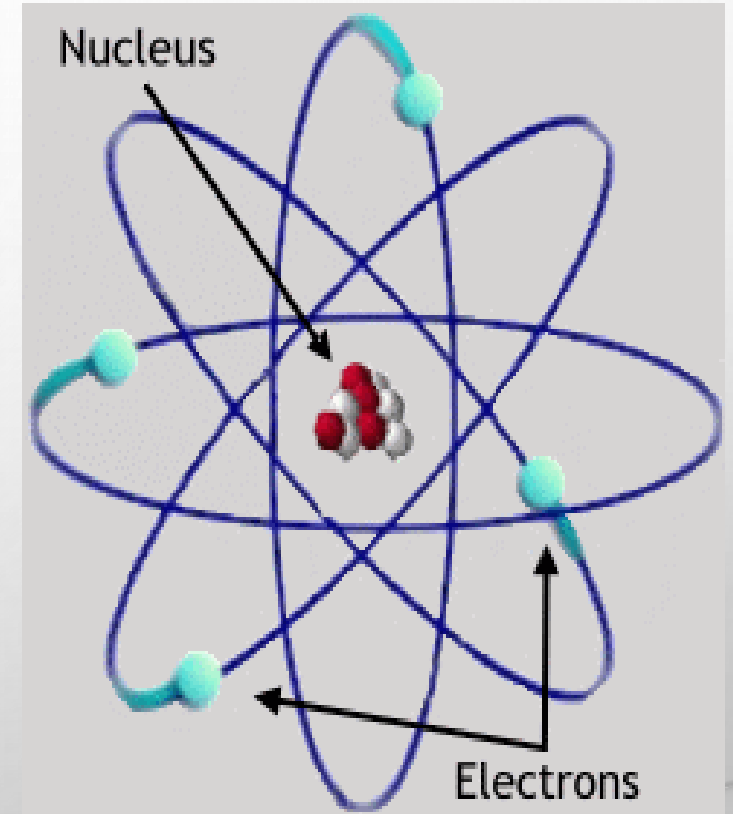


# **Electronic structure of free atom**

## **Crystal growth**

## What Is An Atom?

- oAtom is the smallest unit of an element.
- oConsists of a central nucleus surrounded by one or more electrons.



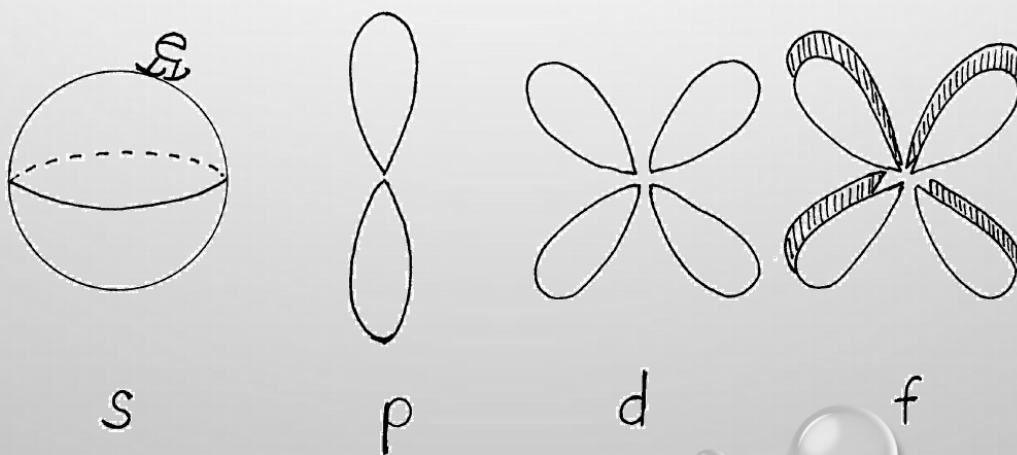
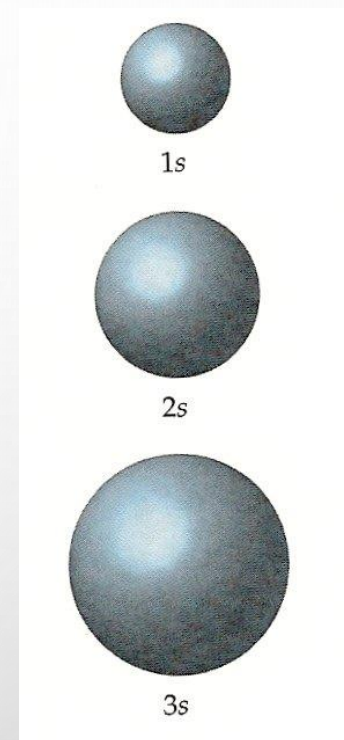
# Quantum numbers

## First (principal) QN (n)

- how far the electron is from the nucleus (larger the number, farther away) – Level or shell

## Second (orbital) QN (l)

- the shape of the orbital



### **Third (magnetic) QN ( $m_l$ )**

- the suborbital

### **Forth (Spin) QN ( $S$ )**

spin of the electron

Two electrons in the same suborbital (ex:  $p_y$ ) must have opposite spins  
Can have values of  $+1/2$  or  $-1/2$



$n$	→	shell	$1, 2, 3, 4, \dots$
$l$	→	orbital	$0, 1, 2, \dots n - 1$
$m_l$	→	subshell	$-l \dots 0 \dots +l$
$m_s$	→	electron spin	$+\frac{1}{2}$ and $-\frac{1}{2}$

# Electron Configurations

1. electron configuration – shorthand notation to tell you the locations of all the electrons in an atom or ion

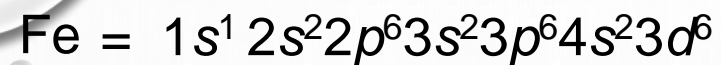
## FILLING RULES FOR ELECTRON ORBITALS

**Aufbau Principle:** Electrons are added one at a time to the lowest energy orbitals available until all the electrons of the atom have been accounted for.

