INTRODUCTION TO SOLID STATE CHEMISTRY

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Introduction to Solid State Chemistry

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Licensing

A detailed breakdown of this resource's licensing can be found in ***Back Matter/Detailed Licensing****.*

CHAPTER OVERVIEW

1: Lectures

Introduction to Solid State Chemistry is a first-year single-semester college course on the principles of chemistry. This unique and popular course satisfies MIT’s general chemistry degree requirement, with an emphasis on solid-state materials and their application to engineering systems.

1.1: Atomic and Electronic Structure
1.2: Chemical Bonding
1.3: Bonding in Metals, Semiconductors and Insulators – Band Structure
1.4: The Nature of Crystalline Solids
1.5: X-rays and X-ray Diffraction
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1.10: Phase Equilibria and Phase Diagrams

1.1: Atomic and Electronic Structure

1.1.1: ATOMS

The familiar model of an atom is that of a small nucleus composed of protons and neutrons surrounded by rapidly moving electrons. Typically, the atomic diameter is on the order of $10^{-10}\ \mathrm{m}$ while that of the nucleus is on the order of $10^{-15}\ \mathrm{m}$. Protons and neutrons have about the same mass (1.00728 and 1.00867 amu respectively) and each is about 1800 times as heavy as an electron. A neutron is electrically neutral, but a proton has a positive charge $\left(+1.6 \times 10^{-19}\right.$ coulomb* $\left.\right)$ which is exactly the opposite of the negative charge of an electron. In a neutral atom, the number of electrons around the nucleus equals the number of protons in the nucleus.

The number of protons in the nucleus (the "atomic number", Z) characterizes a chemical element. Atoms of a given element all have the same number of protons, yet may have different masses. The atomic mass number of an atom, A, is given by $A=Z+N$, where N is the number of neutrons in the nucleus. Since an element is characterized solely by Z, it follows that atoms of a given chemical element may have a varying number of neutrons. Subspecies of chemical elements with the same Z but differing N and A are called *isotopes*. The atomic weight of an element is the weighted average of the atomic masses of the various naturally occurring isotopes of the element, and the atomic weight scale is based on a value of exactly 12, after the carbon isotope that has an atomic mass number of 12.

*****

Generally adopted International Unit System.

1.1.2: NUCLEI

The nucleus of an atom weighs less than the sum of the weights of its isolated component particles. The difference between the actual mass and that of the components is called the mass defect. The mass defect, $\Delta \mathrm{m}$, is related to the binding energy within the nucleus, $\Delta \mathrm{E}$ (in Joules), through Einstein's equation:

$$\Delta \mathrm{E}=\Delta \mathrm{mc}^2 \tag{1.1.1}$$

where c is the velocity of light (in $\mathrm{m} \cdot \mathrm{s}^{-1}$) and $\Delta \mathrm{m}$ is the mass defect (in kg). The nuclear forces which bind protons and neutrons together are strong, and the binding energy per nuclear particle (nucleon) amounts to about 1.4×10^{-12} Joules. The greatest nuclear binding energy is found in nuclei of medium atomic number (such as Fe) where N is approximately equal to Z. For nuclei of larger atomic number, such as uranium, N is about equal to $1.5 \mathrm{Z}$, and the binding energy per nucleon is less. As a consequence of this decreased nuclear stability, some isotopes (of uranium, for example) are unstable. That is, if the uranium isotope, ${}_{92}U^{235}(Z=92, A=235)$, is bombarded with neutrons, the following reaction can take place:

$$ {}^{235}_{92}\mathrm{U}+{}^1\mathrm{n} \longrightarrow {}^{94}_{39}\mathrm{Y}+{}^{140}_{53}\mathrm{I}+2\,{}^1\mathrm{n} \tag{1.1.2}$$

Here the reaction products are smaller nuclei of increased stability. (In the above convention, subscripts indicate the atomic number and the superscripts the mass number.) Notice that one incident neutron generates fission products including two neutrons - the basis for chain reactions in nuclear reactors and nuclear explosions.

Heavy nuclei (even light nuclei) which have an unfavorable ratio in the number of protons and neutrons can spontaneously *decay* by the emission of α particles (helium ions) or β particles (electrons). These nuclei are referred to as *radioactive*. The rate at which the decay of such unstable nuclei takes place varies greatly and is indicated by the *half-life* of the material. In one half-life period, half of the unstable nuclei will have emitted radiation and thus will have changed their character (atomic number). In two half-life periods, only $1/4$ of the nuclei will have survived. In three half-lives, only $1/8$ of the original nuclei remain, etc. For example, the half-life of gamma-emitting "radio" cobalt, ${}_{27}\mathrm{Co}^{60}$ (used for X-ray therapy), is 5.3 years, whereas that of radioactive ${}_6\mathrm{C}^{14}$ is 5700 years. (Much more radiation is emitted per second by a given number of Co^{60} atoms than by the same number of C^{14} atoms.)

1.1.3: EXTRA-NUCLEAR ELECTRONS IN ATOMS

The first atomic theory in quantitative agreement with some experimentally determined facts was proposed in 1913 by Niels Bohr. He postulated (for atomic hydrogen) that:

- The (extra-nuclear) electron can assume only distinct (quantized) energy levels or states.

- In such energy levels, the electrons in motion will not radiate (loose) energy; on changing energy levels, radiation equivalent to the energy difference between the levels is involved.

  $\mathrm{E}_{\mathrm{rad}}=\mathrm{E}_2-\mathrm{E}_1=h v$

- The stable states of the atom involve motion of the electrons in circular orbits.
- The angular momentum of electrons in orbit (mvr) is an integral number of $\mathrm{h}/2\pi$ units:

  $\mathrm{mvr}=\mathrm{n}\dfrac{\mathrm{h}}{2\pi}$

- Newtonian mechanics applies to orbiting electrons.

A pictoral view of the Bohr atomic model visualizes electrons orbiting at a velocity (v) in well-defined spherical orbitals of radius (r) around the nucleus. The angular momentum of the orbiting electrons can, as stated above, only assume certain values of $n \times h/2\pi$ where n (called the principal quantum number) can assume any positive integer value, i.e.1, 2, 3, 4, etc. to infinity (fig. 1).

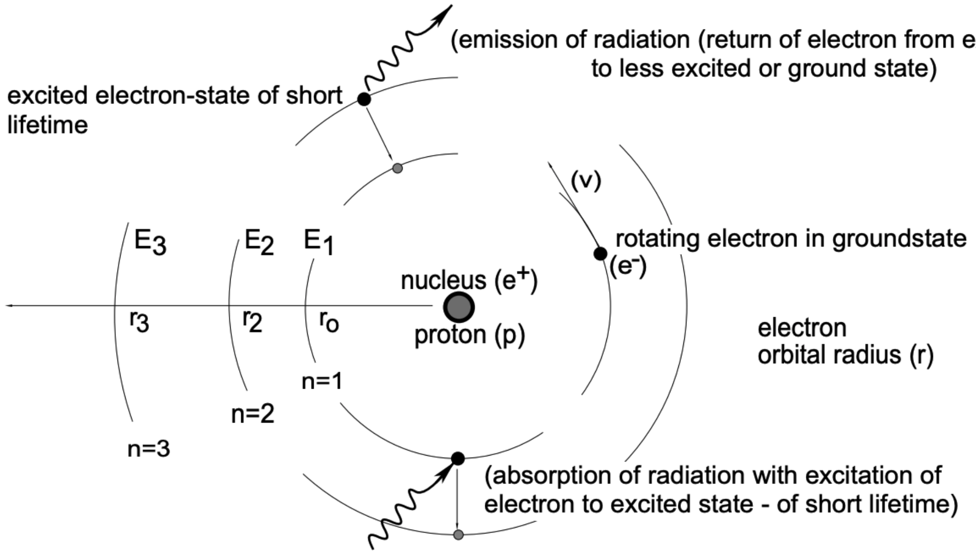


Figure 1 The Hydrogen Atom According to Bohr.

1.1.3.1: Hydrogen Atom

Assuming coulombic interaction and the applicability of Newtonian mechanics, the following values may be directly obtained for the hydrogen atom:

- The radius of an electron orbit (spherical) in hydrogen is given by:

  $$r_n=\frac{n^2 h^2 \varepsilon_0}{\pi m^2} \quad (n=1,2,3,4, \text{ etc. })$$
  $$r_n=n^2 \times \text{ constant } =n^2\left(0.529 \times 10^{-10}\right) m$$

  It can be seen that the smallest electron orbit in hydrogen - the stable orbit - is given for $n=1$ at $r_0=0.529$Å. It is also seen that r increases with n^2 $\left(r=n^2 r_0\right)$.

- The energy of an orbiting electron characterized by the principal quantum number (n) is given as:

  $$E_n=-\frac{1}{n^2} \times \frac{m e^4}{8 h^2 \varepsilon_0^2}=-\frac{1}{n^2} \times \text{ constant [Joule]}$$

  This relationship indicates that electron orbits with increasing principal quantum number (n) assume decreasing negative values $\left(1/n^2\right)$ with the limiting value $(n \rightarrow \infty\ )$ being zero. For convenience, it is frequently customary to express electronic energies in terms of *wave numbers* $(\bar{v})$ with the units of $\left[\mathrm{m}^{-1}\right]$. This conversion may readily be made since $E = hv$. Thus:

$$\bar{v} = \frac{1}{\lambda} = -\frac{1}{n^2} \times \frac{me^4}{8h^3c\varepsilon_0^2}\left[m^{-1}\right]$$

Upon substituting numerical values for all the constants, we obtain:

$$\bar{v} = -\frac{10973500}{n^2} = -\frac{1}{n^2} \times 10973500\left[\mathrm{~m}^{-1}\right]$$

(where n is again the principal quantum number which may assume the values 1,2,3,4, etc. The value of 10973500 is referred to as the Rydberg constant (R; also R_{H} and R_{∞}) to honor the man who obtained its value from spectroscopic studies prior to the establishment of the Bohr model.)

The energy changes associated with electronic transitions and the accompanying emission of radiation (or absorption of radiation) may simply be calculated as follows:

$$\text{Emission } = \Delta\mathrm{E} = \left(\mathrm{E}_{\mathrm{n}_1} - \mathrm{E}_{\mathrm{n}_2}\right) = hv$$

Here n_2 is the principal quantum number of the outer orbit and n_1 is that of the inner orbit. In terms of $\bar{v}$, the wave number, we obtain for emission of radiation:

$$\bar{v} = \left[\left[-\frac{10973500}{n_1^2}\right] - \left[-\frac{10973500}{n_2^2}\right]\right]$$

or

$$\begin{aligned}
&\Delta\mathrm{E} = 10973500\left[\frac{1}{\mathrm{n}_2^2} - \frac{1}{\mathrm{n}_1^2}\right] \times \mathrm{hc} \\
&\Delta\mathrm{E} = \mathrm{R}\left(\frac{1}{\mathrm{n}_2^2} - \frac{1}{\mathrm{n}_1^2}\right] \mathrm{xcc} \\
&\Delta\mathrm{E} = 2.1798 \times 10^{-18}\left[\frac{1}{\mathrm{n}_2^2} - \frac{1}{\mathrm{n}_1^2}\right] \mathrm{J} \\
&\Delta\mathrm{E} = \mathrm{E}_{\mathrm{n}_2} - \mathrm{E}_{\mathrm{n}_1} \\
&\text{Absorption} = \Delta\mathrm{E} = \mathrm{E}_{\mathrm{n}_2} - \mathrm{E}_{\mathrm{n}_1} \\
&\bar{v} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right]
\end{aligned}$$

Electronic transitions (fig. 2) are conveniently represented in so-called term schemes.

