

● Chapter 9: Atomic Model+more

❖ LIGHT:

- Visible light is only a very tiny portion of a massive spectrum of radiation
- It includes radio waves, microwaves, infrared radiation, ultraviolet radiation, x-rays, and even gamma rays.
- This is called the electromagnetic spectrum

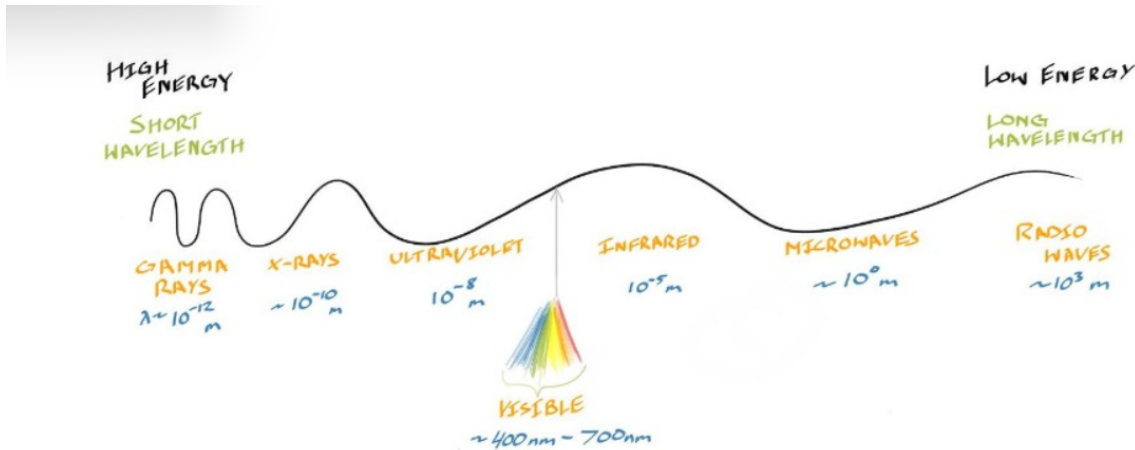


Figure 1. The electromagnetic spectrum. Visible light is only a tiny little bit of the spectrum.

- Another feature of electromagnetic radiation is that the energy within the electromagnetic spectrum exists as chunks of energy, or photons.
- When things exist only as individual, non-divisible units we say that they are quantized.
- So, energy in the electromagnetic spectrum is quantized, and it turns out that the amount of **energy** in each so-called quanta or photon is **inversely proportional** to the **wavelength** of the radiation.
- Frequency is inversely proportional to wavelength
- radio waves are less energetic and ultraviolet waves, x-rays and gamma rays are more energetic.
- As humans we worry more about exposure to higher energy radiation than low energy radiation.

➤ The value of energy in quanta can be calculated as:

$$E = \frac{hc}{\lambda}$$

- h is the Planck constant = 6.626×10^{-34} Js
- c is the speed of light = 3×10^8 m/s
- λ is the wavelength in m/s

OR

$$E = h\nu$$

- ν is frequency of light
- As speed = frequency x wavelength

❖ $1\text{eV} = 1.6 \times 10^{-19} \text{ C} = 1.6 \times 10^{-19} \text{ J}$

❖ THE ATOM:

- A central nucleus contains positively charged particles called protons.
- The nucleus also contains particles having no charge, neutrons
- Mass proton = mass neutron = 1.67×10^{-27} kg
- Orbiting around the nucleus are negatively charged particles called electrons.
- Mass electron = 9.1×10^{-31} kg
- making each of protons and neutrons roughly 1800 times more massive than electrons.
- Most mass is in nucleus
- Protons = atomic number
- Differing numbers of neutrons in an atom give us so-called isotopes of an element.

❖ The Bohr Model of an Atom:

- The essential features of the Bohr model are a central nucleus with orbiting electrons
- electrons orbit at fixed distances from the nucleus
- electrons may jump to **higher** orbits if they **absorb** a quanta of energy exactly equal to the difference in energy between the two orbits
- similarly **release** a quanta of energy if the electron **drops** back down to a lower orbit

❖ PROBLEMS:

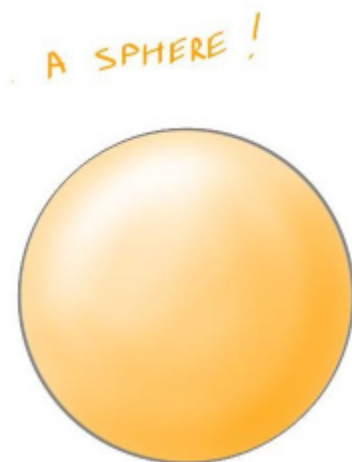
- It only allows calculations of atoms with one electron.
- That is, hydrogen H, a helium ion, or a doubly ionized lithium ion
- not being able to predict line splitting experiments, where closely spaced energy levels were revealed within the orbits further away from the nucleus than the first orbit.

❖ QUANTUM-MECHANICAL MODEL OF AN ATOM:

- In this model, to fully describe the energy state of an electron, we must use four quantum numbers
- PRINCIPLE QUANTUM NUMBER:
 - The principal quantum number describes the **size** of the electron orbit.
 - Sometimes you'll see the principal quantum number described with letters instead of numbers.
 - The letters are always upper case and start at K and move along the alphabet from there so the
 - *K shell* is $n=1$,
 - the *L shell* is $n=2$,
 - the *M shell* is $n=3$, and so on.
- ANGULAR MOMENTUM NUMBER:
 - describes the **shape** of the electron orbital
 - the angular momentum quantum number can have any value ranging from zero to one less than the principal quantum number, that is
 - $\ell=0,1,2,\dots n-1..$
 - $\ell=0$ is the *s subshell*,
 - $\ell=1$ is the *p subshell*,
 - $\ell=2$ is the *d sub-shell*, and

- $\ell=3$ is the *f subshell*.