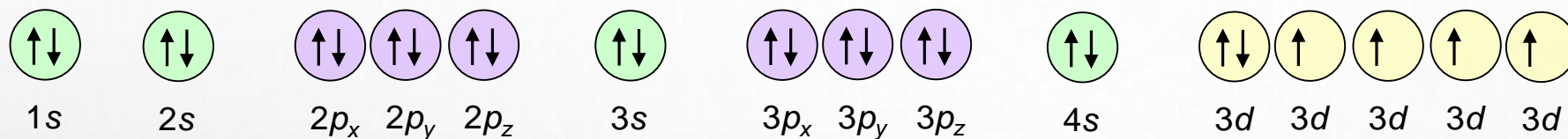
**Pauli Exclusion Principle:** An orbital can hold a maximum of two electrons. To occupy the same orbital, two electrons must spin in opposite directions.

**Hund's Rule:** Electrons occupy equal-energy orbitals so that a maximum number of unpaired electrons results.





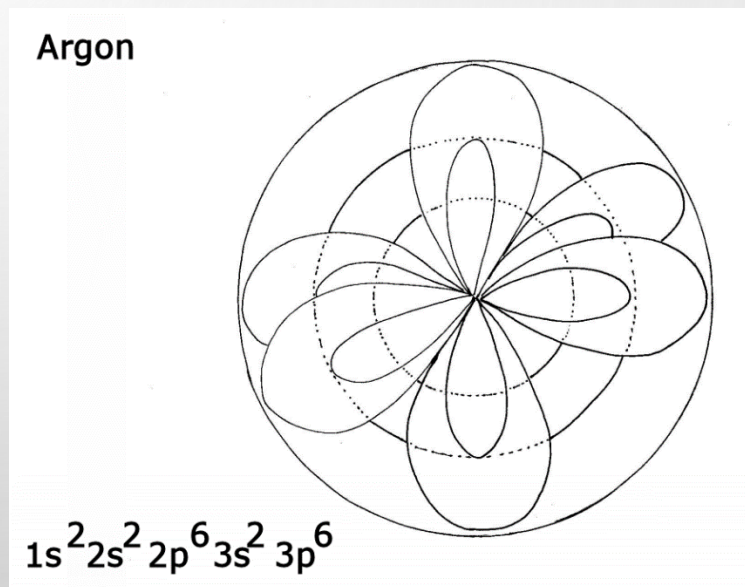
Iron has 26 electrons.