1.1.3.2: Multi-Electron Systems

The limitations of the Bohr atom became apparent soon after its establishment. For example, the uranium atom would require 92 electronic orbits and it would have to assume a size which is incompatible with the experimental facts. The first modifications of the Bohr model were made by Sommerfeld, who introduced additional quantum conditions: Taking into account that individual sharp spectral lines split into several lines (of slightly differing λ) if light emission takes place in a magnetic field (Zeeman effect), the following picture emerged from the Bohr atom: electronic spherical orbits (shells)

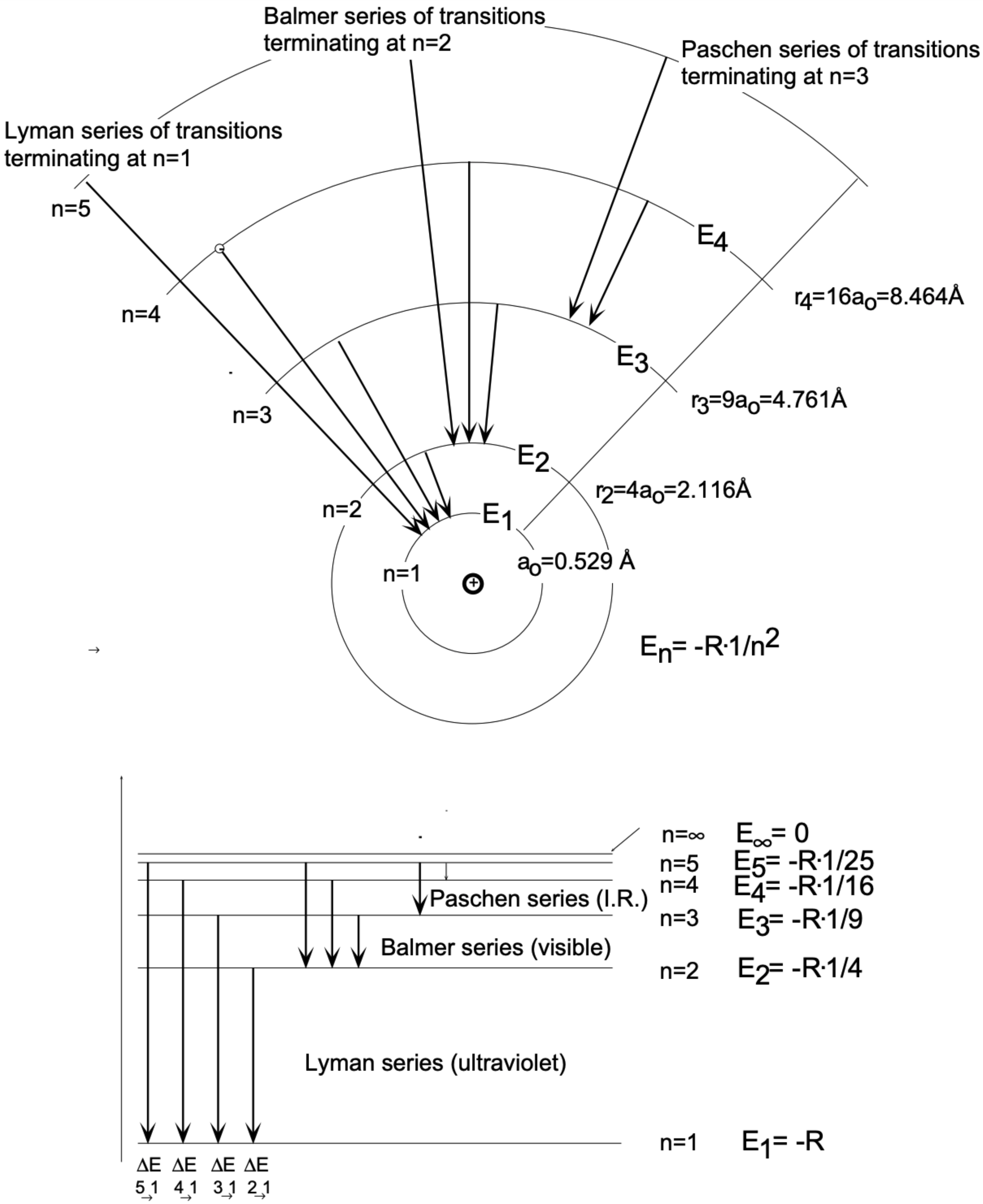


Figure 2 Electron Transitions and Related Optical Spectra in Atomic Hydrogen

may have suborbitals (orbits) which are elliptical of varying eccentricity - controlled by an additional quantum number, the orbital quantum number (I). The eccentric orbitals may assume only particular spatial orientations controlled by the magnetic number (m), in an external magnetic field. The observed magnetic behavior of the elements required an additional quantization (Uhlenbeck) - the introduction of the spin quantum number (s).

According to the Bohr-Sommerfeld quantum theory, electrons move about the nucleus of an atom in well-defined orbits, each of which is characterized by four numbers, called *quantum numbers*. An electron moving in an orbit close to the nucleus has a larger (negative) energy than one in an outer orbit. Energy is therefore necessary to move an electron from an inner to an outer orbit (with smaller negative energy). Conversely, energy is released (as radiation) during the transition of an electron from an outer to an inner orbit. The (electromagnetic) radiation released consists of discrete entities or quanta, which are called *photons*. The energy of emitted photons is given by the difference in energy between the two orbits involved and is related to the frequency, v, or the wavelength, λ, of the electromagnetic radiation by:

$$\mathrm{E}_{\text{photon}}=\mathrm{E}_2-\mathrm{E}_1=\mathrm{hv}=\mathrm{h}(\mathrm{c}/\lambda) \quad (\mathrm{c}=\lambda v)$$

where h is called the Planck's constant, E_2 and E_1 are the energies of the outer and inner orbits, respectively, and c is the velocity of light. Through (spectroscopic) observations of the frequencies or wavelengths of radiation emitted by an excited atom (atom with an excited electron), the differences of electron energy levels can be determined. Figure 1 shows such energy levels obtained from measurements of the wavelengths of radiation emitted by atomic hydrogen excited electrically in a gas discharge tube.

To specify the spatial location and energies of electrons in an atom requires the use of four *quantum numbers*. The "principal quantum number", (n), determines the size of the shell in which a particular electron orbits around the nucleus; it also largely determines its energy. The value of n is restricted to integral values: $n=1,2,3$ and so forth. A value of $n=1$ signifies that the electron exists in the lowest energy state and its *orbit* is in the innermost allowed *shell*, as close to the nucleus as possible. Successively higher energy states are represented by $n=2,3$, etc. It should thus be clear that the principal quantum number of the outermost orbiting electron determines, in principle, the size of a given atom. For convenience, letters are frequently used to characterize the electronic shells of $n=1,2,3,4$, etc. In letter notation:

$$\begin{aligned}&\mathrm{n}=1=\mathrm{K}\text{ shell}\\&\mathrm{n}=2=\mathrm{L}\text{ shell}\\&\mathrm{n}=3=\mathrm{M}\text{ shell}\\&\text{etc.}\end{aligned}$$

The second quantum number, (I), is referred to as the "orbital" or "azimuthal quantum number". It specifies the angular momentum of orbiting electrons and, to a minor extent, their energy. "I" can only assume integral values ranging from $I=0$ to $I=(n-1)$ (where n is the principal quantum number). Accordingly, for $n=1$ (the K shell), I can only assume a value of 0. For $n=2$, either $I=0$ or $I=1$ is possible, etc. For convenience again, letters are used to specify the electronic state (orbit) in a given shell (characterized by n) corresponding to the second quantum number:

$$\begin{aligned}&I=0=\mathrm{s}\ (\text{orbit})\\&I=1=\mathrm{p}\ (\text{orbit})\\&I=2=\mathrm{d}\ (\text{orbit})\\&I=3=\mathrm{f}\ (\text{orbit})\end{aligned}$$

An electron with $I=0$ is in an s-quantum state (in short, it is an s-electron), one with $I=1$ is in a p-state, etc. Thus, an electron with a principal quantum number $n=3$ and an orbital quantum number $I=1$ is called a $3p$ electron (the electron in the M shell is in a p orbital).

The third quantum number, (m), called the "magnetic quantum number", controls the number of allowed spatial orientations ("degeneracy") of each orbit characterized by I in a given shell [characterized by (n)]. (Degenerate states are of identical energy. The "degeneracy" disappears in the presence of a magnetic field where different spatial orientation of orbits assume different energy values.) The total number of allowed orbital orientations for any orbital characterized by l is $(2I+1)$, corresponding to m values of I, $(I-1),(I-2),\ldots,0,-1,-2,\ldots,-l$. An electronic state with $I=0$ necessarily has only $\mathrm{m}=0$ and thus has no directional orientation in space; it is a spherical orbit. On the other hand, a p-state $(I=1)$ allows m values of $-1,0,+1$. The resulting three possible orientations are perpendicular to one another (as shown in fig. 4).

The first three quantum numbers $(\mathrm{n}, /$ and $\mathrm{m})$ define atomic electron orbitals. They are related respectively to the size, shape, and spatial orientation of the orbital. The fourth quantum number, s, (called the "electron spin quantum number"), can be interpreted as determining for an orbiting electron the direction of electronic spin around its own axis. " s " can assume values of $+1/2$ (parallel spin) and $-1/2$ (anti-parallel spin). For notational purposes, a positive s is conveniently represented as ↑ and a negative s as ↓.

We may now summarize our findings about the electronic states in atoms. Any electron in an atom is defined by four quantum numbers, viz.:

- The principal quantum number (n), which may have any positive integral value except zero. (In practice, because of the instability of heavy nuclei, atoms containing electrons with n values greater than 7 are unknown.)
- The orbital or azimuthal quantum number (I), which is an integer and may have any positive value less than n, including zero.

$$0 \leq I < n$$

- The magnetic quantum number (m), which is also an integer and may have any positive or negative value equal or less than I, including zero.

$$-l \leq m \leq +l$$

- The spin quantum number (s) which may only assume one of two values, namely $+1/2$ and $-1/2$.