➤ S-subshell:



➤ P-subshell:



❖ MAGNETIC QUANTUM NUMBER:

- The magnetic quantum number describes how many different ways each subshell can be **orientated**.
- Each of the unique orientations is called an *orbital*.
- These are twice the angular momentum quantum number plus one and are written as integers ranging from the negative to the positive value of l
- For example, for the *p* subshell, or $\ell = 1$, there are three orbitals and the magnetic quantum number could be -1, 0, or 1.
- Within each of these orbitals, or any orbital for that fact, there may be a maximum of two electrons.

- These electrons are distinguished from one another by the spin quantum number.

❖ The Spin Quantum Number:

- The spin quantum number reflects the slightly different energy level for two electrons within a specific orbital.
- The values of the spin quantum number are either positive or negative one half

❖ MAGNITUDES OF ELECTRON ENERGY LEVEL:

- at this point that the electron shell closest to the nucleus, having the **highest** value of **energy** ($n=1$) **s subshell**



Figure 5. A common sketch used to describe and memorize the general rule for the relative energy levels of subshells. The shells and subshells are first drawn out using numbers for the principal quantum number and letters (s, p, d, f) for the angular momentum quantum number. Leftwards and downwards arrows are then drawn through these subshell labels, showing the order of filling of electrons into isolated atoms.

❖ ELECTRON CONFIGURATION:

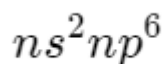
- Carbon: $1s^2 2s^2 2p^2$
- Ca: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
- Titanium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
- Titanium $2+$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

➤ EXCEPTIONS;

- Chromium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
- Copper: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

❖ OCTET STABILITY:

Inert gasses, in fact what makes them inert or unreactive, is that their electron configurations are very stable. This stable configuration involves eight electrons in their outermost shell. Sometimes the so-called octet rule is written as



❖ ATOMIC BONDING:

➤ IONIC BONDING:

- involves a transfer of electrons followed by a subsequent charge attraction between oppositely charged ions.
- charge attraction is general, between all oppositely charged ions.
Furthermore, the charge on an ion is not depleted by its participation in an ionic bond. For this reason, ionic bonding is said to be non-directional.
- We can explain the fact that ionic solids do not conduct electricity by noting the stability of these ions, with all their electrons strongly bound to their respective nuclei.

➤ COVALENT BONDING:

- involves the sharing of electrons.

➤ METALLIC BONDING:

- the sea-of-electrons model, and the band theory of solids.
 - In the sea-of-electrons model the valence electrons are not bound to a specific nucleus, but are instead thought to be free to move around while the nuclei are bound into their lattice positions
 - METALLIC BOND: collection of delocalised electrons holding together the ion cores

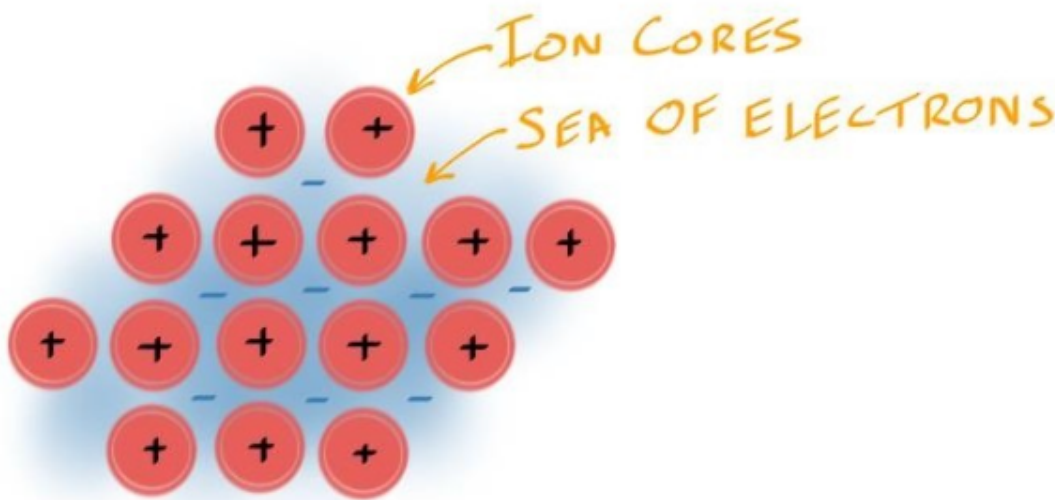


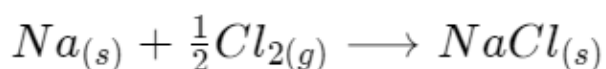
Figure 9. A cartoon depiction of a slice through a metal showing the sea-of-electrons bonding together the ion cores in a lattice.

- The sea-of-electrons model can also help to explain the ductility of most metals.
- If a sufficiently high stress is applied to a metallic crystal, eventually one plane of atoms will move past another
- There is an energy requirement to move the planes, however, it is generally possible for the planes to move past one another since they are always held together by the sea of negatively charged electrons.
- In a ceramic, for one plane to move past another we would need to have similarly charged ions pass through an intermediate position in which they come closer to one another.
- This significantly raises the stress required to move a plane of atoms in a ceramic and typically leads to fracture before deformation.

- When we consider the electrical properties of polymers we can quite easily explain their electrically insulating properties due to the lack of any free electrons; all of the valence electrons are tightly bound in the strong covalent bonds.

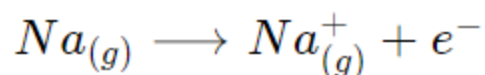
❖ Why does salt form a crystal?

- let's consider the formation of solid crystalline salt from gas phase chlorine and solid sodium:

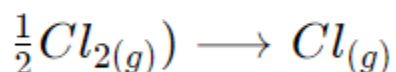


1.