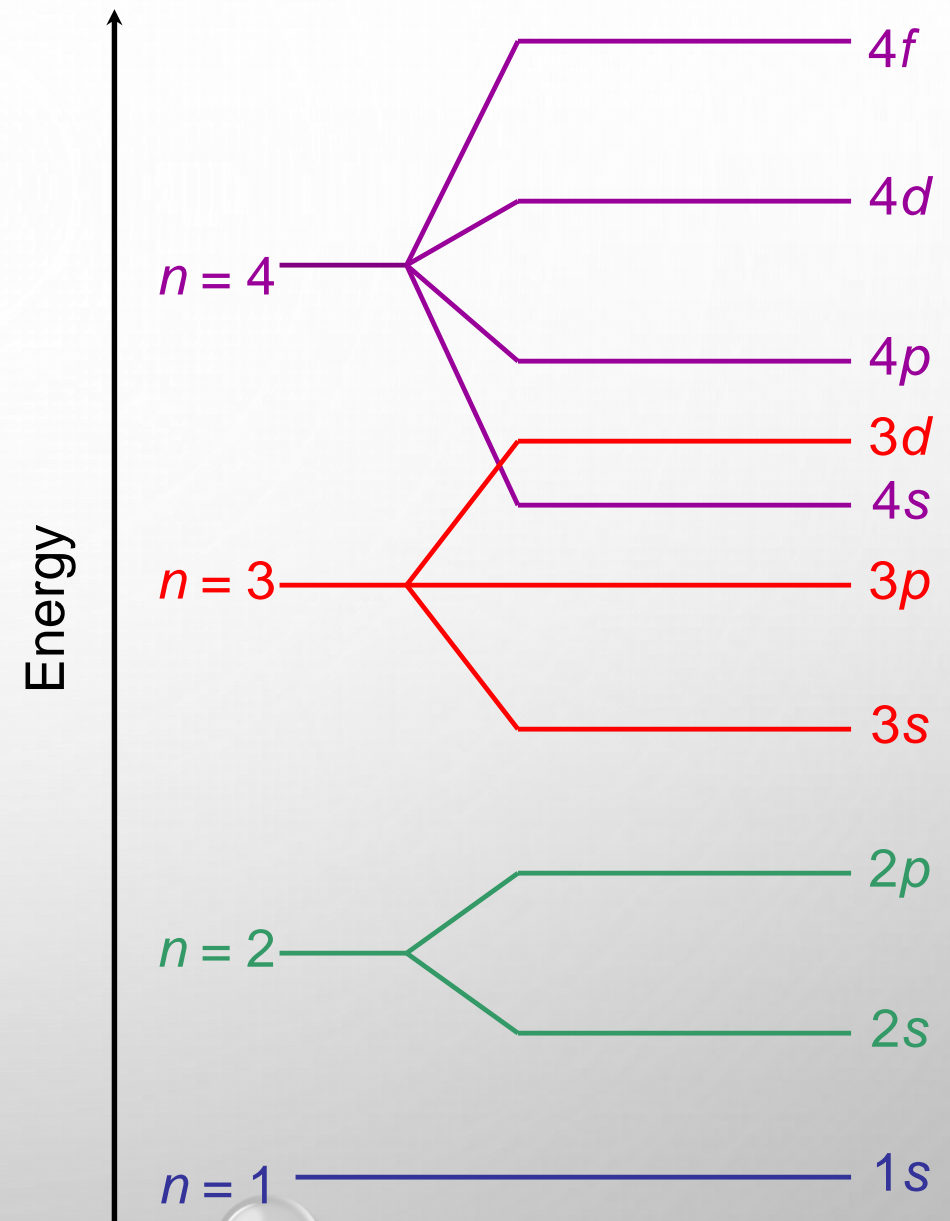


**Why is “d” one less?**

Energy is slightly above the next s orbital

**Ar has 18 electrons**







# Atomic Bonding

*What kind of forces hold the atoms together in a solid?*

Why do atoms bond with each other to form compounds?

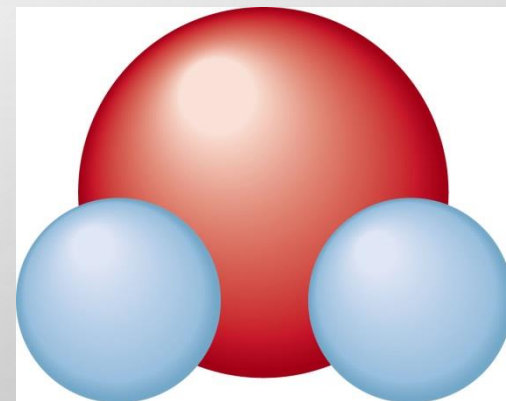
How do atoms bond with each other to form compounds?

-Forces that hold groups of atoms together and make them function as a unit.

-A bond results from the attraction of nuclei for electrons

-A bond will form if the energy of the aggregate is lower than that of the separated atoms.

**Bond energy** – energy required to break a chemical bond



# Energies of interactions between atoms

*The energy of the crystal is lower than that of the free atoms by an amount equal to the energy required to pull the crystal apart into a set of free atoms. This is called the binding (cohesive) energy of the crystal.*

**NaCl is more stable than a collection of free Na and Cl.**

**Ge crystal is more stable than a collection of free Ge.**

# General Considerations

## There must be an attractive force

An apparent candidate is the Coulomb Force

$$F = -\frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r^2}$$

Here  $r$  is a distance between atoms (ions) forming a solid

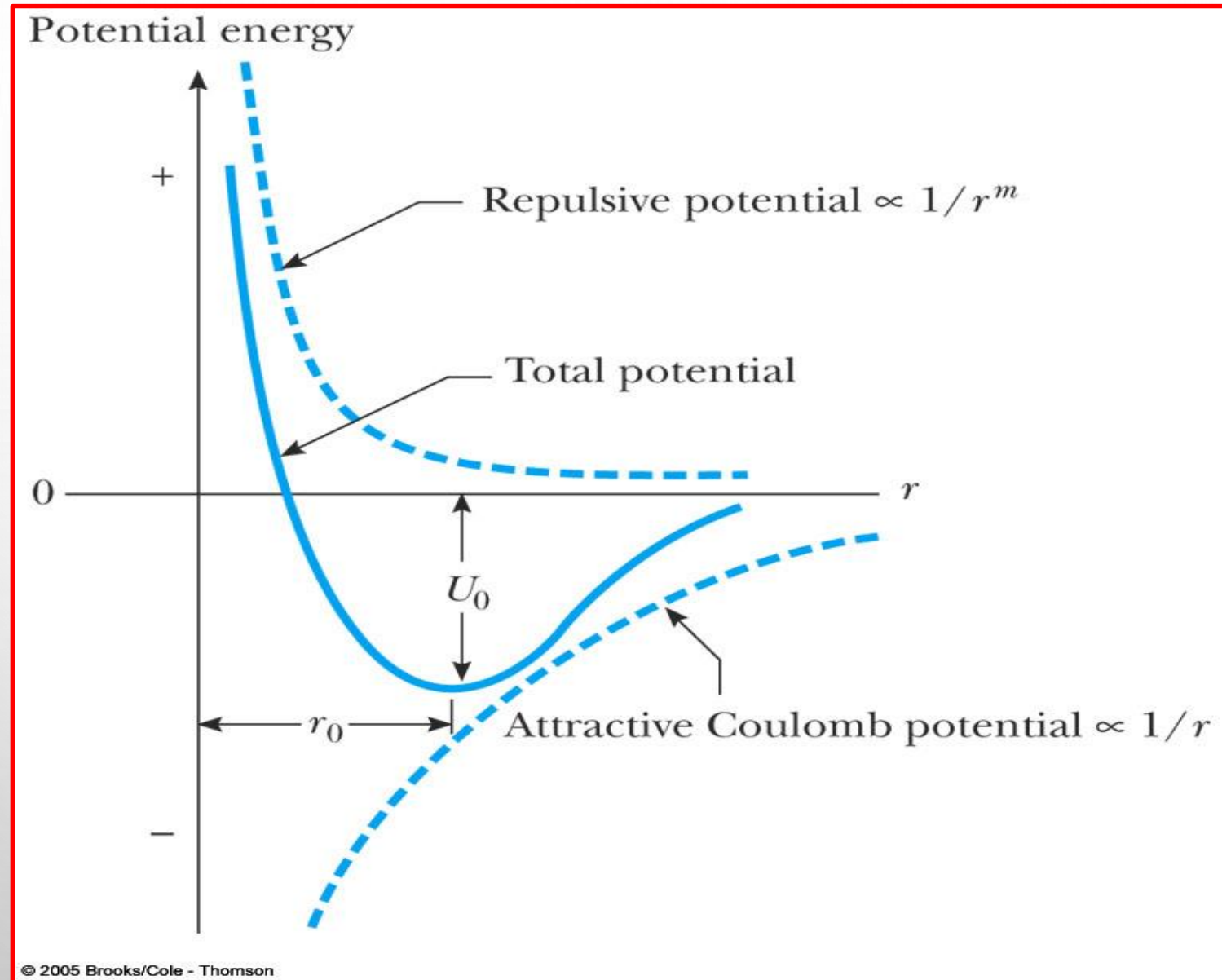
## What stops atoms (ions) from getting closer than they do?