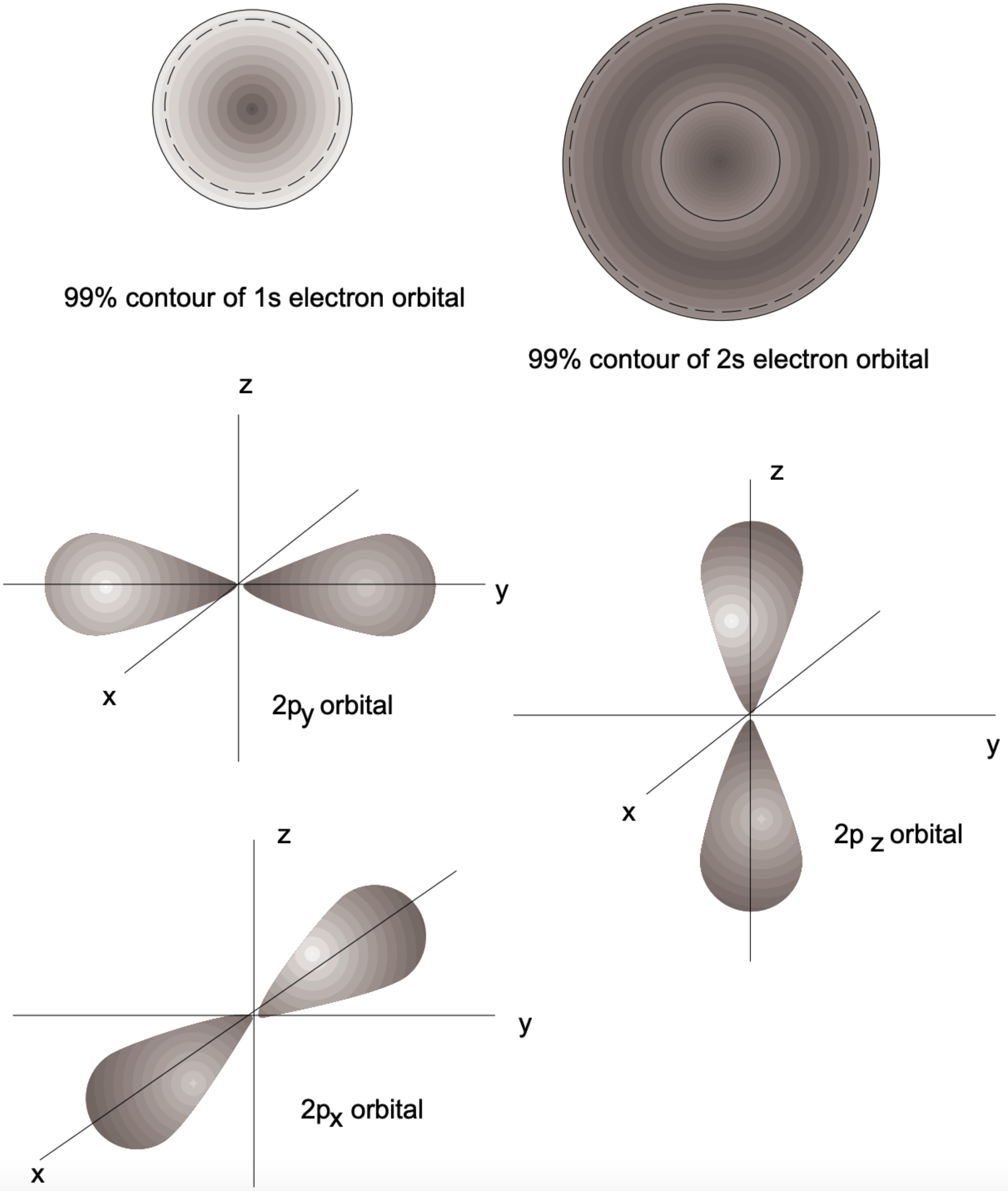
$$s = \pm 1/2$$

An important law enables us to make use of these quantum rules for the characterization of electronic states in multi-electron systems: the *Pauli Exclusion Principle*. It states that in any atom no two electrons may have the same four quantum numbers. From this principle it follows that each electronic orbital can accommodate at most two electrons differing by their spin quantum number which will be $+1/2$ for one electron and $-1/2$ for the other electron. (The Pauli principle is based on the fact that the separate existence of any electron depends upon its non-destruction by interference, i.e. on its wave nature.)

A further useful fact that generally simplifies understanding electronic structures is that (with exceptions stated shortly) *the quantum states for electrons follow the rule (Aufbau Principle) that the lowest* m, *I and* n *numbers, consistent with Pauli's exclusion principle, are selected first by electrons in multi-electron atoms.* (For the spin quantum numbers, the $+1/2$ value is given priority over the $-1/2$ value.) Applicability of this rule is restricted to systems in which the orbitals, defined by a selected set of quantum numbers with lowest possible numerical value, correspond to orbitals of lowest energy since in all instances the lowest energy levels are filled first. The build-up of the electronic states of an atom is obtained by placement of the electrons first in the orbitals of lowest energy (the *aufbau principle* or "construction principle").

Wave mechanics (introduced by Schrödinger), unlike the quantum theory based on a planetary model, asserts that an electron in an atom cannot be considered as a particle having an orbit with a definite radius. Instead, there is a *probability* of an electron being at certain spatial positions. Hence, the location of an electron is best described in terms of its *probability density distribution*, which is sometimes called an *electron cloud*. The spatial symmetry of the probability distribution depends upon the electronic state. The electron cloud is spherically symmetric for s-electrons, but more complicated for electrons in a p-state. Examples of these distributions are shown in fig. 3 for 1 s and $2p$ electrons.

Figure 3 Conclusions on Electron Orbital Shapes based on Wave Mechanics:



99% contour of 1s electron orbital

99% contour of 2s electron orbital

$2p_y$ orbital

$2p_z$ orbital

$2p_x$ orbital

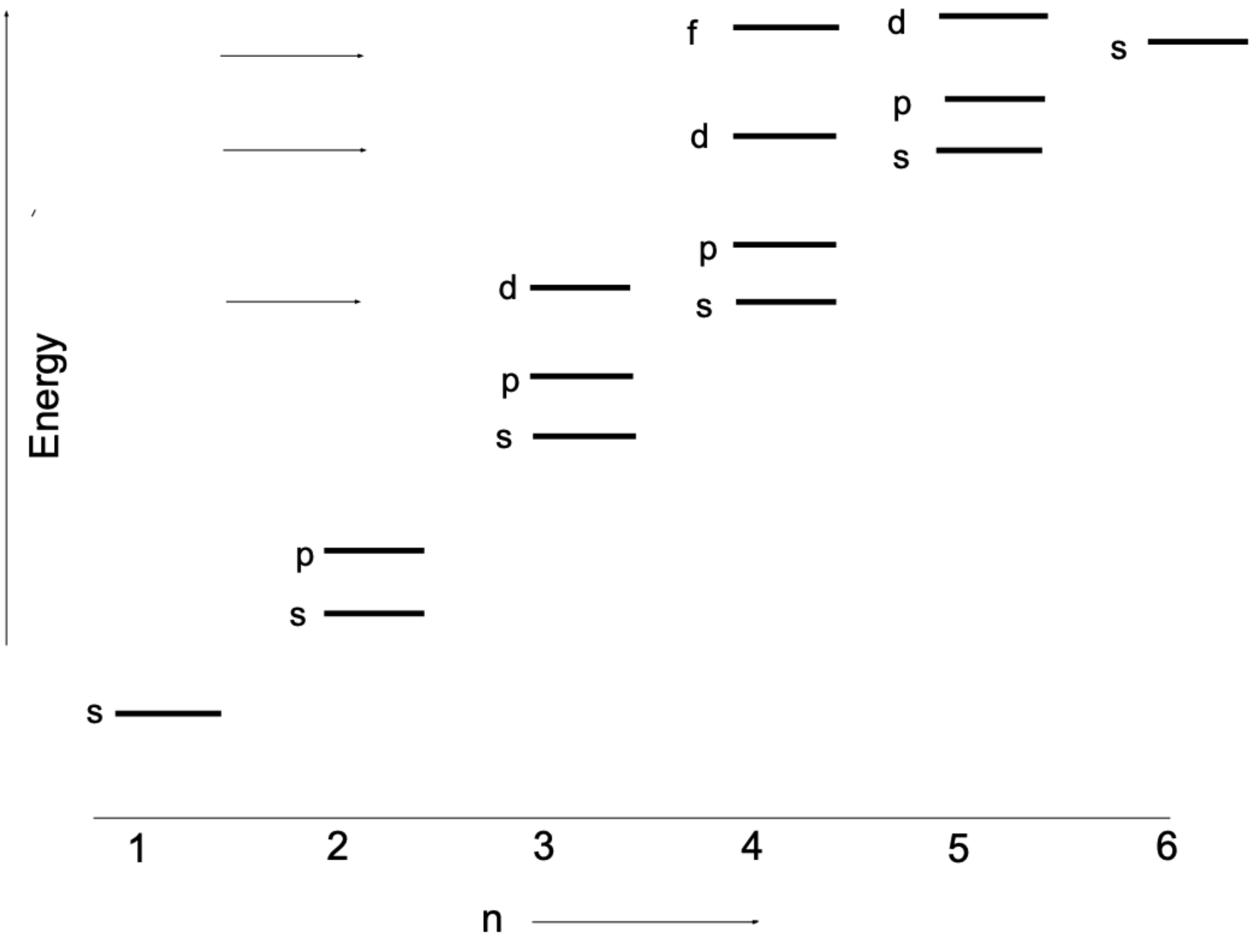
1.1.4: ENERGY LEVELS AND THE AUFBAU PRINCIPLE

Consider the atom of an element containing one extra-nuclear electron: hydrogen; for electro-neutrality the charge on the nucleus must be $+1$. This orbiting electron (in the ground state - the lowest possible, most stable state) will have the lowest available quantum numbers in n, I and m. That is, $n=1$; hence $I=0$ and $m=0$; also, $s=+1/2$.

In the two-electron atom helium, one electron will have the same quantum numbers as the electron in hydrogen and the other electron will have quantum numbers $n=1, I=0$, $m=0$ and $s=-1/2$. The element of atomic number 3 (lithium) will have two electrons with the same quantum numbers as the helium electrons, plus one electron with the quantum numbers $n=2, I=0, m=0, s=+1/2$. [Note that n must be 2 for the third electron since states such as $(n=1, I=1)$ or $(n=1, I=0, m=1)$ or $(n=1, I=0, m=-1)$ are not allowed. Similarly, the quantum numbers for the additional electron in beryllium (atomic number 4) are $n=2, I=0, m=0, s=-1/2$. The next electron for boron (atomic number 5) has the values $n=2, I=1, m=-1, s=+1/2$, and so on.

In applying the aufbau principle to the orbital filling with increasing atomic number we have thus far inferred the tendency of the energies of electrons to follow in the same order as the principal quantum numbers; that is, successive electron shells are filled with increasing Z. This concept does not hold in all instances. For example, electrons with the quantum numbers $n=3, I=2$ (and various m values) are of higher energy than those with $n=4, I=0$. Other *inversions* occur with $n=4$ and higher. These apparent irregularities in the aufbau principle, the result of an energetic overlap of orbitals in successive shells, lead to partial shell fillings and the appearance of groups of so-called transition elements. The groups are characterized (with minor exceptions) by identical outermost electron shell configurations and therefore do not exhibit, with increasing atomic number, the (expected) change in properties observed on regular shell filling for elements 2-18. (In the transition elements, with increasing atomic number the electrons are accommodated in lower lying shells which remained empty because of the above mentioned energy overlap of their orbitals.) The energy levels of the various orbitals in shells with increasing n are schematically indicated in fig. 4.

Another factor in the application of the aufbau principle is Hund's Rule which states that in atoms the electrons tend at first to fill up given orbitals (m levels) singly (with unpaired spins and spin quantum number equal to $+1/2$). Only after all m levels associated with a particular I value in a given shell have been used for single-electron occupation does doubling of electrons into m levels occur. Thus the extra electron for carbon (atomic number 6) has the quantum numbers $n=2, I=1, m=0, s=+1/2$ rather than $n=2, I=1, m=-1, s=-1/2$. Both the effects of energy inversion and Hund's rule are very apparent when considering the electronic configuration of the elements $Z=18, 19, 20$ and 21.



Relative energies of the orbitals in neutral, many-electron atoms. Electrons will always assume lowest available energy states. Accordingly, with increasing atomic numbers, the 4s states will be filled prior to the 3d states, for example.

The s, p, d, and f orbital sets:

Types of orbitals	Orbital quantum numbers	Total number of orbitals in set	Total number electrons accommodated.
s	$I = 0; m = 0$	1	2
p	$l = 1; m = 1, 0, -1$	3	6
d	$I = 2; m = 2, 1, 0, -1, -2$	5	10
f	$l = 3; m = 3, 2, 1, 0, -1, -2, -3$	7	14

Figure 4

The presently used notation is not the most convenient way of designating the energy levels (and wave functions) occupied by the electrons in atoms. The more informative way is a code written as follows: The principal quantum number is given first, followed by the conventional letter which designates the azimuthal (orbital) quantum number and, in a superscript, the number of electrons with that azimuthal quantum number. The code for the electronic ground state in hydrogen, therefore, is 1 s^1, for helium 1 s^2, lithium $1s^22s^1$, beryllium $1s^22s^2$, boron $1s^22s^22p^1$, etc. (See fig. 5 for example.) You will note that the magnetic quantum number has not been specified, but this can be done when required by writing p_x when $m = -1, p_y$ when (m=+1\) and p_z when $m = 0$. Similar codes exist for the d and f levels. Usually such subscripts are not specified and in that case a consideration of Hund's rule will not be required.