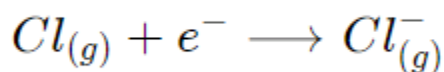
- look at the energy changes here to confirm that this was energetically favorable.
- solid going directly to a gas, without melting first is called sublimation and the so-called *sublimation enthalpy*
- Positive values mean that we need to put energy into our system for the reaction to proceed from left to right.



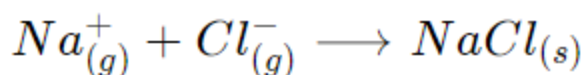
2.



3.



4.



5. crystallization
6. It is energetically favorable for salt to form a crystal at room temperature.

❖ THE BAND THEORY:

- When atoms begin to get atomically close to one another, the electrons in each atom run the risk of having the same energy levels.
- This is called degeneracy
- Instead, as the atoms approach one another, the energy levels begin to spread out slightly so that, for a given electron energy level in an isolated atom, there are two corresponding energy levels when two atoms are close to one another, three for three atoms, four for four atoms, and so on.

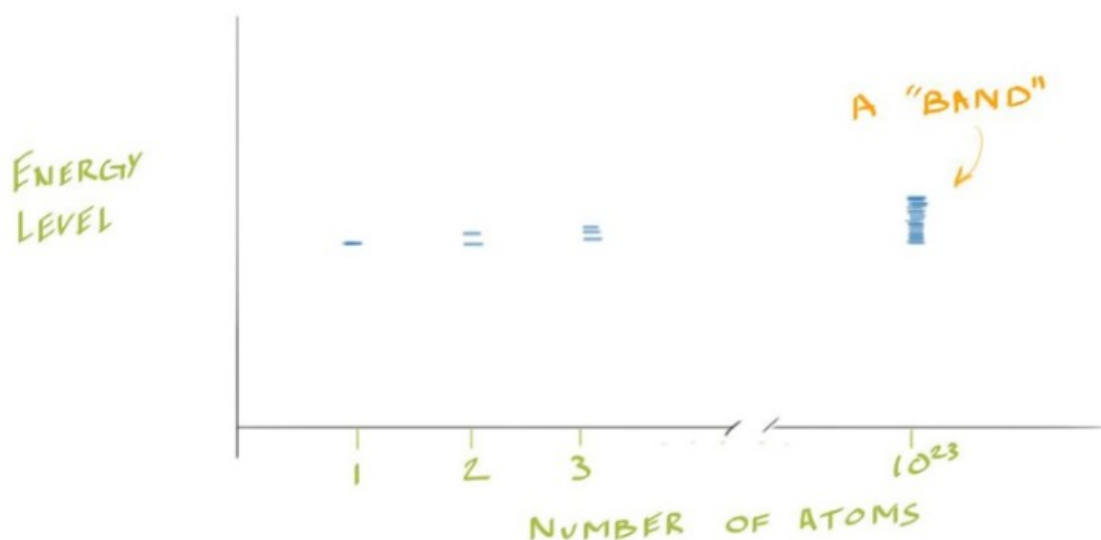
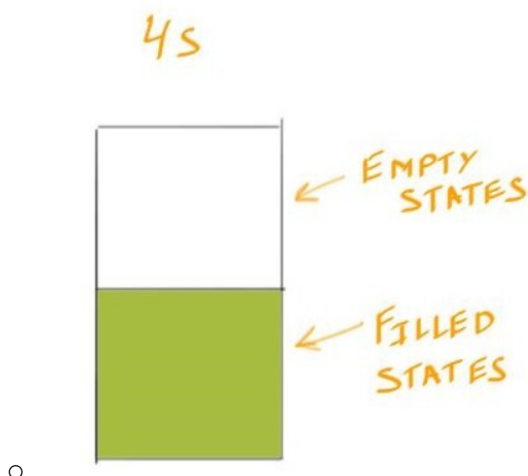


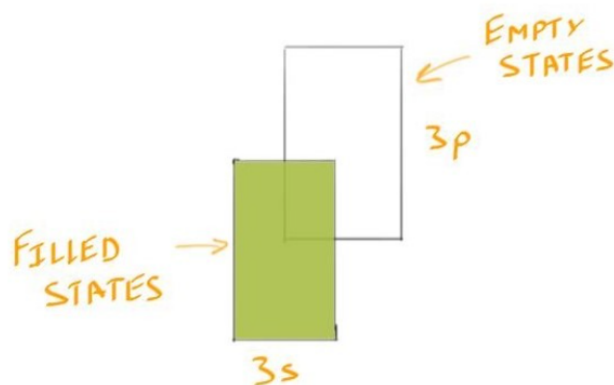
Figure 11. A schematic depiction of a particular energy level in an isolated atom, two atoms, three atoms, and so on up to a massive collection of atoms, as in a solid. The number of energy levels in a solid, for a corresponding single energy level in an isolated atom, is equal to the number of atoms, so that when we have a solid there are so many closely spaced energy levels as to be essentially continuous. We call this a band.

- Bonding in metals like copper:
 - Cu electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
 - When a massive collection of copper atoms come together in a solid,
 - The 4s energy levels spread out into a band, but notice that only half of these states will be filled.
 - 4s can accept two electrons, one spin up and one spin down.
 - Each of these states has a corresponding level in the band structure, even though only half are filled.



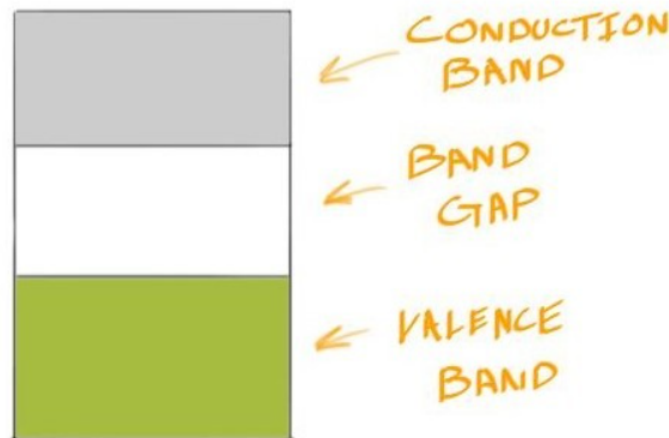
- This means that it is very easy to promote an electron up within the band structure into one of the empty states.