When ions are very close to each other, other forces arise.

These are the so-called **short-range repulsive forces**, due to rearrangement of electrons as nuclei approach

*All bonding is a consequence of the electrostatic interaction between the nuclei and electrons.*

## Leonard-jones model



# Electronegativity

- The ability of an atom in a molecule to attract shared electrons to itself.
- For a molecule HX, the relative electronegativities of the H and X atoms are determined by comparing the measured H–X bond energy with the “expected” H–X bond energy.
- On the periodic table, electronegativity generally increases across a period and decreases down a group.
- The range of electronegativity values is from 4.0 for fluorine (the most electronegative) to 0.7 for cesium and francium (the least electronegative).

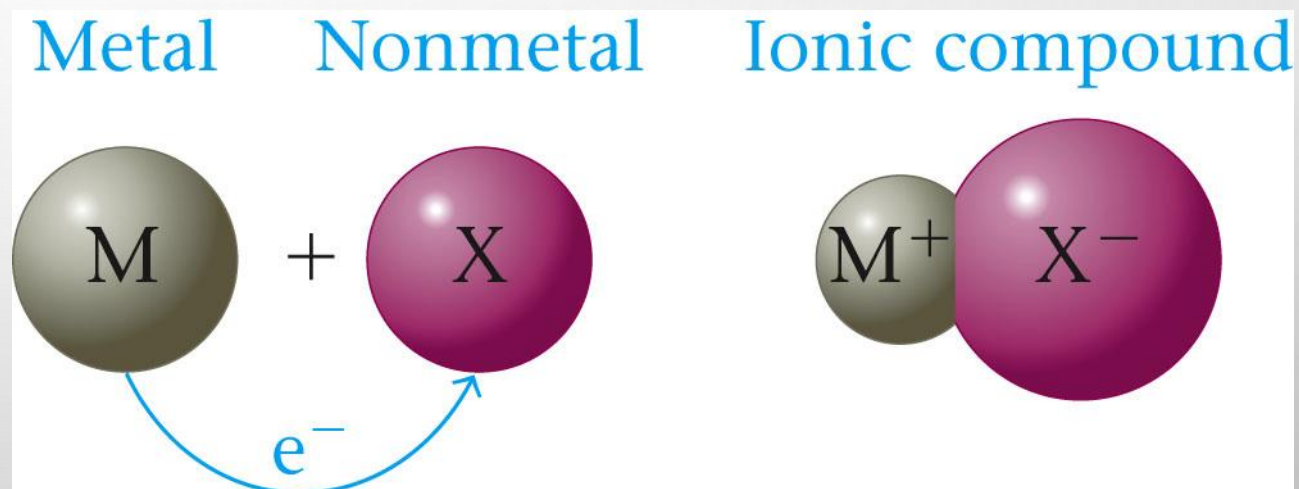


# Ionic Bonding

## Metal with nonmetal

- Ionic compound results when a metal reacts with a nonmetal.
- Electrons are transferred between **valence shells** of atoms
- Ions are packed together to maximize the attractions between ions.

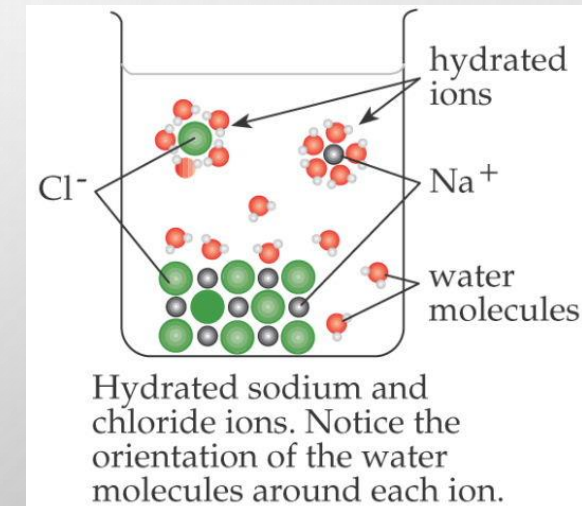
- Electronegativity difference **> 2.0**  
Look up e-neg of the atoms in the  
bond and subtract





# Properties of **Ionic Compounds**

- Very hard solid at RT but can be cleaved
- high melting point and boiling point temperatures because of **very strong inter-particle attractions** (electrostatic attractions)
- **non**conductors of electricity in **solid** phase (no free ions or electrons)
- **good** conductors in liquid phase or dissolved in water (aqueous) (as ions are free to move)
- **Soluble** in polar substances as polar solvents overcome the electrostatic forces between ions



# Covalent Bonding

## Nonmetal with nonmetal

Covalent bonding takes place between atoms with small differences in electronegativity which are close to each other in the periodic table.