An important fact to remember is that the number of electrons in any s, p, d or f level is limited: There are, as you know, a maximum of two electrons in any level with spin numbers $+1/2$ and $-1/2$. For the p levels, / is one and, therefore, three m values $(-1, 0, +1$) are permitted, each with two electrons of spin number $+1/2$ and $-1/2$, resulting in a maximum of six p electrons in any p orbital system. The reader should confirm that ten electrons are the maximum in a d system of orbitals and 14 in an f system of orbitals.

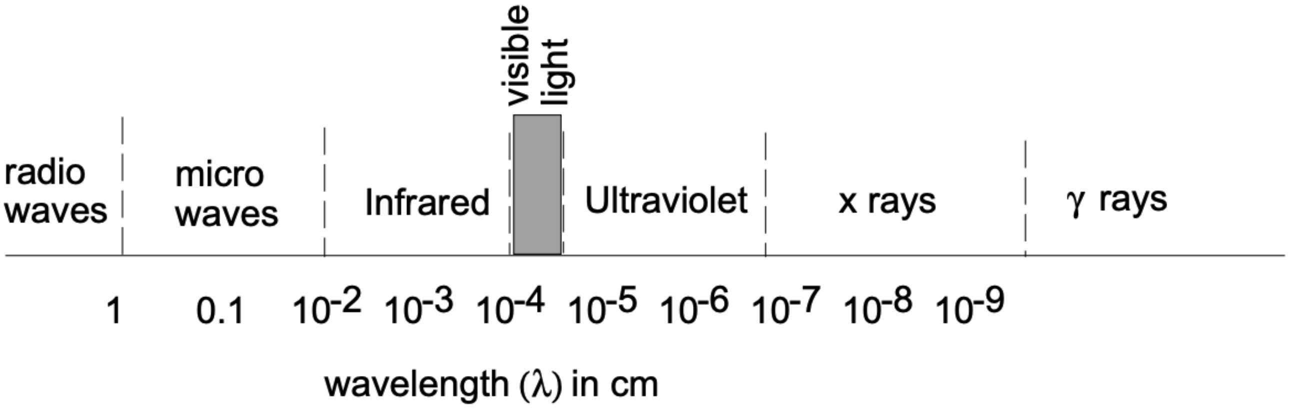
1.1.5: IONIZATION POTENTIAL

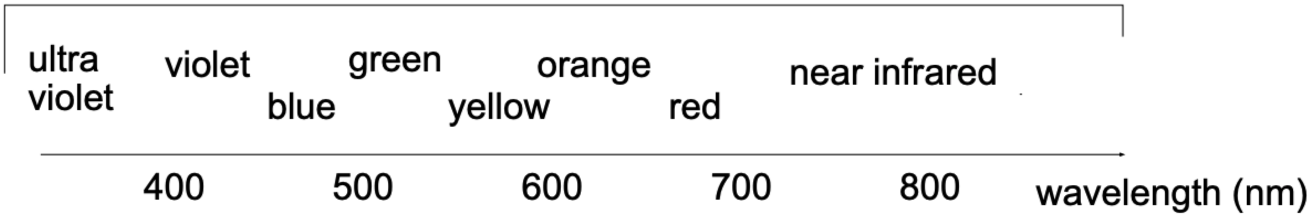
Electrons may be removed from isolated atoms by bombardment with other electrons and by heat, for examples. The work (energy) required to remove the most weakly bound (outermost) electron from an isolated atom is known as the "ionization energy". This energy is sometimes listed in units of Joules. More often ionization energies are given in terms of the "ionization potential". The ionization potential is the potential (V) that will accelerate an electron at rest so that it acquires a kinetic energy, sufficient to extract the outermost (most loosely bound) electron from an atom. This potential is 13.595 Volt (as listed in the PT) for the ionization of a hydrogen atom. You can also say the electron is bound to the proton by an (negative) energy equivalent to the energy of an electron accelerated by a potential of 13.595 Volt. [If you make a dimensional analysis, you will recognize that charge (e) times potential (V) has the dimensions of energy $\left(\mathrm{kg}^2\ \mathrm{m}^2 \cdot \mathrm{sec}^{-2}\right)$ and 1 electron Volt $(1 \mathrm{eV})$ corresponds to 1.6×10^{-19} Joules.] (Note that the first ionization energies are given as first ionization potentials (V) in the Periodic Table of the Elements; see also the 3.091 courseware menu.)

It is significant that inert or noble gases have some of the highest ionization potentials. This reflects the fact that these elements have just enough electrons to completely fill a shell or a subshell which form stable configurations. On the other hand, the ionization potentials of alkali metal atoms (Li, Ni, etc.) are low - the lowest, that of Cs, is only $3.89 \mathrm{eV}$. The reason for this is that alkali metal atoms have one outer s-electron beyond the stable electronic structure of an inert gas atom. Consequently this single electron in

Figure 5 Atomic Electron Affinities (EA)

Atom	Orbital electronic configuration	EA, electron volts	Orbital electronic configuration of anion
H	$1s^1$	0.756	(He)
F	(He) $2s^22p^5$	3.45	(Ne)
Cl	(Ne) $3s^23p^5$	3.61	(Ar)
Br	(Ar) $4s^2\ 3d^{10}4p^5$	3.36	(Kr)
I	(Kr) $5s^24d^{10}5p^5$	3.06	(Xe)
O	(He) $2s^22p^4$	1.47	(He)$2s^22p^5$
S	(Ne) $3s^23p^4$	2.07	(Ne)$3s^23p^5$
Se	(Ar) $4s^23d^{10}4p^4$	(1.7)	(Ar)$4s^23d^{10}4p^5$
Te	(Kr) $5s^24d^{10}5p^4$	(2.2)	(Kr)$5s^24d^{10}5p^5$
N	(He) $2s^22p^3$	(-0.1)	(He)$2s^22p^4$
P	(Ne) $3s^23p^3$	(0.78)	(Ne)$3s^22p^4$
As	(Ar) $4s^23d^{10}4p^3$	(0.6)	(Ar)$4s^23d^{10}4p^4$





The visible spectrum

the outermost new shell can be removed relatively easily. (The second and successive ionization potentials of such atoms are increasingly greater.)

From a chemical and physical viewpoint, it is found that whether an atom is neutral or ionized as well as isolated or combined leads to distinctly different characteristics. It should be recognized that the notation used previously for neutral atoms can also be employed for electronic structures of ions. The electronic configurations of an iron atom and two iron ions are shown below.

$$\begin{array}{lll} \mathrm{Fe}: & 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2 & \text{(neutral atom)} \\ \mathrm{Fe}^{+2}: & 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 & \text{(ferrous ion)} \\ \mathrm{Fe}^{+3}: & 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 & \text{(ferric ion)} \end{array}$$

1.1.6: ELECTRON AFFINITY

As we shall see later, the tendency of some atoms to accept, as well as to lose, electrons is important in determining how atoms combine with each other. Whereas removal of an electron always requires the expenditure of energy, acceptance of one extra electron by an atom generally is accompanied by the release of energy. The amount of energy released on acquisition of an electron is called the electron affinity (or "first electron affinity"). The elements on the left of the periodic table (metals) and the inert gases on the outer right have low electron affinities, whereas the non-metals have higher ones. The particularly high electron affinities of halogen atoms $(\mathrm{F}, \mathrm{Cl}$, etc.) may be attributed to the fact that these elements all lack one electron which would provide the stable electronic structure of an inert gas. By acquiring an additional electron, they increase their stability since the additional electron goes into the orbital lacking one electron and thus results in a stable, s^2p^6, octet configuration. (See fig. 5.)

1.1.7: ATOMIC SIZE

The size, or volume, of an isolated atom is difficult to define explicitly since, in the electron cloud model of the atom, the probability density distribution theoretically reaches zero only at infinity. Nevertheless, the electron density falls off so rapidly at a short distance from the nucleus that some approximation of size can be made. In the hydrogen atom, for example, the electron density is very nearly zero at a distance of $1.2\text{Å}\left(1.2 \times 10^{-10}\ \mathrm{m}\right)$ from the nucleus. The problem of defining atomic size is simplified in molecules and solids in that rather precise dimensions can be determined from interatomic distances which can be measured by diffraction techniques. Thus, in the H_2 molecule the atoms are only 0.72Å apart, as determined from the distance between the nuclei. In this case the radius of the hydrogen atoms is taken to be 0.37Å, even though the size of the H_2 molecule is considerably more than four times this value.

It should be apparent that the atomic radius depends upon whether an atom is isolated or combined with other atoms. The radius of an isolated atom is called the *van der Waals radius*, that of a bound atom in a molecule is the *covalent radius*, and that of a bound atom in a metal is the *metallic radius*. Van der Waals, covalent and metallic radii for some elements are listed in some periodic tables of the elements. The radii of positive ions (cations) and those of negative ions (anions) differ from the van der Waals radii. (See the 3.091 courseware menu on Athena.)

1.1.8: SAMPLE PROBLEM

For hydrogen, calculate the radius (r) and energy level (E_T) of the electron in the lowest energy state (ground state).

Solution

The size of the first allowed orbit can be calculated by requiring that the centrifugal force of the orbiting electron be balanced by the coulombic attraction to the nucleus.

$$F_{\text{centr}} = \frac{mv^2}{r} \quad F_{att} = \frac{e^2}{4\pi\varepsilon_0 r^2} \quad \frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

According to Bohr, the angular momentum of the electron (mvr) is quantized in units of $\mathrm{h}/2\pi$:

$$mvr = \frac{\mathrm{nh}}{2\pi} \quad \mathrm{n} = 1, 2, 3, \ldots$$

With these quantum conditions, r for the first allowed orbit becomes:

$$\begin{aligned} \frac{mv^2}{r} &= \frac{e^2}{4\pi\varepsilon_0 r^2} \\ m^2v^2r^2 &= \frac{me^2 r}{4\pi\varepsilon_0} \\ \frac{n^2h^2}{4\pi^2} &= \frac{me^2 r}{4\pi\varepsilon_o} \\ r &= \frac{n^2h^2\varepsilon_0}{\pi me^2} = n^2 x \text{ constant} \end{aligned}$$

For $n = 1$:

$$r_0 = 0.529 \times 10^{-10} \text{ m} = 0.529\text{Å}$$

The kinetic energy of the electron is $1/2\text{mv}^2$. The potential energy as a function of distance from the nucleus is given by Coulomb's law as:

$$-\frac{e^2}{4\pi\varepsilon_0 r}$$

The total energy is the sum of the kinetic and potential energies.

$$\begin{aligned} \text{E}_\text{T} &= \text{E}_\text{K} + \text{E}_\text{P} \\ \text{E}_\text{T} &= \frac{1}{2}m\text{v}^2 - \frac{\text{e}^2}{4\pi\varepsilon_0 r} \end{aligned}$$

The balance of attractive and repulsive forces requires that:

$$\begin{aligned} F_{\text{centr}} &= F_{\text{att}} & \text{Since:} \quad \frac{mv^2}{r} &= \frac{e^2}{4\pi\varepsilon_0 r^2} \\ \frac{mv^2}{r} &= \frac{e^2}{4\pi\varepsilon_0 r^2} & \text{Then:} \quad \frac{mv^2}{2} &= \frac{e^2}{8\pi\varepsilon_0 r} \end{aligned}$$

Therefore:

$$\text{E}_\text{T} = \frac{\text{e}^2}{8\pi\varepsilon_0 \text{r}} - \frac{\text{e}^2}{4\pi\varepsilon_0 \text{r}} = -\frac{\text{e}^2}{8\pi\varepsilon_0 \text{r}}$$

Substitution for r now gives:

$$E_T = -\frac{1}{n^2} \times \frac{me^4}{8h^2\varepsilon_0^2}$$

For $n = 1$:

$$\begin{aligned} \text{E}_\text{T} &= -2.179 \times 10^{-18} \text{ J} \\ \text{E}_\text{T} &= -13.6\text{eV} \end{aligned}$$

1.1.9: DEFINITIONS

ATOM: The basic constituent of matter, consisting of a nucleus surrounded by electrons.