- Bonding in metals like Magnesium:
 - Mg electronic configuration: $1s^2 2s^2 2p^6 3s^2$
 - Even though the 3s band is filled, the energy levels for the 3p states actually spread out enough that they overlap with the 3s levels.
 - Just because the 3p levels are empty doesn't mean that they are not available.



○

- We can see that the unfilled states from the 3p levels provide available energy levels for electrons to be easily promoted into, from the 3s levels.
- Because of the overlap between the 3s and the 3p states, Mg still behaves like a metal
- Bonding in Ceramics and Polymers:
 - ceramics and polymers are electrically insulating
 - Ceramics tend to be held together by ionic bonds and ionic bonds involve electrons being transferred from one atom to another.
 - Remember also that this electron transfer happened so that each atom could achieve a filled valence shell.
 - Since the valence shell is filled there are no electron energy states immediately adjacent to filled states.
 - Also, these electrons are tightly bound to the nucleus, so there are no free electrons.
 - The same is true for polymers, except that the bonding is covalent.
 - Of course, in covalent bonds the valence electrons are shared between two atoms and are bound tightly to them.
 - Both of these types of materials are insulators.
 - Band structure for insulator:



-
- In order for electrical conduction to occur in an insulator, an electron would have to be given enough energy to cross the band gap.
- In such a case we say that it is promoted into the conduction band, where it is free to move.
- The valence band states arise from the valence electrons on the outermost parts of the atoms in the solid, which is why we call it the valence band.

- Bonding in Semiconductors:
 - semiconductors have a band gap that isn't as large as in an insulator.
 - This is important because it means that we can control the flow of electrons in these materials.
 - If a material has a band gap that is larger than 4 eV, we can consider it to be an insulator,
 - and if the band gap is less than 4 eV (but isn't zero) we can consider the material to be a semiconductor.
 - This means that, in many cases, thermal energy or photons of visible light can promote electrons across the band gap in semiconductors.
- DEFINING CONDUCTORS, SEMICONDUCTORS AND INSULATORS

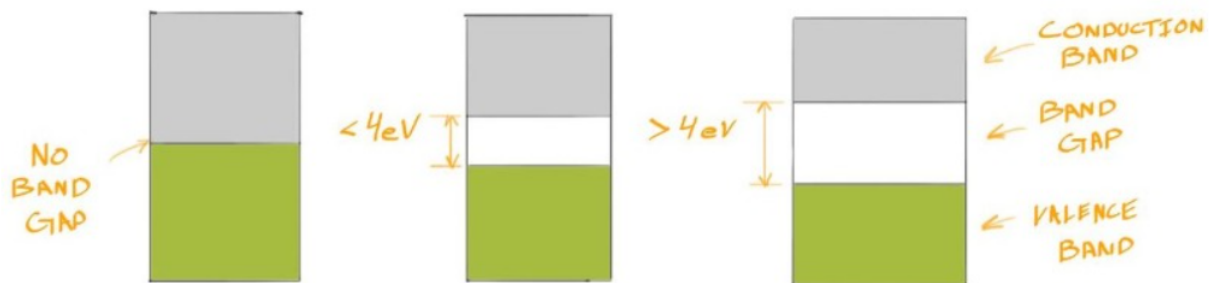


Figure 16. The band structures of conductors, insulators and semiconductors. For our purposes, we'll consider the dividing line between semiconductors and insulators to be 4 eV.

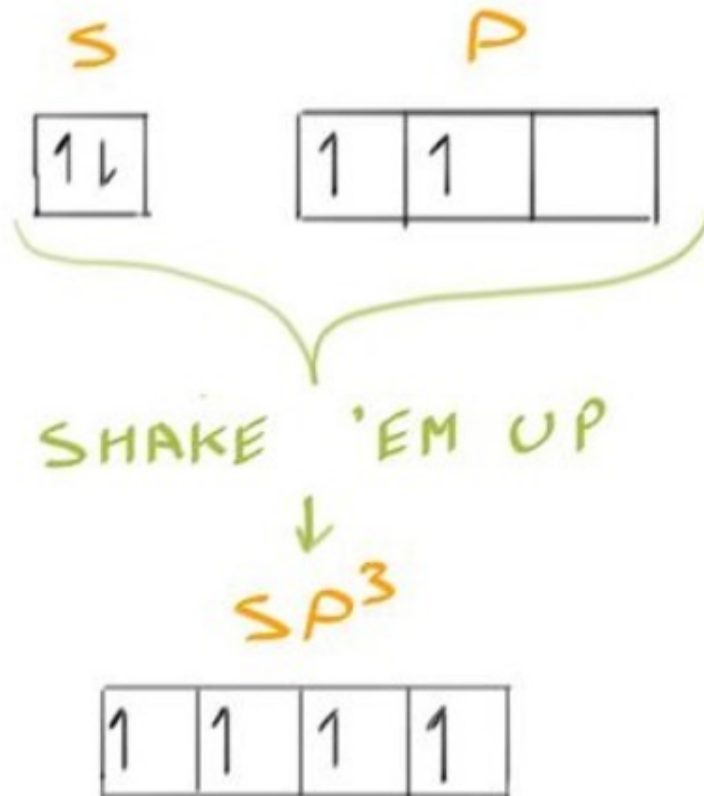
- if the material has a high band gap (greater than 3 eV) the photons will pass through and the material, barring any internal diffraction events, will be optically transparent.
- The visible photons will have no trouble promoting electrons, since there is no band gap in a metal.
- As a result, metals are opaque.
- The electron promotions are temporary and when the electrons drop back down to their lower energy states they re-emit the photons.
- As a result, metals are shiny.

