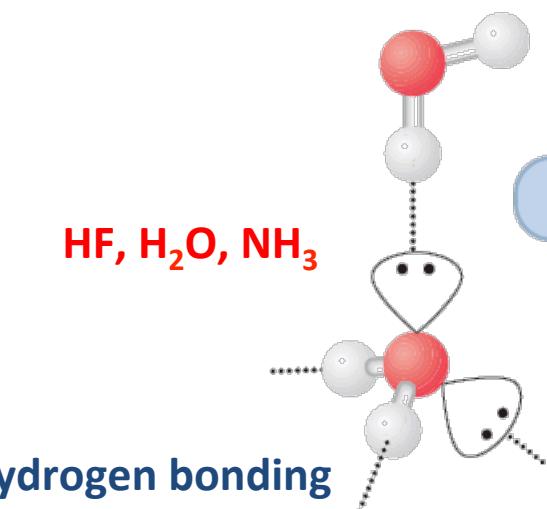
Network solid

Diamond, SiO<sub>2</sub>



Metallic solid

Au, Fe, Ba, ...

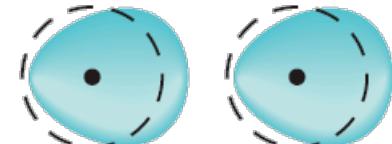


HF, H<sub>2</sub>O, NH<sub>3</sub>

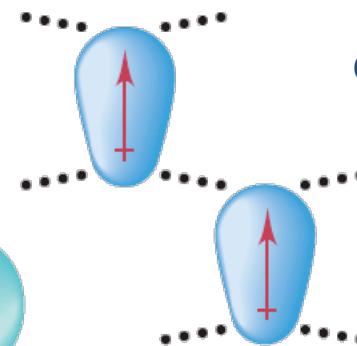
Hydrogen bonding

Molecular solid

O<sub>2</sub>, Noble gases



Van der Waals bonds



dipole bonds

HCl, CO<sub>2</sub>

# Strength of the bonds

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- If you make covalent solids (atoms with covalent bonds between them, like diamond,  $\text{SiO}_2$ ); they form a “*solid network*” and they have the highest melting point.
- After that, we have *ionic solids*, and then *metallic solids*. Sometimes metallic solids has higher melting point, it is case by case.
- Then we have secondary bonding; hydrogen bonding is the highest, then dipole bonding (between polar molecules), and then van der Waals bonds (between non polar molecules). They all make *molecular solids*.

Case by case

- Network solids > “*ionic solids > metallic solids*” > “*hydrogen bonds > dipole > van der Waals*”

Molecular solids

# Example

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Indicate what type of solid (ionic, network, metallic, or molecular) each of the following forms on solidification:

(a) Br<sub>2</sub> (b) KBr (c) Ba (d) SiO<sub>2</sub> (e) CO<sub>2</sub>

- A. molecular
- B. ionic
- C. metallic
- D. network
- E. molecular

Example: compare melting points of following compounds

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HF, HCl, NaCl, diamond, SiO<sub>2</sub>, CH<sub>3</sub>OH, CH<sub>4</sub>

Answer:

Diamond > SiO<sub>2</sub> > NaCl > HF > CH<sub>3</sub>OH > HCl > CH<sub>4</sub>

# Example: type of bonding in the following materials

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- Brass (Copper-zinc alloy) metallic Metallic solid
- BaS ionic Ionic solid
- Xenon Van der Waals
- HF Hydrogen bonding between molecules,  
(covalent between atoms)
- HCl Dipole-dipole between molecules,  
(covalent between atoms)
- F<sub>2</sub> Van der Waals between molecules,  
(covalent between atoms)

Molecular  
solids

# Properties of the Major Classes of Solids

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## Network solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous

\*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.

The general order of increasing strength of interactions in a solid is molecular solids < ionic solids ≈ metallic solids < network solids.

# Comparison of bond types and typical properties (general trends)

	Typical Solids	Bond Energy eV/atom	Melt. Temp. (°C)	Elastic Modulus (GPa)	Density (g cm <sup>-3</sup> )	Typical Properties
<b>Ionic</b>	NaCl, (rock salt)	3.2 10	801 2852	40 250	2.17 3.58	Generally electrical insulators. May become conductive at high temperatures. High elastic modulus. Hard and brittle but cleavable.
	MgO, (magnesia)					Thermal conductivity less than metals.
<b>Metallic</b>	Cu	3.1	1083	120	8.96	Electrical conductor.
	Mg	1.1	650	44	1.74	Good thermal conduction. High elastic modulus.
<b>Covalent</b>	Si	4	1410	190	2.33	Generally ductile. Can be shaped.
	C (diamond)	7.4	3550	827	3.52	Large elastic modulus. Hard and brittle. Diamond is the hardest material. Good electrical insulator. Moderate thermal conduction, though diamond has exceptionally high thermal conductivity.
<b>van der Waals:</b> <b>Hydrogen bonding</b>	PVC, (polymer)	- 0.52	212 0	4 9.1	1.3 0.917	Low elastic modulus. Some ductility. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.
	H <sub>2</sub> O, (ice)					
<b>van der Waals: Induced dipole</b>	Crystalline Argon	0.09	-189	8	1.8	Low elastic modulus. Electrical insulator. Poor thermal conductivity. Large thermal expansion coefficient.

From *Principles of Electronic Materials and Devices, Second Edition*, S.O. Kasap (© McGraw Hill, 2002)

<http://Materials.Utsc.ca>