ATOMIC MASS NUMBER (A): The combined number of protons and neutrons in a specific nucleus.

ATOMIC NUMBER (Z): The number of protons in a specific nucleus, characteristic of a chemical element.

ATOMIC WEIGHT:

(1) The weighted mass of the naturally occurring atoms which constitute an element, relative to the value of exactly 12 for C^{12}.
(2) The mass, in grams, of one mole of a chemical element.

ELECTRON: A negatively charged subatomic particle.

ELECTRON AFFINITY: The amount of energy released when an electron is added to the lowest possible energy level of a neutral atom.

ELECTRON DENSITY DISTRIBUTION/PROBABILITY DENSITY DISTRIBUTION: The spatial distribution of an electron in an atom, depending upon its set of quantum numbers.

ELECTRONIC CONFIGURATION: The shorthand notation used to designate the occupancy of energy levels in an individual atom.

ENERGY LEVEL: The discrete energy state of an electron in an atom, depending upon its set of quantum numbers.

FIRST IONIZATION POTENTIAL: The work which must be expended to remove an electron from a neutral atom in its ground state.

GROUND STATE: The lowest energy state of an atom. All electrons occupy energy levels sequentially from the lowest level.

HALF–LIFE: The time required for half of the atoms of an unstable, radioactive isotope to decay or for a reaction to go to 50% completion.

ION: A charged atom having either an excess or a deficiency of electrons relative to its nuclear charge.

ISOTOPE: The form of an element having the same atomic number but different atomic mass number (or atomic weight) than other forms of the element. As a rule, isotopes of an element exhibit virtually identical chemical behavior, but may exhibit quite different nuclear and physical behaviors.

NEUTRON: A neutral subatomic particle having approximately the same mass as a proton.

NUCLEUS: An extremely dense, small portion of an atom, with a radius of about 10^{-5} that of an atom and containing in excess of 99% of the atomic mass.

ORBITAL: A pictorial designation pertaining to the existence of an electron within a subshell, depending upon the magnetic quantum number, m. Each orbital may contain a maximum of two electrons having opposite spins- i.e., electron spin quantum numbers of $+1/2$ or $-1/2$.

PAULI EXCLUSION PRINCIPLE: The statement that each electron in an atom must have a specific set of unique quantum numbers.

PERIODIC TABLE: A chart arraying the chemical elements in order of increasing atomic number and in groups having similar chemical behavior and similar outer electronic configurations.

PHOTON: A quantum, or minimum unit, of electro magnetic energy. The energy is equal to Planck's constant, h, times the frequency, ν, of the radiation.

PROTON: A positively charged subatomic particle whose charge is exactly opposite that of an electron and whose mass is about 1800 times that of an electron.

QUANTUM NUMBERS: A series of discrete numbers which catalog the state of an electron and which can be derived from wave mechanics.

SHELL: A pictorial designation pertaining to electrons having the same principal quantum number, n, often indicative of the overall energy level of the electron.

SUBSHELL: A pictorial designation pertaining to the state of electrons within a shell, depending upon the second quantum number, l, and indicative of the spatial distribution of the electron.

1.2: Chemical Bonding

The electronic configurations of the elements, as specified in the previous chapter, apply in principle only to *isolated atoms* - atoms separated by distances over which no *mutual interactions* of their electronic orbitals can occur (*infinite distance*). This condition is never met in *condensed phases* (i.e., liquids and solids); it is only encountered in high vacua where atoms move over long distances without mutual interaction. Under normal conditions, particularly in the mentioned condensed phases, atoms are separated over distances controlled, in essence, by the dimension of their respective outermost occupied electronic orbitals. Whenever the outer electron shells of two or more atoms come in contact with each other (overlap to any extent), the *potential* for interaction (reaction) exists. Spontaneous reaction (consisting of a rearrangement of the electronic orbitals and/or actual transfer of electrons from one atom to another) will take place whenever such a rearrangement results in a *lower energy configuration*. This means that the driving force for mutual interaction and rearrangement of electronic configurations is in most instances (but not always) manifested through the release of heat (a form of energy) to the environment. [Typical case: $\mathrm{Mg}+1/2\mathrm{O}_2 \rightarrow$ Reaction Product $(\mathrm{MgO})+($light + heat) i.e. energy.] Since the same amount of energy must be supplied to the system if the original state - i.e., separation of the species – is to be reestablished, the reaction partners are "*bonded* together" by comparable energies. The "strength" of the bonds can obviously vary from system to system with the nature of the electronic rearrangement.

Even the inert gases, particularly the heavier ones like xenon, are capable of forming associations with other atoms. Sometimes we find that two atoms assume a more stable state by sharing electrons; at other times, an atom may transfer electrons to another atom in order to achieve a greater stability. In still other instances, the rearrangement may simply be an orbital distortion or an internal charge redistribution. In either event the mutual benefit that accrues is the formation of what is commonly called a *chemical bond*. Through these bonds atoms combine with each other to form very different kinds of particles referred to as *molecules* and *ions*.

1.2.1: NATURE OF CHEMICAL BONDS

In order for a chemical bond to be formed between two atoms, there must be a net decrease in the energy of the system (the two atoms): the ions or molecules produced by electronic rearrangements must be in a lower energy state than the atoms were prior to interaction, prior to bond formation.

Since atoms of each of the elements have different electronic structures, the variety of possible chemical bonds (differing from each other in at least some small way) is considerable and is even further increased by the effects of neighboring atoms on the bond under consideration. The modes of bond formation can be categorized into two basic types, each representing a type of bonding. The bonding types are called *electrovalent (or ionic) bonding and covalent bonding. Electrovalent bonding arises from complete transfer of one or more electrons from one atom to another; covalent bonding arises from the sharing of two or more electrons between atoms*. Since these models represent the limiting cases, we can anticipate that most real bonds will fall between these two extremes. (Two additional types of bonding, metallic bonding and Van der Waals bonding, will be discussed later.)

Before discussing these models in detail it is appropriate to consider the relationships between the electronic structures of atoms and their chemical reactivity. The inert gases (Group VIII) are the most stable elements with regard to bond formation, i.e. toward electronic rearrangements. It is therefore useful to examine the reasons for their stability. Inert gases all have electronic structures consisting of filled subshells. For all but helium the outer (or valence) shell contains eight electrons, with filled s and p sublevels $\left(ns^2p^6\right)$. The electronic structure of helium is $1s^2$, which is equivalent to the structure of the other inert gases since there is no $1\mathrm{p}$ sublevel. Inert gases have high ionization energies because each electron in the sublevel of highest energy is poorly screened from the nucleus by other electrons in its same sublevel. Each electron "sees" relatively high positive charge on the nucleus, and a large amount of energy is required to remove it from the atom. Inert gases have very low *electron affinity* because any added electron must enter a significantly higher energy level. We find, therefore, that the electronic structures of inert gases are particularly resistant to changes by either loss or gain of electrons and, further, that atoms of other elements with fewer or more electrons than inert gas configuration tend to gain or lose electrons, respectively, to achieve such inert gas structure.

1.2.2: ELECTROVALENT (IONIC) BONDING

An electrovalent bond is formed by the transfer of one or more electrons from one atom to another. Consider first atoms that have electronic structures differing from an inert gas structure by only a few, (1, 2 or 3) electrons. These include the representative elements of Groups I, II and III in the Periodic Table, which have respectively 1, 2 and 3 electrons more than a neighboring inert gas, and the representative elements of Groups V, VI and VII, which have respectively 3, 2 and 1 electrons less than a neighboring inert gas (fig. 1).

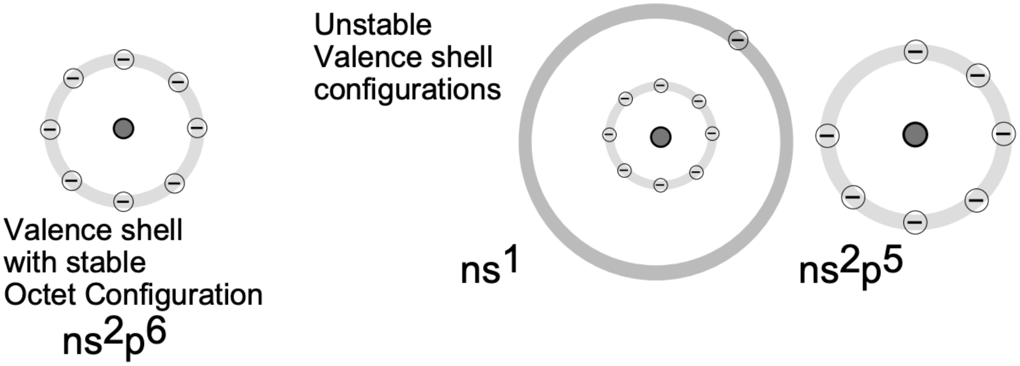
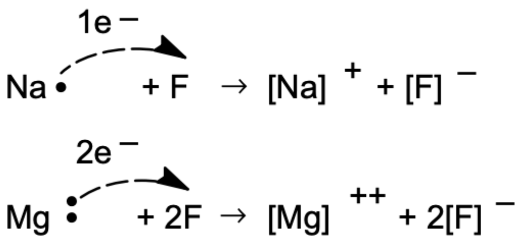


Fig.1 Stable and Unstable Valence Shell Configurations.

The elements of Groups I, II and III can form the electronic structure of an inert gas by losing their outer 1, 2 and 3 (valence) electrons. (The resulting species are positively charged ions.)

In a similar electron transfer which, however, involves the acquisition of electrons in the outer valence levels, elements of Groups V, VI and VII form an inert gas electronic structure (by formation of negatively charged ions).

It is through the electron transfer between an electron-losing element and an electron-gaining element that *compounds* are formed which involve electrostatic attraction (*electrovalent bonds*) of oppositely charged species called *ions*.



(In the notation [Na•], the dot indicates the outermost electron which is in excess of the rare gas configuration. It is referred to as a *valence electron*.)

Elements immediately following the inert gases (in the horizontal columns of the Periodic Table) lose electrons, and those immediately preceding the inert gases gain electrons on interaction. The resulting compounds are called electrovalent; the valence number (charge on the ion) of a particular element when it forms an electrovalent compound is given by the number of electrons lost or gained in changing from the atomic to the ionic state.

The stoichiometric formula of an electrovalent compound reflects the ratio (usually very simple) of positive to negative ions that gives a neutral aggregate. Hence, the ions Na^{+} and F^{-} form a compound whose formula is NaF because these ions are singly charged and are present in the compound in a one-to-one ratio. Magnesium nitride, composed of Mg^{2+} and N^{3-}, has the formula $Mg_3\ N_2$ because this composition represents electroneutrality.

The electrovalent bond is the result of electrostatic attraction between ions of opposite charge. This attractive force accounts for the stability of these compounds, typified by $NaF, LiCl, CaO$, and KCl. The ions individually possess the electronic structures of neighboring inert gases; their residual charge arises from an imbalance in the number of electrons and protons in their structures. Isolated ions and simple isolated pairs of ions, as represented by the formula $NaCl$, exist only in the gaseous state. Their electrostatic forces are active in all directions; they attract oppositely charged species and thus can form regular arrays, resulting in ordered lattice structures, i.e. the solid state (fig. 2). Even in the liquid state and in solutions (where disruptive thermal forces reach values close to that of the attractive electrostatic bonding forces) attraction between ions and with other species remains effective.