❖ SILICON STRUCTURE:

- $1s^2 2s^2 2p^6 3s^2 3p^2$
- 4 valence electrons in 3s and 3p
- The problem is that we have four electrons at two different energy levels that need to form four identical bonds

● sp^3 hybridization

- let's just take the one s orbital and the 3 p orbitals and blend them together to form four equivalent energy levels,
- We call these new orbitals hybrid orbitals, and since we blended one s with 3 p orbitals we call the resulting orbitals sp^3 hybridized orbitals.



❖ DIAMOND CUBIC

➤ TETRAHEDRAL:

- Coordination number = 4

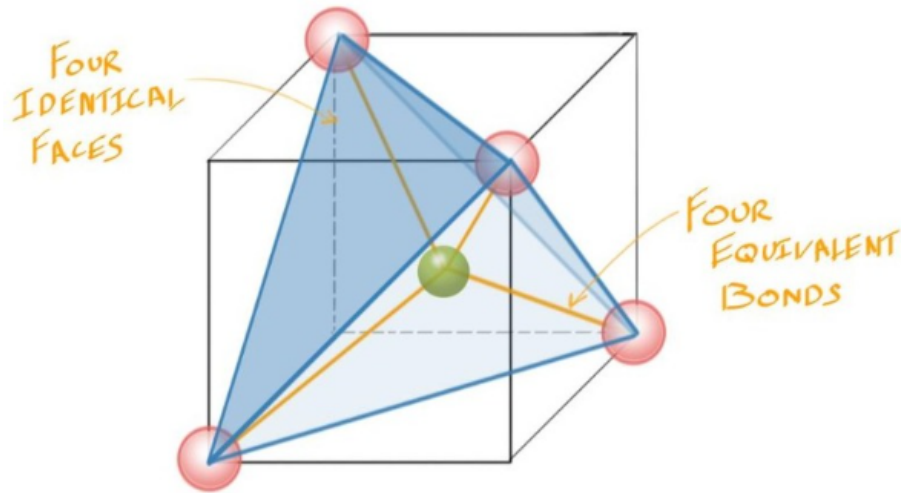


Figure 18. The tetrahedral interstitial site at the centre of a cube. Note that the coordination number is also 4, in addition to the number of faces on the solid formed by this site, however the name comes from the solid geometry, not the coordination number.

- with diamond cubic we will place atoms into the tetrahedral interstitial sites
- we can't fill each of the **eight** available tetrahedral interstitial sites.
- If we did this, we'd have too many bonds on each atom.
- Instead, we fill only half of the sites, and we place them as far apart from each other as possible,
- giving us the alternating arrangement shown with the shaded cubes:

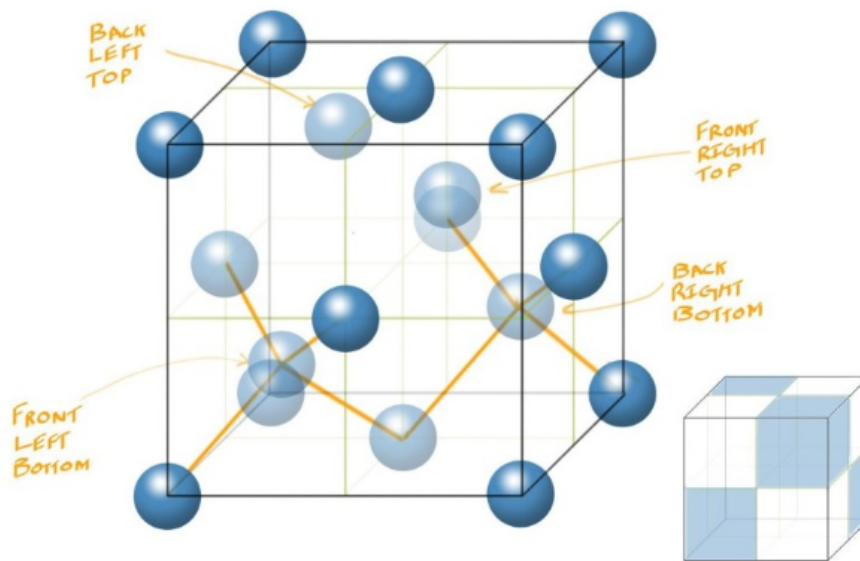


Figure 19. The structure of diamond cubic. This structure can be thought of as an FCC lattice of atoms with the same atoms occupying half of the available tetrahedral interstitial sites, in alternating positions. The alternating positions are illustrated with the shaded "sub-cube" faces in the second cube.

❖ SEMICONDUCTORS:

➤ INTRINSIC SEMICONDUCTORS:

- Everything that is available to conduct electricity comes from the semiconductor itself, not from anything that we add to it.
- when the temperature is raised, or a voltage is applied and we get some promoted electrons.
- When an electron is promoted into the conduction band, it leaves behind a broken bond.
- This broken bond is really a neutral charge, amongst an array of negative charges.
- When everything else is negative, something neutral looks positive and so we often refer to this missing electron as being a positive "thing"
- Since it is a missing electron, it looks a little bit like a hole in the structure, so we call this a **hole**
- if a hole is created for every promoted electron, these features are created in pairs.