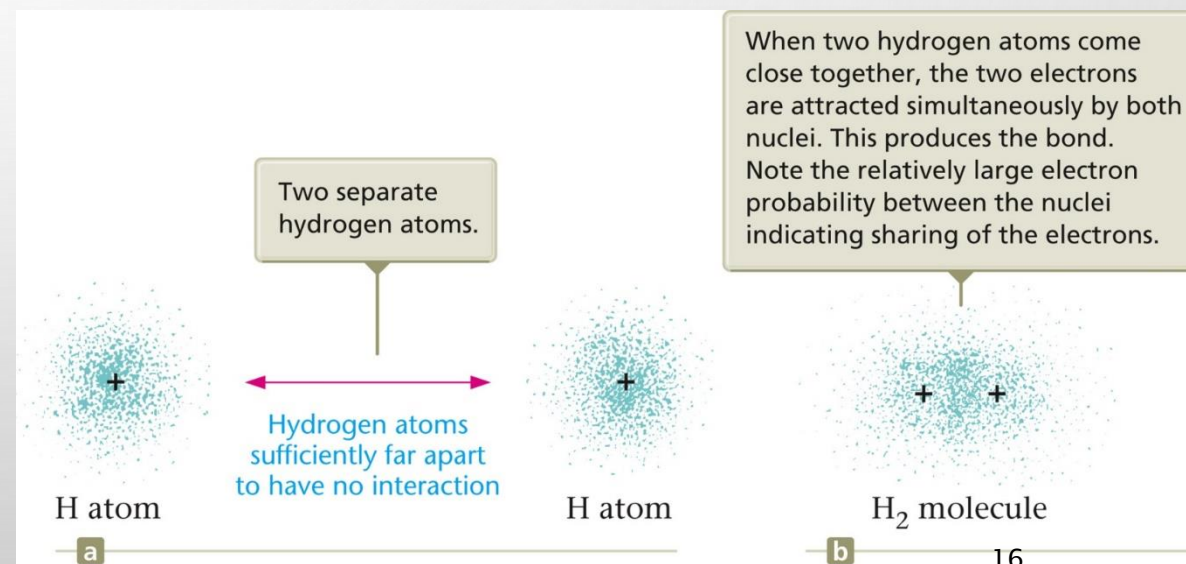
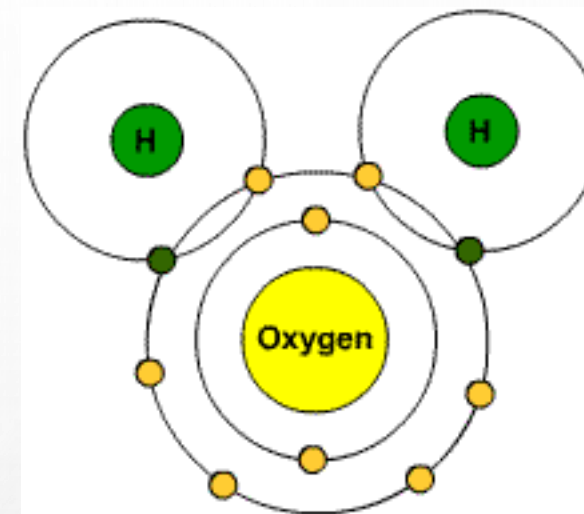
- A covalent bond results when electrons are shared by nuclei.

-Pairs of e<sup>-</sup> are shared between non-metal atoms

-electronegativity difference < 2.0

•They move back and forth between the outer energy levels of each atom in the covalent bond.

•So, each atom has a stable outer energy level some of the time.



# Properties of Molecular Substances

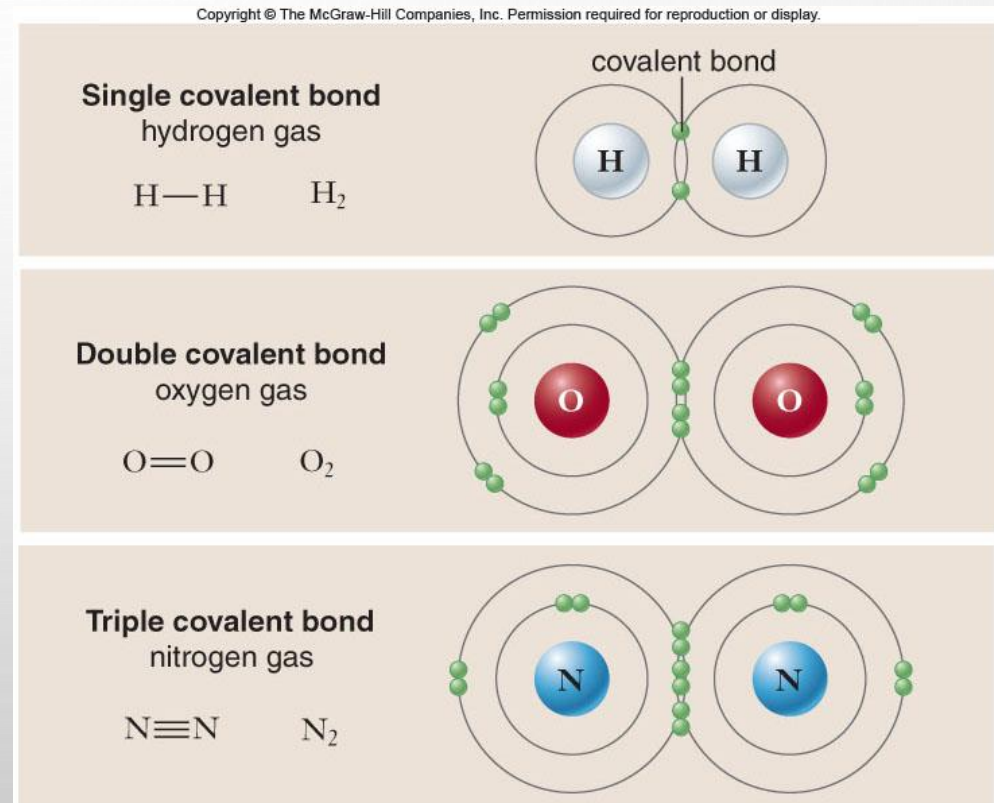
- Low melting and boiling point temperature.
- relatively soft solids as compared to ionic compounds
- nonconductors of electricity in any phase even when molten (no free ions or electrons)
- Insoluble in water and other polar substances

## Examples

- methane (CH<sub>4</sub>)
- ammonia (NH<sub>3</sub>)
- oxygen (O<sub>2</sub>)
- nitrogen (N<sub>2</sub>).