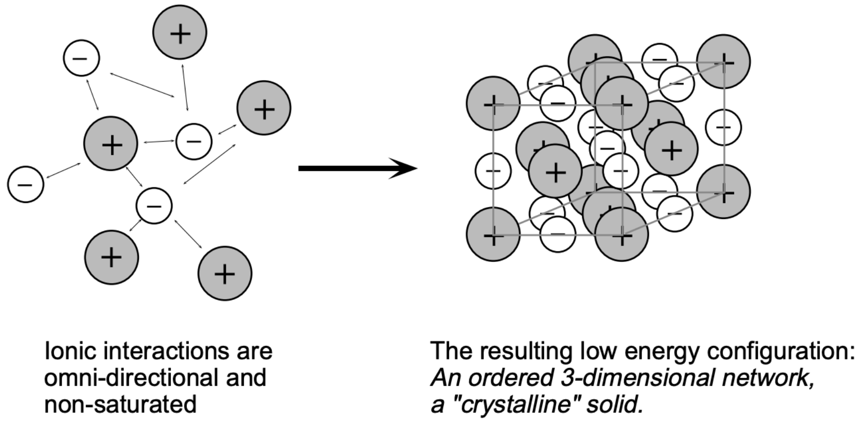


Figure 2 Formation of a crystalline, ordered body (a SOLID), a direct consequence of ion interaction in conjunction with energy minimization..

1.2.2.1: Energetics of Ionic Bonding

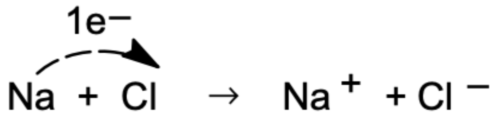
Ionic bonding is the simplest type of chemical bonding to visualize, since it is totally (or almost totally) electrostatic in nature. The principle of the energetics of ionic bond formation is realized when considering the formation of NaCl (our common salt) from its constituents Na (metal) and $\mathrm{Cl_2}$ (chlorine gas). Formally, this reaction is:

$$\begin{aligned}
&\mathrm{Na(s)} + 1/2\mathrm{Cl_2(\,g)} \rightarrow \mathrm{NaCl(s)} \\
&\Delta\mathrm{H} = -414\ \mathrm{kJ/mol}
\end{aligned}$$

The equation as written indicates that 1 mole sodium reacts with $1/2$ mole chlorine $(\mathrm{Cl_2})$ under formation of 1 mole (ionically bonded) sodium chloride; this reaction is accompanied by the release $(-)$ of $414\ \mathrm{kJ}$ of energy $(\Delta\mathrm{H})$, referred to as the *heat of reaction*. From earlier considerations it is clear that electronic rearrangement (reaction or *bond formation*) takes place because the resulting solid product (NaCl) is at a lower energy state than the sum total of the energies of the original components.

The energetics associated with ionic bond formation may be determined quantitatively by considering the energy changes associated with the individual steps leading from the starting materials to the final product (*Haber-Born cycle*).

The bond formation in NaCl may be formally presented as an electron-transfer reaction:



The reactions involved in this process which result in the formation of 1 mole of solid salt are:

(1) Ionization of Na:

Na (gas) $\rightarrow \mathrm{Na}^{+} + 1\mathrm{e}$ $(\mathrm{E.I.} = +497\ \mathrm{kJ/mole})$

The energy change associated with this step, energy of ionization (E.I.), is

$+497\ \mathrm{kJ}/$ mole.

(2) Acquisition of one electron by Cl:

Cl (gas) $+1\mathrm{e} \rightarrow \mathrm{Cl}^{-}$ $(\mathrm{E.A.} = -364\ \mathrm{kJ/mole})$

The energy change associated with this step, *electron affinity* (E.A.), is $-364\ \mathrm{kJ/mole}$. The minus sign reflects an energy release, a lowering of the energy state associated with the achievement of stable rare gas configuration by chlorine.

So far, the energy balance appears positive ($\Delta\mathrm{E} = +133\ \mathrm{kJ}$); this means the reaction is not favored since the final products are at a higher energy state than the starting products. However, there are additional steps involved since:

(3) Vaporization of Na:

Na (metal) $\rightarrow \mathrm{Na}$ (gas) $(\Delta\mathrm{H_V} = +109\ \mathrm{kJ}/$ mole)

The energy required to transform Na (metal) into Na (gas), the latent heat of vaporization $(\Delta \mathrm{H_v})$, is $109\ \mathrm{kJ}/$ mole (now reaction appears even less favorable).

(4) Dissociation of $\mathrm{Cl_2}$:

$\mathrm{Cl_2} \rightarrow 2\mathrm{Cl} \quad (\text{ E.D. } = +242\ \mathrm{kJ}\ )$

The energy associated with breaking up the (stable) chlorine molecule into two reactive chlorine atoms, *dissociation energy* (E.D.), is $+242\ \mathrm{kJ/mole}$. (Since the formation of one mole NaCl involves only 1 mole Cl, and since 2 moles are formed from one mole $\mathrm{Cl_2}$, the energy required in this step is $1/2\mathrm{E}.\,D.$, or 121 kJ.)

The total energy change associated with reactions (1) through (4), $\Delta \mathrm{H_T} = +364\ \mathrm{kJ}$ This indicates that one or more basic reactions which lead to an overall decrease in energy are still unconsidered.

(5) Unconsidered as yet is the coulombic attraction of the reaction products which are of opposite charge and an energy term associated with the formation of the "solid state" product, NaCl. The two ionic species, originally at zero energy (infinite distance of separation), attract each other with an accompanying energy change (decrease).

The energetics associated with the approach of the reaction partners (fig. 3) is best considered by fixing the position of one, for example $\mathrm{Na^+}$, and letting the other $(\mathrm{Cl^-})$ approach: as $\mathrm{Cl^-}$ approaches $\mathrm{Na^+}$, E decreases according to Coulomb's law with $\mathrm{e}^2/4\pi\varepsilon_0 r$. With the approach of the two oppositely charged ions, the outermost electronic shells will come into contact and a repulsive force will become active as the shells interpenetrate. The repulsive force $(E_{\text{rep}}\,)$ increases with $+b/r^{12}$ and thus is only active in the immediate vicinity of the sodium ion, but at that stage increases rapidly. The two ions at close proximity are under the influence of both attractive and repulsive forces and will assume a distance of separation at which the two forces balance each other - a distance which is referred to as the equilibrium separation (r_o) and which corresponds to the energy minimum for the NaCl molecules:

$$E_{\text{coul}} = -\frac{e^2}{4\pi\varepsilon_0 r_0} + \frac{b}{r_0^{12}}$$

where $e =$ electronic charge, $\varepsilon_0 =$ permittivity of free space $\left(8.85 \times 10^{-12}\ \mathrm{F/m}\right)$ and (b) is a constant. (r_0 for gaseous molecules may be obtained from physical measurements.)

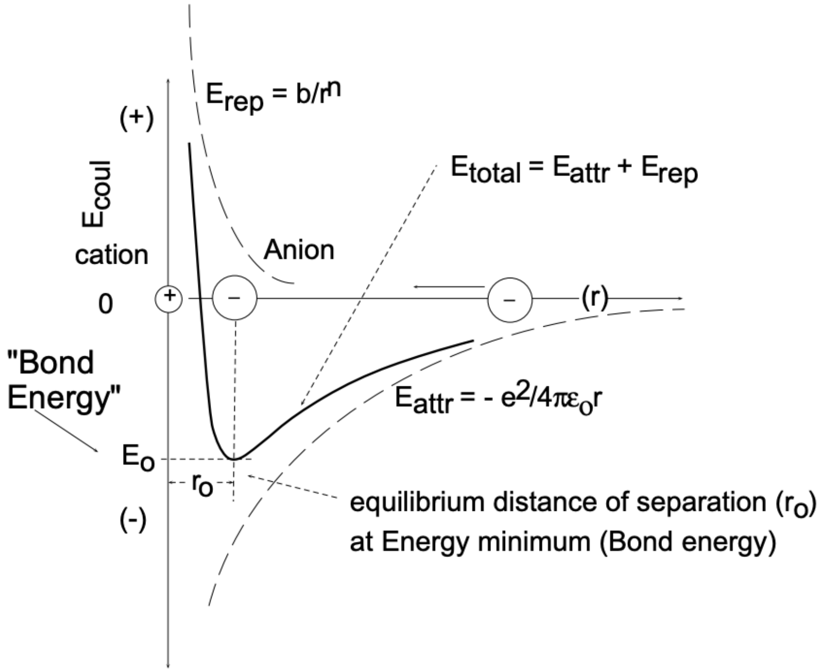


Figure 3 Energetics of ionic bonding.

If the presently considered coulombic (attractive) energy term is taken into consideration as reaction (5), it will decrease the overall positive energy change, $\Delta \mathrm{H}_{\bar{T}}$; it will, however, not make it change sign from (+) to (-). Thus, NaCl molecules in gaseous form are not the final reaction product; nor would reaction occur if $\Delta \mathrm{H_T}$ remained positive.

Considering an ionically bonded, gaseous Na^+Cl^- molecule, it is clear that its electrostatic forces $(+)$ and $(-)$ are not saturated - they remain active in all possible directions. This means that Cl^- will attract Na^+ ions from other directions as will the Na^+ atoms attract additional Cl^- ions. The result of these attractive forces in all directions is the formation of a "giant size" ionic body - a "solid" body of macroscopic dimensions. From the preceding it is recognized that the minimum energy configuration is given by a body in which Na^+ and Cl^- are arranged with extreme periodicity and order since any ion located outside of its "equilibrium position" will be in a "higher energy configuration"; such an ordered body is referred to as a *crystalline solid*, or frequently just called a solid (fig. 2).

The total energy change associated with the formation of one mole of crystalline ionic solid from its ionic constituents is given as:

$$\mathrm{E}_{\text{cryst}}=-\frac{M\,\mathrm{N}_{\mathrm{A}}\mathrm{e}^2\left(\mathrm{Q}_1\mathrm{Q}_2\right)}{4\pi\varepsilon_0 r_o}\left(1-\frac{1}{\mathrm{n}}\right)$$

where $\mathrm{M}=1.747$ ("Madelung" constant for NaCl, reflecting multiple interactions for the particular geometric arrangement of ions in the solid), $\mathrm{N}_{\mathrm{A}}=$ Avogadro's number, $\mathrm{Q}=$ number of charges per ion $\left(1 \text{ for } \mathrm{Na}^+ \text{ and } \mathrm{Cl}^-\right)$, $\mathrm{r}_0=$ equilibrium distance of separation of ions, and $n=$ repulsive exponent ($n=12$ for NaCl).