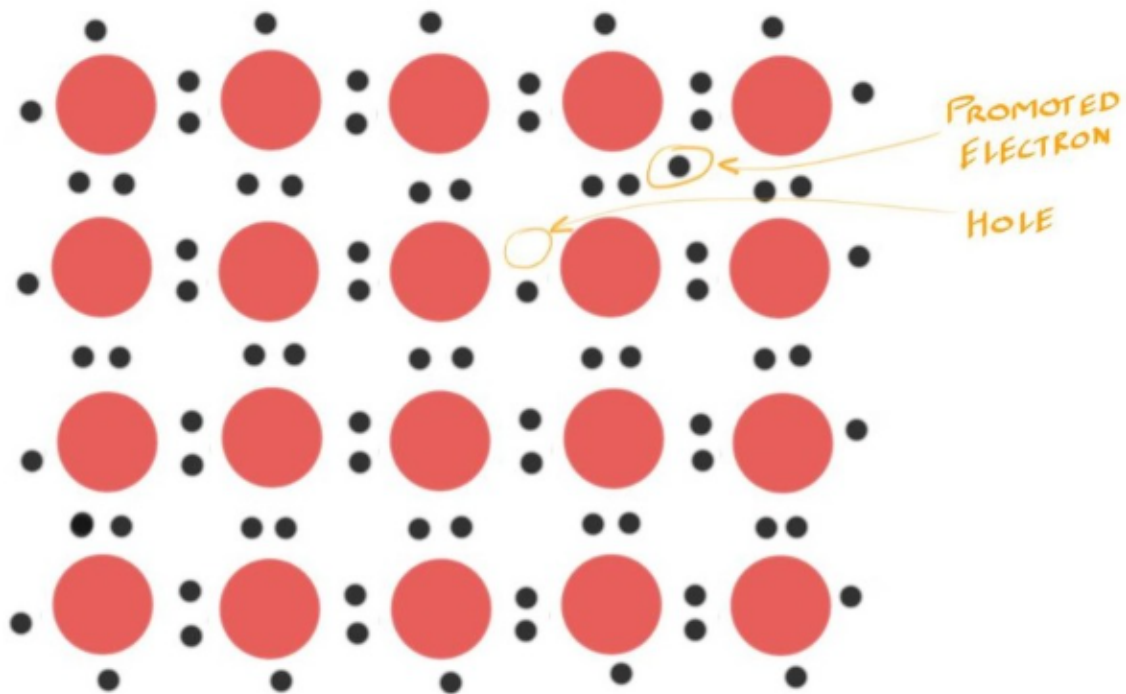


Figure 21. A cartoon depiction of the bonding in crystalline silicon with an electron promoted into the conduction band, leaving behind a broken bond, or a so-called *hole*.

- Since both the electron and the hole can be thought of as charged particles, it is possible for both of them to conduct electricity, just in opposite directions.
- CALCULATING CONDUCTIVITY OF INTRINSIC SEMICONDUCTOR:

$$\sigma = nq\mu_n + pq\mu_p$$

- $n(-ve)$ =concentration of electrons (m^{-3})
- $p(+ve)$ =concentration of hole (m^{-3})
- μ_n electron mobility (m^2/Vs)

- μ_p hole mobility (m^2/Vs)
- q =charge on electrons and holes= $1.6 \times 10^{-19}\text{C}$
- Conductivity unit: ohms/m or S/m

- Since one hole is created for every promoted electron $n=p$

$$\sigma = nq(\mu_n + \mu_p)$$

➤ EXTRINSIC SEMICONDUCTORS:

- When impurities(DOPANTS) are added to semiconductors to control their conductivity
- When we add even a very small amount of dopant to a semiconductor, the conductivity introduced by the dopant overpowers any of the intrinsic semiconductor
- Two ways to dope a semiconductor
 - Extra electrons (n-type semiconductor)
 - Extra holes (p-type semiconductor)

1. Extrinsic n-type semiconductor:

- We need to add impurity atoms (point defects) that bring along with them some extra electrons.
- Example: Silicon semiconductor
 - Knowing that silicon has 4 valence electrons we need only look at atoms to the **right of silicon** in the periodic table to find atoms that will carry along **extra electrons**.
- DOPING SILICON WITH PHOSPHORUS:
 - Phosphorus: $1s^2 2s^2 2p^6 3s^2 3p^3$
 - P has 5 valence electrons and so when added as a point defect in a silicon lattice there will be one extra electron kicking around when four covalent bonds have been formed with the neighboring silicon atoms

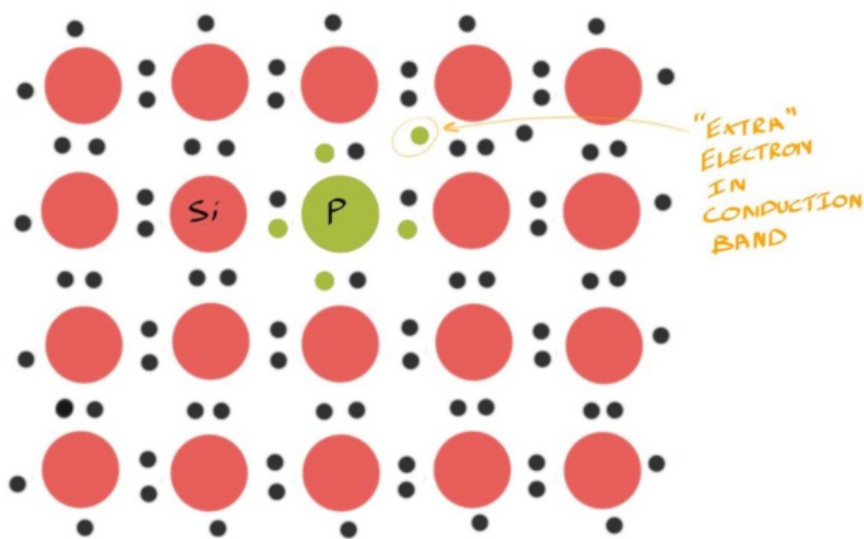


Figure 22. A cartoon depiction of the bonding in crystalline silicon with a phosphorous dopant atom. I've color coded the electrons for conceptual clarity, but remember that all of the electrons are actually equivalent. That is, a silicon electron is the same as a phosphorous electron.