Occasionally, they can share 2 or even 3 electrons pairs.

These are called double and triple bonds.



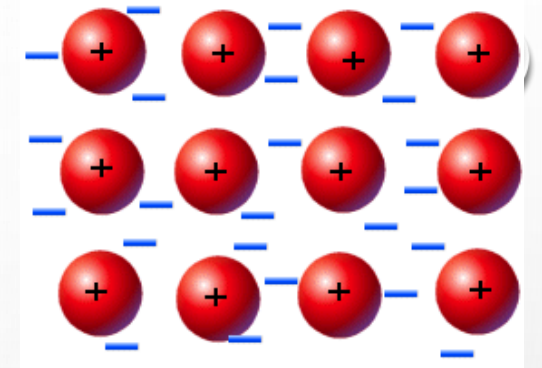


# Metallic bonding

## Metal with metal

- Occurs between *like* atoms of a metal in the free state
- Valence e- are mobile (move freely among all metal atoms)
- Positive ions in a sea of electrons
- The metallic bond is **weaker** than the ionic and the covalent bonds.
- A metal may be described as a **low-density** cloud of free electrons.
- Therefore, metals have **high** electrical and thermal **conductivity** due to density and mobile electrons.
- High melting and boiling points** due to strong metallic bonds
- Not soluble**

The strength of metallic bonds varies and so consequently the melting and boiling points of different metals varies.



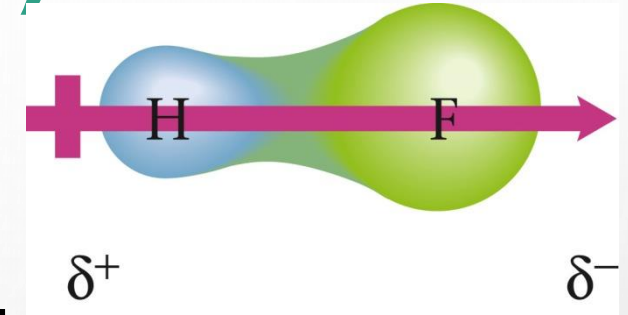
**It's the mobile electrons (sea of electrons) that enable metals to conduct electricity**

# Intermolecular Forces

- intermolecular forces are weaker than ionic or covalent bonds.
- intermolecular forces are responsible for the physical state of a compound (solid, liquid or gas).
- **Van der Waals Forces**
- **Hydrogen Bonds**

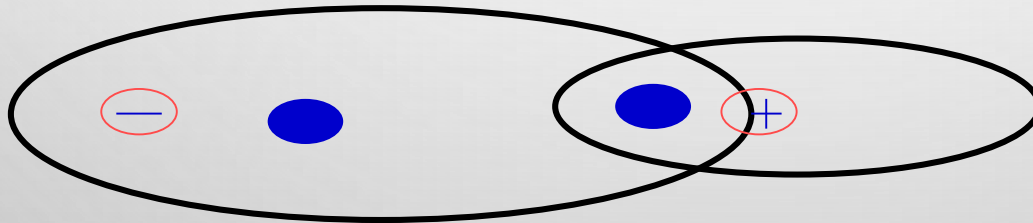
## Molecular Bonds (Van der Waals bonds)

- They are the weakest attractions between molecules with a typical strength of 0.2 eV/atom.
- Electrostatic interaction between the oppositely charged regions of polar molecules (dipoles).
- Van der Waals bonds occur between **neutral atoms and molecules**.
- Weak forces of attraction result from the natural fluctuations in the electron density of all molecules that cause small temporary dipoles to appear within the molecules.
- It is these temporary dipoles that attract one molecule to another. They are called van der Waals' forces.





- The **shape** of a molecule influences its ability to form temporary dipoles. Long thin molecules can pack closer to each other than molecules that are more spherical.
- The **bigger** the '**surface area**' of a molecule, the **greater** the **van der waal's forces** will be and the higher the melting and boiling points of the compound will be.
- Van der waal's forces are of the order of 1% of the strength of a covalent bond.
- These forces are due to the electrostatic attraction between the nucleus of one atom and the electrons of the other.



# Hydrogen Bonding

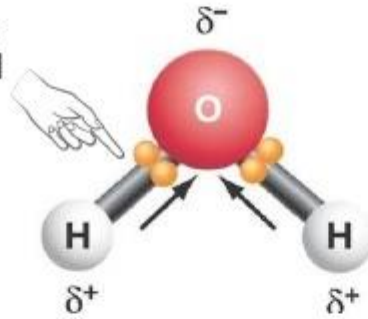
- Hydrogen bonding is the attraction between a hydrogen atom of a molecule to an unshared pair of electrons in another molecule.
- Hydrogen bonding occurs in molecules where hydrogen is covalently bonded to a very electronegative element.
- Hydrogen bonding occurs in molecules containing N, O, F.
- The strength of hydrogen bonding varies from 0.1 to 0.5 eV/atom.
- Hydrogen bonds are the strongest of all intermolecular forces.
- Hydrogen bonds are possible because in hydrogen atoms there is no shielding of the nucleus.
- Hydrogen bonds are responsible for the physical properties of many biological substances and, more importantly, water.