[The relationship for the crystal energy $\left(\Delta\mathrm{E}_{\text{cryst}}\right)$ is readily obtained from equilibrium energy considerations:

$$\mathrm{E}_{\text{coul}}=-\frac{\mathrm{e}^2}{4\pi\varepsilon_0 r}+\frac{\mathrm{b}}{4\pi\varepsilon_0 r^n}$$

At equilibrium distance of ion separation $\left(r_0\right)$, $(\mathrm{dE}/\mathrm{dr})=0$. Thus:

$$\left(\frac{dE}{dr}\right)_{r_0}=\frac{e^2}{4\pi\varepsilon_0 r_o^2}-\frac{nb}{4\pi\varepsilon_0 r_o^{n+1}}=0$$

and

$$\mathrm{b}=\frac{\mathrm{e}^2\mathrm{r}_{\mathrm{o}}^{\mathrm{n}-1}}{\mathrm{n}}$$

and

$$\begin{aligned}E_{o(\text{ Coul })}&=-\frac{e^2}{4\pi\varepsilon_o r_o}+\frac{e^2}{n4\pi\varepsilon_o r_o}\\E_{o(\text{ Coul })}&=-\frac{e^2}{4\pi\varepsilon_o r_o}\left(1-\frac{1}{n}\right)\end{aligned}$$

For a "molar" crystal with ionic charges Q_1 and Q_2, the molar $\Delta\mathrm{E}_{\mathrm{o}(\text{ Coul})}$ is thus given as:

$$\Delta\mathrm{E}_{\text{cryst}}=-\frac{\mathrm{MN}_{\mathrm{A}}\mathrm{Q}_1\mathrm{Q}_2\mathrm{e}^2}{4\pi\varepsilon_{\mathrm{o}}\mathrm{r}_{\mathrm{o}}}\left(1-\frac{1}{\mathrm{n}}\right)$$

Here M and N_A stand, as indicated above, for the conventional terms, the Madelung constant and Avogadro's number.]

For the present system (NaCl):

$$\Delta\mathrm{E}_{\text{cryst}}=-777\ \mathrm{kJ}/\text{ mole.}$$

Now considering reactions (1) through (5):

$$\Delta\mathrm{H}_{\text{Total}}=-414\ \mathrm{kJ}/\text{ mole}$$

which is identical with the value experimentally determined and given for the reaction:

$$\begin{aligned}&\mathrm{Na}(\text{ metal })+\mathrm{Cl}_2\text{ (gas) }\rightarrow\mathrm{NaCl}\text{ (solid)}\\&\Delta\mathrm{H}_{\text{Reaction}}=-414\ \mathrm{kJ}/\text{ mole}\end{aligned}$$

In the Haber-Born cycle, the reaction energy $(\Delta\mathrm{H})$ associated with the formation of NaCl from $\mathrm{Na}+\mathrm{Cl}_2$ may be summarized as:

$$\Delta\mathrm{H}=\text{ E.I. }+\text{ E.A. }+\Delta\mathrm{H}_{\mathrm{V}}+1/2\text{ E.D. }+\Delta\mathrm{H}_{\text{cryst}}$$

$\Delta\mathrm{H}$, the heat of reaction, may thus be obtained from the energetics of the steps leading to the end product. In most instances, however, the reaction energy $(\Delta\mathrm{H})$ is determined experimentally in a calorimeter and the Haber-Born cycle is used to obtain the value of $\Delta\mathrm{E}_{\text{cryst}}$ or E. A., which are both extremely hard to come by.

Conclusions: A primary drive for atomic interactions leading to "bonding" is the achievement of valence shell octets which exhibit a high degree of stability. If atoms on the left and right side of the Periodic Table interact, i.e. atoms with a large difference in electron affinity ($\triangle \mathrm{E.A.}$), stabilization is achieved by electron octet formation through charge transfer. The reaction products exhibit opposite charges ($\oplus$ cations, $\ominus$ anions) and are subject to Coulombic attraction - ionic bonds are formed. Since the electrostatic forces are non-directional and non-saturated, energy minimization will result in the formation of macroscopic bodies that are highly ordered on the atomic scale, crystalline ionic solids. Ionic solids have mostly predictable, basic properties:

- atomic arrangements are a function of the ion size ratio, the charge ratio of ions, and their electronic structure;
- electrical and thermal conductivities are expected to be low because the high stability of the octets formed results in bound electrons which do not contribute to conduction (there is a large "energy gap" to be crossed for electrons to move into a higher energy state);
- optically, ionic solids are mostly transparent, or translucent, reflecting octet stability of the electrons and macro- or micro-crystallinity;
- melting points are high, increasing with the electronic charges on the cations and anions;
- ionic solids are normally hard and brittle.

1.2.3: COVALENT BONDING

1.2.3.1: Mechanical Concepts and Conclusions

In 1924 L. DeBroglie advanced the hypothesis that all matter in motion possesses wave properties and can be attributed a *particle wavelength*

$$\lambda_P = \mathrm{h}/\mathrm{mv}$$

where h is the Planck constant, m is the mass of the matter and v is its velocity.

The credibility of this hypothesis was established by Davisson and Germer in 1927 when they demonstrated that electrons (like electromagnetic radiation) are diffracted by crystal lattices. An important consequence of the dual nature of matter (it exhibits both particle and wave properties) is the *uncertainty principle* established in 1927 by W. Heisenberg. It states that it is impossible to simultaneously know with certainty both the momentum and position of a moving particle:

$$(\Delta p_x)(\Delta x) \gtrsim h$$

We can paraphrase the uncertainty principle in the following manner: *If the energy of a particle is known (measured) with high precision, its location is associated with a high degree of uncertainty*.

If electrons occupied simple orbits (as postulated by Bohr-Sommerfeld), their momentum and position could be determined exactly at any moment - in violation of the uncertainty principle. According to Heisenberg, if the energy of an electron is specified with precision (sharpness of spectral lines), its location can only be specified in terms of the probability of finding this electron in a certain location (volume element). These arguments give rise to the concepts of *probability density* and *electron cloud* which are inherent to the wave-mechanical electron concept emanating from the solutions of Schrödinger’s wave equation which relates the energy of an *orbiting* electron to its wave properties. When solving exactly the Schrödinger wave equation for an electron in a hydrogen atom, a quantization results according to which electrons can only assume certain energies which are in quantitative agreement with those obtained from the Bohr theory.

In comparison to the Bohr theory, significant differences are observed for the orbital quantization (orbital quantum number I) which specifies the orbital shape. For $n=1, I=0$ (1s orbital), wave mechanics predicts a spherical electron density distribution with a maximum probability density $\left(\psi^2\right)$ at a distance of $0.529\,\text{Å}\left(\mathrm{a}_0\right)$ from the nucleus. For $I=1$ (p orbitals), however, it is found that the orbitals (three) form lobes aligned with rectangular coordinates (see LN-1, fig. 3). For $I=2$ (d orbitals), five complex orbital configurations are obtained.

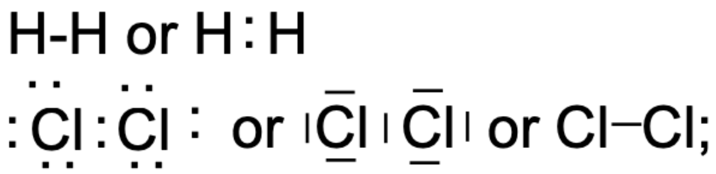
Previous considerations suggest that all elements attempt to assume a stable octet configuration with eight electrons in the valence shell. (For hydrogen, with only one shell occupied, the stable configuration consists of two electrons in the K shell - which is the maximum number of electrons that can be accommodated.) Stable octet formation is possible through electron transfer (and ionic bond formation) when, for example, elements in columns IA, IIA and IIIA react with elements in columns VA, VIA and VIIA, respectively. In these instances, the reaction partners exhibit rather pronounced differences in *electron affinity* and upon reaction one assumes octet configuration by losing one or more electrons while the other does so by acquiring the missing number of electrons.

This mechanism is clearly not possible if H reacts with H to form an H_2 molecule where two atoms are bonded together. The same argument holds for the formation of N_2, Cl_2 and O_2 molecules. Inert gas configuration (octet configuration) in such elements is achieved by a mechanism called *orbital sharing* and the resulting bond is called *covalent*, or electron-pair bond.

A covalent bond is somewhat more difficult to visualize than an ionic or electrovalent bond because it involves the sharing of a pair of electrons between atoms. The stability of this bond can be attributed to the complex mutual attraction of two positively charged nuclei by the shared pair of electrons. *In principle, the bond can be understood if it is recognized that both electrons in the bonding orbital spend more time between the two nuclei than around them and thus must exercise attractive forces which constitute the bond*. In this arrangement it is clear that each electron, regardless of its source, exerts an attractive force on each of the “bonded” nuclei. The pair of electrons in a covalent bond is unique to the extent that the Pauli exclusion principle precludes the presence of additional electrons in the same orbital. Furthermore, the pairing phenomenon neutralizes the separate electronic spins of the single electrons, and the resulting electron pair with its zero spin momentum interacts less strongly with its surroundings than do two independent electrons. [Covalent bonds are conveniently symbolized through the *dot notation*, introduced first by Lewis (fig. 4).]

1.2.4: LEWIS NOTATION:

In LEWIS notation the covalent molecular bond is indicated as a BAR or as two DOTS (standing for the paired electrons)



Formal valence shell octet stabilization can be achieved by electron sharing, H whereby one electron from each reaction partner share - spin paired - the molecular bonding orbital.

Quantum mechanics makes it possible to rigorously describe these bonds for very simple cases such as the hydrogen molecule, which is composed of two protons and two electrons. It can thus be shown that the potential energy for the system reaches a minimum for a certain equilibrium distance between the nuclei, with increased electron density between the nuclei. At shorter distances between the nuclei repulsive forces are found to increase very rapidly.

In the hydrogen molecule (H_2), the two hydrogen atoms are effectively linked together by *one* molecular electron orbital, termed a σ orbital, which comprises both atoms and contains two electrons. (fig. 5) Each of these two electrons can be considered to have originated from one of the two atoms - they were originally both 1 s electrons with the same spin value $(s = +1/2)$. In the molecular orbit comprising both atoms, the spins of

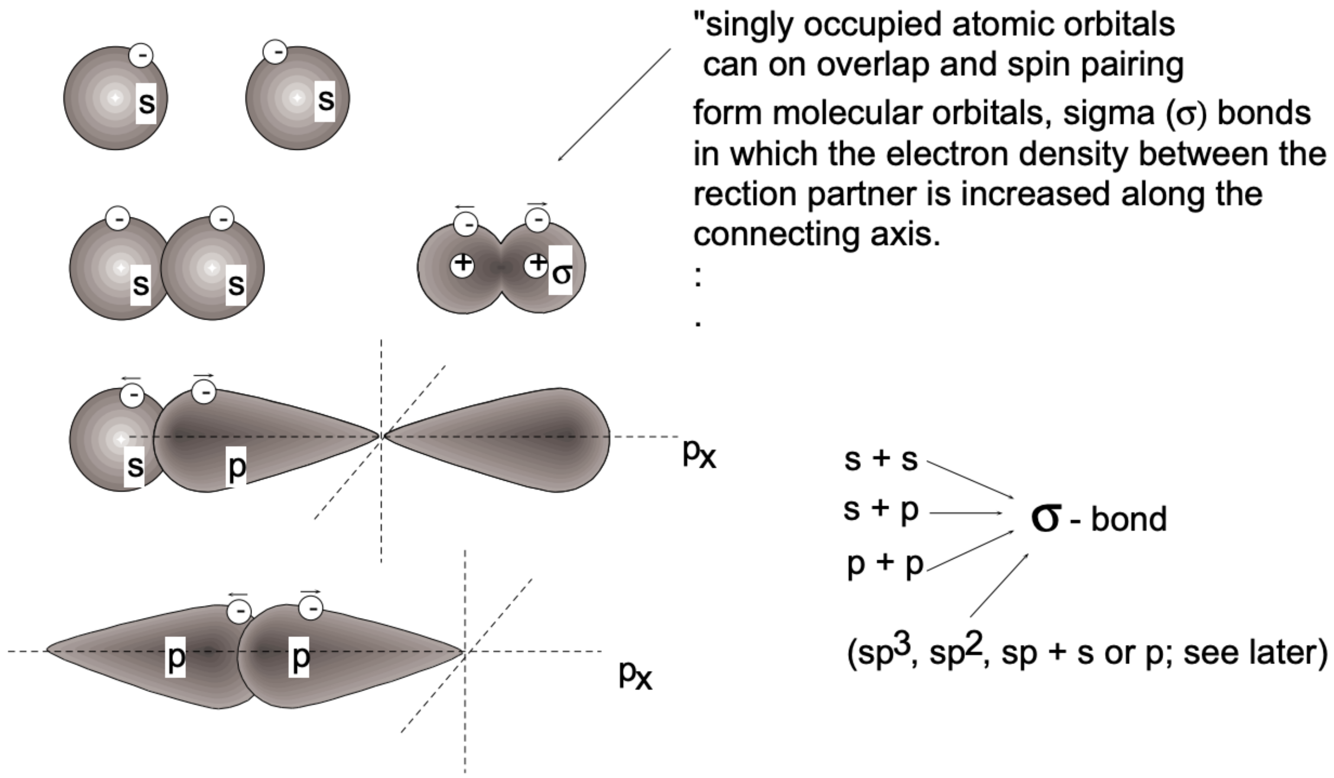


Figure 5 Covalent bond formation

the two electrons must align anti-parallel (opposite spin). This spin-pairing process results in a considerable release of energy and thus contributes significantly to the stability (strength) of the covalent bond formed. It is interesting that according to Newtonian mechanics, no stable configuration can arise from the placement of two electrons into the same region (orbit) - wave mechanics (see below), however, predicts increased stability from such configurations. (Similar spin-pairing occurs in the filling of atomic orbitals.) In the molecular case, spin-pairing has the consequence that both the probability distributions $\left(\psi^2\right)$ and spatial distribution of electrons are such that maximum overlap of orbitals of combining atoms occurs.