- The extra electron from phosphorus is only weakly bound and can be easily promoted, and made available for conduction.
- That is, only a small amount of energy is required to get this extra electron, donated by the dopant, into the conduction band.
- For this reason, a n-type semiconductor is said to have a **donor energy level** within the band gap, close to the bottom of the conduction band

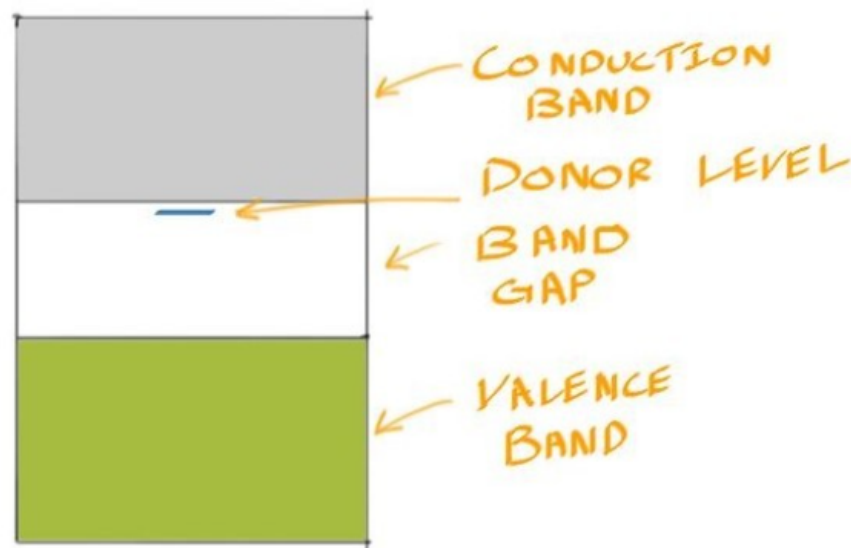


Figure 23. The band diagram for a n-type semiconductor, showing the donor level within the band gap, close to the bottom of the conduction band. Only a small amount of energy is required to free up that electron and get it conducting.

- Since the dopant atoms contribute so many more charge carriers to the semiconductor than are created through intrinsic promotion we can neglect the intrinsic semiconductor and calculate the conductivity of a n-type semiconductor with only the **electron concentration and mobility**:

$$\sigma_{n-type} = nq\mu_n$$

2. Extrinsic p-type semiconductor:

- If we dope with elements to the left of silicon there will be less than 4 valence electrons and there will be broken bonds, or holes introduced.
- For example, if we dope **silicon with boron**, the boron will only bring along 3 valence electrons, $2s^2 2p^1$
- This means that there will be **one broken bond**, or hole for every dopant atom

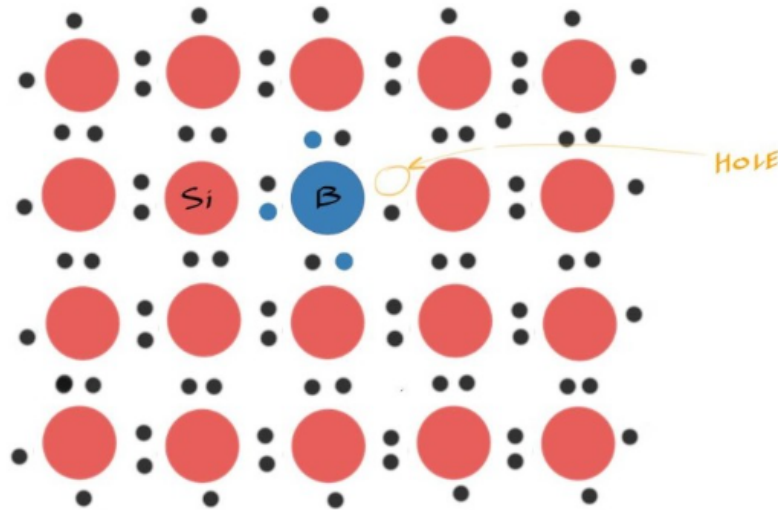


Figure 24. A cartoon depiction of the bonding in crystalline silicon with a boron dopant atom, creating a hole.

- Since the hole is now a place that an electron can be promoted into, we describe the energy level from the hole as an **acceptor level**
- this acceptor level is located within the band gap, close to the top of the valence band

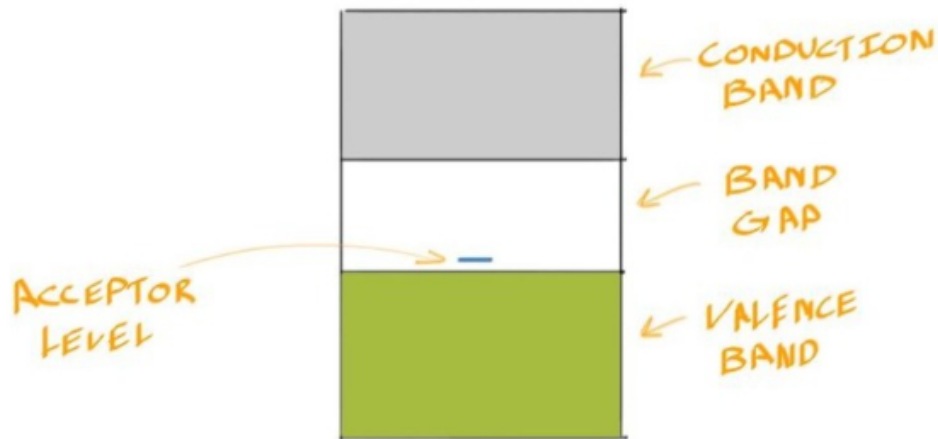


Figure 25. The band diagram for a p-type semiconductor, showing the acceptor level within the band gap, close to the top of the valence band. Only a small amount of energy is required to promote an electron up into that level.