**Do not confuse with  
hydrogen covalent  
bond!!!!!!**

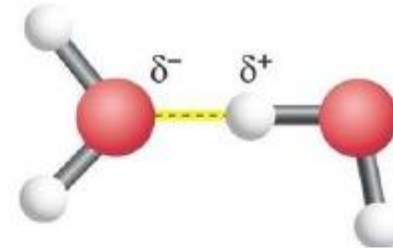
# Water Molecules and Hydrogen Bonding

(a) Water is polar.

Electrons are  
pulled toward  
oxygen



(b) Hydrogen bonds form  
between water molecules.



# Crystal growth

- Why do crystals form?
- What controls their shape and size?
- Three aspects to the growth of a crystal are
  - **Nucleation**: formation of a stable nucleus
  - **Diffusion** of material to the nucleus
  - **Growth** of the crystal by adding atoms

The **slowest** of these three aspects  
generally **controls** the shape and size



## Lots of variables in “recipe” to be determined

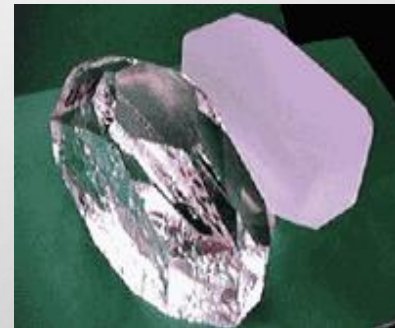
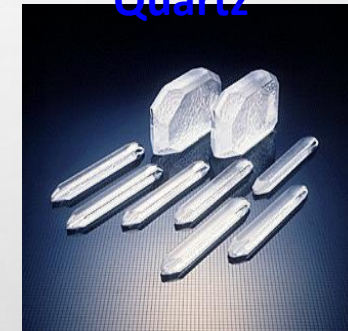
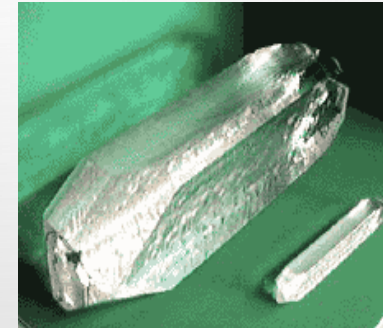
Method to use, temperature, pressure, atmosphere, cooling rate, crucible material, choice of flux / solvent, choice of starting compounds, control oxygen content, doping levels, size/shape of starting materials, optimize for desired crystal size / orientation.

**Isotropic** – same properties in every direction

**Anisotropic**- different properties in different directions → most minerals are this type



Natural  
Quartz



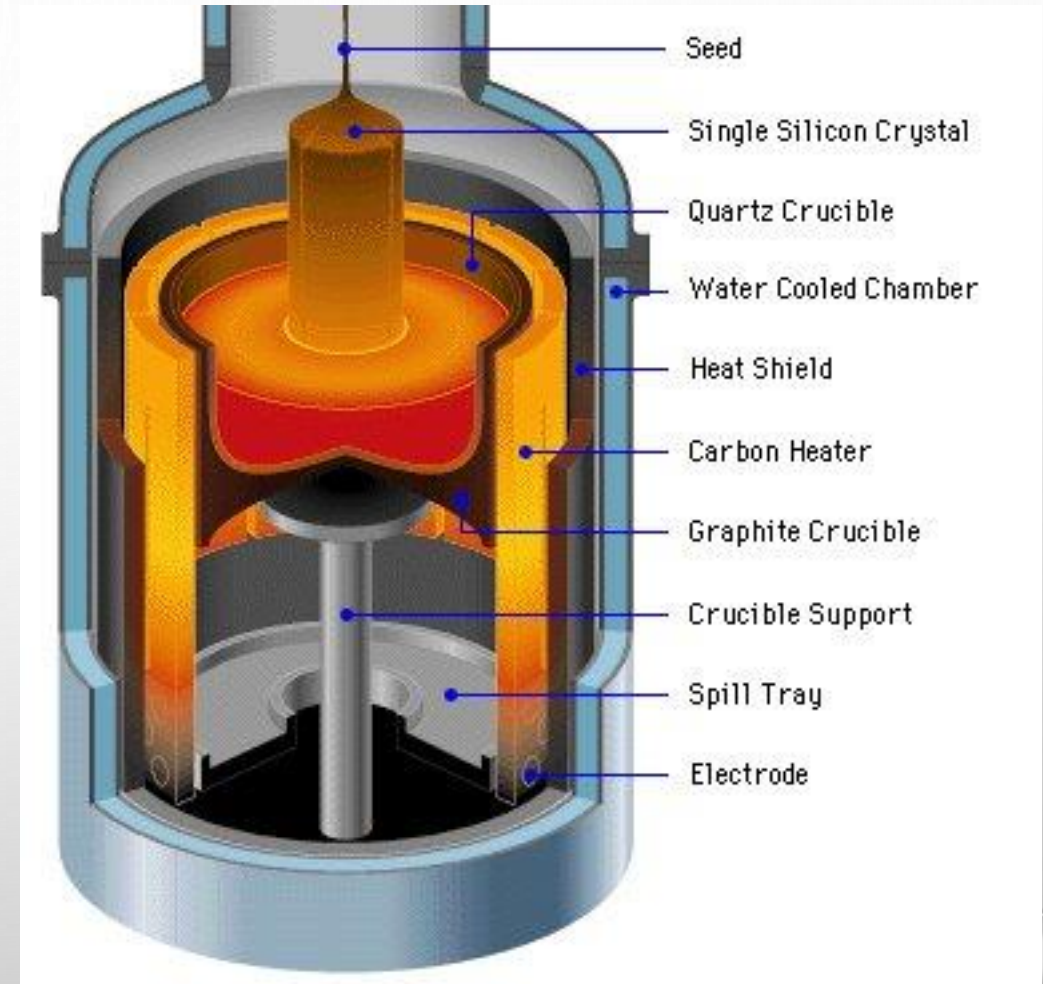
Synthetic  
Quartz

# Czochralski method

Developed 1917, Jan Czochralski

- the material to be grown is melted by induction or resistance heating under a controlled atmosphere in a suitable non-reacting container.
- By controlling the furnace temperature, the material is melted.
- A seed crystal is lowered to touch the molten charge.
- the temperature of the seed is maintained very low compared to the temperature of the melt.
- by suitable water cooling arrangement, the molten charge in contact with the seed will solidify on the seed.
- Then the seed is pulled with simultaneous rotation of the seed rod and the crucible in order to grow perfect single crystals.

abeer alshammari,2016







Used for industrial  
metals: Pd, Pt, Ag, Au  
Some salts

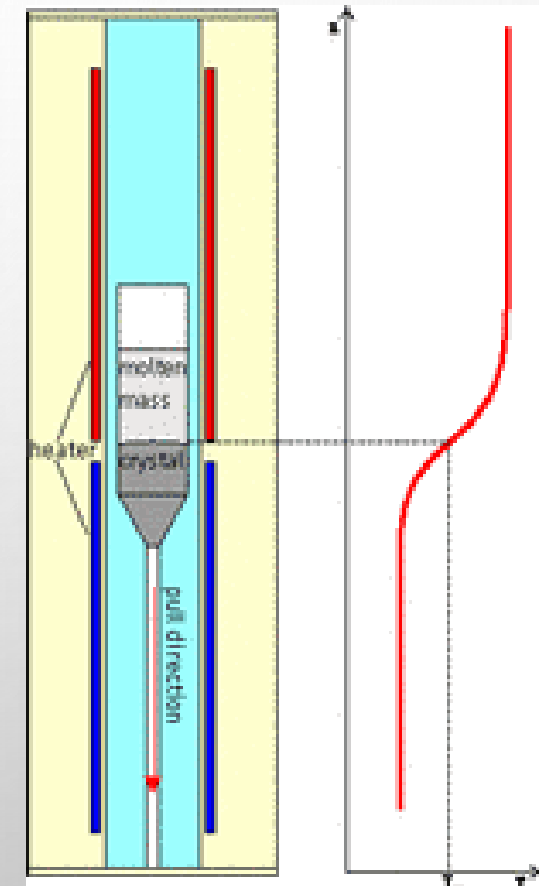
SC's: Si, Ge

# Bridgman method

developed at 1940's

- the material is melted in a vertical cylindrical container, tapered conically with a point bottom.
- The container is lowered slowly from the hot zone of the furnace in to the cold zone.
- The rates of movement for such processes range from about 1 – 30 mm/hr.
- Crystallization begins at the tip and continues usually by growth from the first formed nucleus.
- This technique cannot be used for materials, which decompose before melting.
- This technique is best suited for materials with low melting point

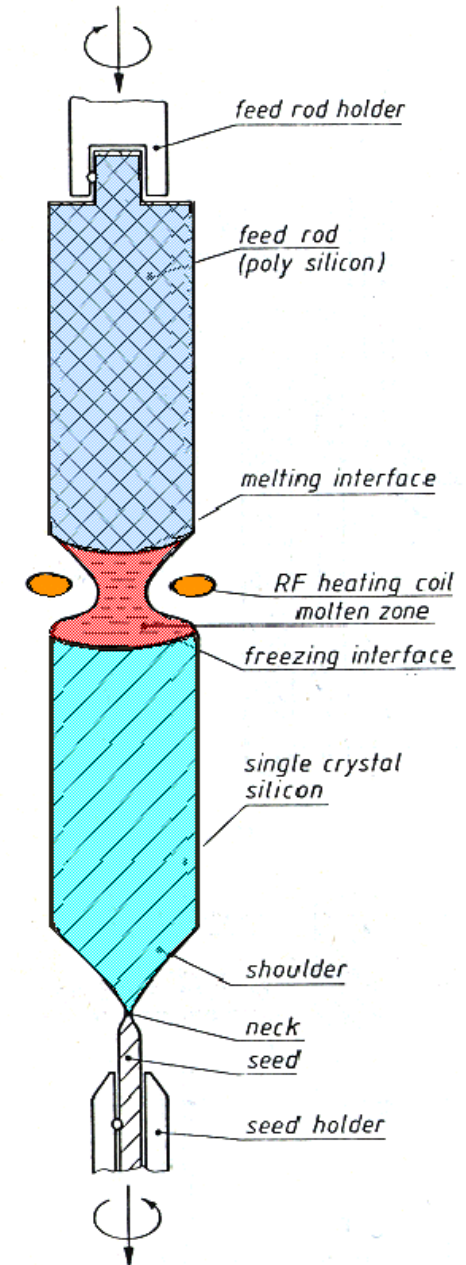
e.g. GaAs



## zone method

- The basic idea in float zone (**FZ**) crystal growth is to move a liquid zone through the material. If properly seeded, a single crystal may result.
- Impurities in the molten region tend stay in the molten region rather than be incorporated into the solidified region

### Float-zone pulling





# Characterization of crystals

- XRD (X-ray diffraction)