- the conductivity of a p-type semiconductor can be calculated assuming that only **the holes are charge carriers**, neglecting any intrinsic semiconductor.

$$\sigma_{p\text{-type}} = pq\mu_p$$

● Chapter 10: Energy

❖ SECOND LAW OF THERMODYNAMICS:

- The entropy of the Universe increases during any **spontaneous** process.
 - Spontaneous: the process proceeds on its own, without the need for an input of energy.

❖ THE ENTROPY:

- it is a measure of how disordered a system is
- When a system becomes more disordered, its entropy will increase
- An increase in entropy means that the system becomes energetically more stable
- For example, during the thermal decomposition of calcium carbonate (CaCO_3) the entropy of the system increases:

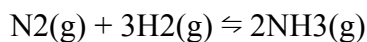


- In this decomposition reaction, a gas molecule (CO_2) is formed
- The CO_2 gas molecule is more disordered than the solid reactant (CaCO_3), as it is constantly moving around
- As a result, the system has become more disordered and there is an increase in entropy
- if the number of gaseous molecules in a reaction changes, there will also be a change in entropy
- The greater the number of gas molecules, the greater the number of ways of arranging them, and thus the greater the entropy
- For example the decomposition of calcium carbonate (CaCO_3)



- The CO_2 gas molecule is more disordered than the solid reactant (CaCO_3) as it can freely move around whereas the particles in CaCO_3 are in fixed positions in which they can only slightly vibrate
- The system has therefore become more disordered and there is an increase in entropy

- Similarly, a decrease in the number of gas molecules results in a decrease in entropy causing the system to become less energetically stable
- For example, the formation of ammonia in the Haber process



- In this case, all of the reactants and products are gasses
- Before the reaction occurs, there are four gas molecules (1 nitrogen and 3 hydrogen molecules) in the reactants
- After the reaction has taken place, there are now only two gas molecules (2 ammonia molecules) in the products
- Since there are fewer molecules of gas in the products, there are fewer ways of arranging the energy of the system over the products
- The system has become more ordered causing a decrease in entropy
- The reactants (N₂ and H₂) are energetically more stable than the product (NH₃)

❖ ENTROPY FORMULA:

$$\Delta S = \frac{q_{rev}}{T} \quad (1)$$

where S is the entropy, q_{rev} is the heat transferred, and T is the *thermodynamic* temperature,

- Rev means that the heat is transferred reversibly.
- the system was at all times in equilibrium.

❖ COMMON ALPHABETS:



❖ SECOND LAW THERMODYNAMICS MATHEMATICAL:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

❖ FIRST LAW THERMODYNAMICS:

- The first law of thermodynamics states that the energy of the universe is constant.
- The change in the internal energy of a system is the sum of the heat transferred and the work done.
- The heat flow is equal to the change in the internal energy of the system plus the PV work done.

$$\Delta U_{sys} = q + w$$

First Law of Thermodynamics

❖ STANDARD STATE:

The most stable form of a pure element at 25°C and 105 Pa.

- STATE FUNCTIONS: a property whose value does not depend on the path taken to reach that specific value. Example: temperature, pressure, density, volume, Gibb's energy, potential energy, enthalpy, **internal energy**, and entropy.
- PATH FUNCTIONS: properties or quantities whose values depend on the transition of a system from the initial state to the final state. The two most common path functions are **heat and work**.

❖ CLOSED VS ISOLATED SYSTEM:

- In an isolated system no heat is exchanged with the surroundings
- In a closed system heat may pass the boundaries.

$$\Delta U = 0 \text{ Isolated System}$$

$$\Delta U = q + w \text{ Closed System}$$

- q is heat transferred into the system
- w is work done on the system
- U is change in internal energy
- IT IS IMPOSSIBLE TO DETERMINE THE ABSOLUTE VALUE OF INTERNAL ENERGY

❖ ENTHALPY

- The enthalpy change is just the heat supplied (or absorbed) by a reaction, when we account for the work done in pushing back the atmosphere.

$$\Delta H = \Delta U + P\Delta V$$

❖ GIBBS ENERGY:

- The Gibbs free energy (G) is the energy change that takes into account both the entropy change of a reaction and the enthalpy change
- The Gibbs equation is:

$$\Delta G_{\square} = \Delta H_{\text{reaction}\square} - T\Delta S_{\text{system}\square}$$

- The units of ΔG_{\square} are in kJ mol⁻¹
- The units of $\Delta H_{\text{reaction}\square}$ are in kJ mol⁻¹
- The units of T are in K
- The units of $\Delta S_{\text{system}\square}$ are in J K⁻¹ mol⁻¹ (and must therefore be converted to kJ K⁻¹ mol⁻¹ by dividing by 1000)

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

$$\Delta S_{\text{surroundings}} = \frac{q_{\text{surroundings}}}{T}$$

$$q_{\text{surroundings}} = -q_{\text{system}}$$

$$\Delta S_{\text{surroundings}} = \frac{-q_{\text{system}}}{T}$$

$$\Delta S_{\text{system}} + \frac{-q_{\text{system}}}{T} > 0$$

$$T\Delta S_{\text{system}} - q_{\text{system}} > 0$$

$$T\Delta S_{system} - \Delta H_{system} > 0$$

$$\Delta H_{system} - T\Delta S_{system} < 0$$

This means that when Gibbs energy decreases, it is just another way of saying that the entropy

increased, specifically $\Delta G = -T\Delta S_{universe}$.

- **-ve G and +ve S means spontaneous**
- A reaction with a **positive** enthalpy change and a **positive** entropy change will be spontaneous under **high** temp
- A reaction with a **positive** enthalpy change and a **negative** entropy change will **NEVER** be spontaneous
- A reaction with a **negative** enthalpy change and a **negative** entropy change will be spontaneous under **low** temp