The bond formed in hydrogen is a single bond, containing two electrons with paired spins. This formulation predicts that there will be a fixed internuclear separation which, for the hydrogen molecule, has the value of $0.74 Å$. [σ bonds are formed not only by s orbital overlap, but also by p-s and p-p orbital overlap as well as by the overlap of s or p orbitals with hybridized orbitals; to be discussed below (see fig. 5).]

It is important to recognize that octet stabilization by electron orbital sharing results in bond properties which differ fundamentally from those encountered in ionic (electrovalent) bonding: with the formation of the covalent bond between the hydrogen atoms $(H_2$ molecule formation) the *bond forming capabilities of the two hydrogen atoms are saturated*; the final product is a *distinct molecule* (H_2) rather than a giant-sized solid body which is obtained as the final product with ionic bond formation. Covalent solid bodies, however, also do exist: they are formed if the elements involved have the capability of forming more than one bond. For example, carbon will form four covalent bonds in tetrahedral configuration - the result is diamond, a covalently bonded, three dimensional network.

1.2.4.1: Diatomic Molecules Involving Dissimilar Atoms

Consider the compound hydrogen chloride (in the gaseous, liquid or solid state). This compound is not ionic (because the energy state on complete ionization would be higher. Instead, bonding between hydrogen and chlorine atoms is accomplished by the sharing of electrons in a molecular orbital, thus forming a single covalent bond (fig. 6).

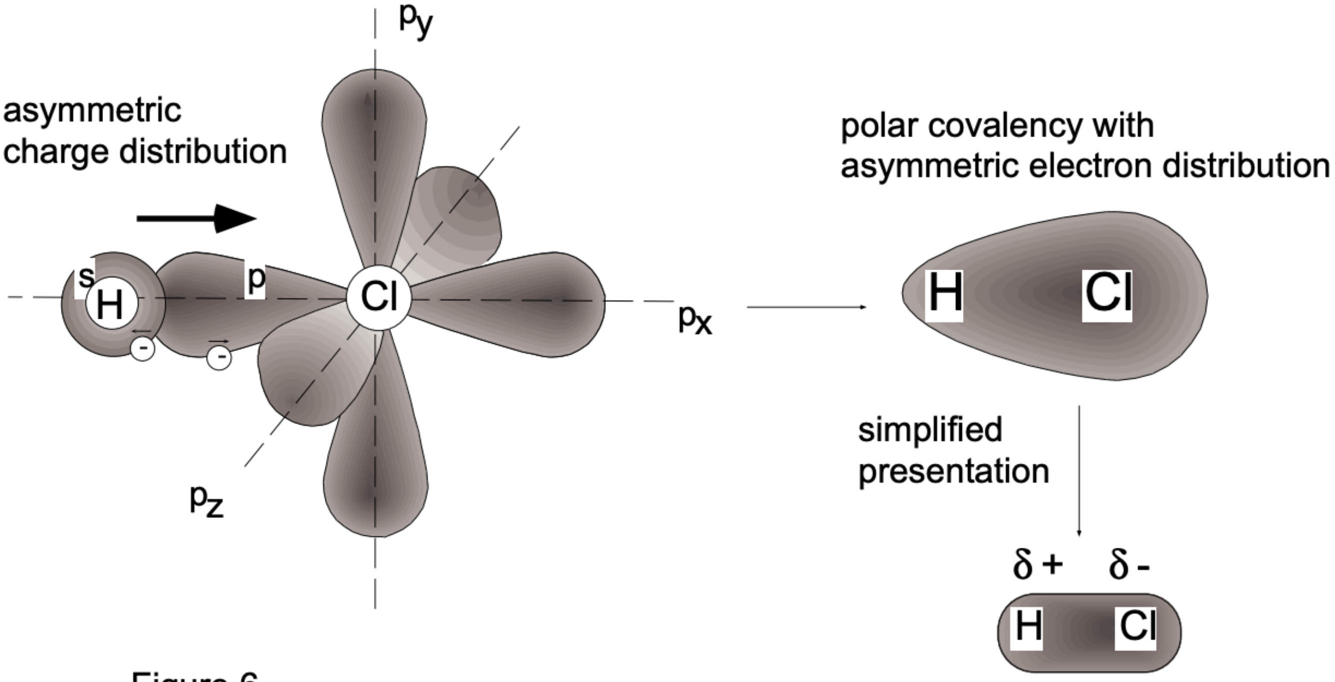


Figure 6

The electrons involved are the 1 s electron of the hydrogen atom and the unpaired $3p_z$ electron of the chlorine atom. After spin-pairing, a typical σ bond results in which each atom attains a noble gas structure: in HCl the hydrogen atom is "involved" with two electrons, as in helium, and the chlorine atom with 18 electrons, as in argon. The other (inner) electrons of chlorine do not participate in the bonding; they are termed *non-bonding*.

According to the above considerations, the bonding of HCl may be taken as very similar to that of $\mathrm{H_2}$. However, in the hydrogen molecule the electrons participating in the σ bond formation do not favor the proximity of either of the hydrogen nuclei - instead, they are equally shared. On the other hand, a preference for one nucleus (chlorine) is shown by the electrons of the σ bond in hydrogen chloride. This is because electrons, for energetic reasons, favor the environment of the more electronegative atom; in hydrogen chloride this is the chlorine atom and, consequently, the σ bond electrons spend more time in the vicinity of the chlorine atom. This situation results in the chlorine end of the molecule being fractionally negatively charged (δ^-) and the hydrogen end being fractionally positively charged (δ^+). We denote such an internal charge redistribution by the symbolism $\mathrm{H}^{\delta+}-\mathrm{Cl}^{\delta-}$, where the δ sign indicates a partial electronic charge; the bond is said to be polar. (The hydrogen molecule does not a priori exhibit such an "asymmetric charge distribution"; it may, however, acquire a temporary polarization.) Molecules with asymmetric electronic charge distribution have a *permanent dipole moment*, the value of which is given by the product of the fractional charge (δ^+ must be equal to δ^-) and the distance of charge separation (L). Although dipole moments can be measured, their values do not allow us to directly calculate the polarity of bonds between atoms since the detailed internal charge distribution is unknown. The direction of electron drift and, to some extent, the magnitude of its effect can be estimated from the magnitude of the difference in electron affinity between the reaction partners. Because of a limited data base on electron affinity, L. Pauling introduced a related term, the *relative electronegativity* (see below). From the above considerations it should be clear that no sharp dividing line exists between ionic and covalent bonding. We might consider a completely ionic bond to result in cases where the electron drift is such that one atom (the cation) becomes entirely deficient in one or more electrons, and the other atom (the anion) becomes correspondingly electron-rich, the bonding electrons being entirely under the influence of the latter. Hydrogen halides are σ bonded and have dipole moments; the bonds are referred to as *polar covalency*. The homonuclear diatomic molecules formed by the halogens, viz. $\mathrm{F_2}, \mathrm{Cl_2}, \mathrm{Br_2}$ and $\mathrm{I_2}$, are all σ-bonded systems involving spin-pairing of the various p_z electrons $(2p_z, 3p_z,$ $4p_z$ and $5p_z$ respectively). They have no permanent dipole moments.

1.2.4.2: Energetics of Covalent Bonding

Pauling extensively treated the energetics of polar covalencies, encountered in all heteronuclear systems (such as $\mathrm{H}-\mathrm{Cl}$) which have permanent dipole moments $\left(\mathrm{H}^{\delta+}-\mathrm{Cl}^{\delta-}\right)$. His approach visualizes the bonding to consist of two components - a pure covalency and an ionic bonding component with attraction resulting from the interaction of the fractional charges on the nuclei involved.

Pauling determines the basic covalent bonding component, for example in the formation of HCl, from the experimentally obtained bond energies associated with the molecular species of the components, $\mathrm{H_2}$ and $\mathrm{Cl_2}$. For this purpose he made the basic assumption that the covalent bond component between the dissimilar atoms is given by the geometric mean of the pure covalent bond energies associated with these molecular species. Thus:

Pure Covalent Bond Energy of HCl:

$$\begin{aligned} \mathrm{BE_{HCl}} &= \sqrt{\mathrm{BE_{H_2}} \times \mathrm{BE_{Cl_2}}} \\ &\mathrm{H_2 : H-H\ (Bond\ Energy\ = BE_{H_2} = 430\ kJ/mole\ )} \\ &\mathrm{Cl_2 : Cl-Cl\ (Bond\ Energy\ = BE_{Cl} = 238\ kJ/mole\ )} \\ &\mathrm{BE_{HCl}} = \sqrt{430 \times 238} = 320\ \mathrm{kJ/\ mole} \end{aligned}$$

The ionic contribution (Δ) to the polar covalent bonding is then obtained from the difference between the experimentally determined bond energy (for HCl, for example), which obviously must contain both components, and the calculated pure covalent bond energy:

$$\Delta = [\mathrm{BE_{HCl}}\ (\text{experimental })] - [\mathrm{BE_{HCl}}\ (\text{theoretical - covalent})\ ]$$

$$(\text{The experimentally determined} \mathrm{BE_{HCl}} = 426\ \mathrm{kJ/mole.}\ )$$

$$\Delta = 426 - 320 = 106\ \mathrm{kJ/\ mole}$$

In connection with the presently discussed work, Linus Pauling established the now generally used *electronegativity scale*, or, better, the *scale of relative electronegativities*. This scale, included in the Periodic Table of the Elements, is extremely helpful since values of the *electron affinity* are known thus far for only very few elements.

The electronegativity (x) scale lists the relative tendency of the neutral elements to attract an additional electron. (The values of x are conventionally listed in electron Volts.) The scale listed was obtained by arbitrarily fixing the value of $x_H = 2.2$. Pauling obtained the values for the other elements by relating differences in electronegativity of reaction partners to the fractional ionic character (ionic bonding component) of the bond established between them:

$$\begin{aligned} &\text{experimental } \mathrm{BE_{AB}} = \sqrt{\mathrm{BE_{AA}} \times \mathrm{BE_{BB}}} + \mathrm{k}(\mathrm{x_A} - \mathrm{x_B})^2 \\ &\text{or} \\ &\Delta = 96.3(\mathrm{x_A} - \mathrm{x_B})^2\ \mathrm{kJ} \end{aligned}$$

According to Pauling, the bonding character between two different elements may be defined as:

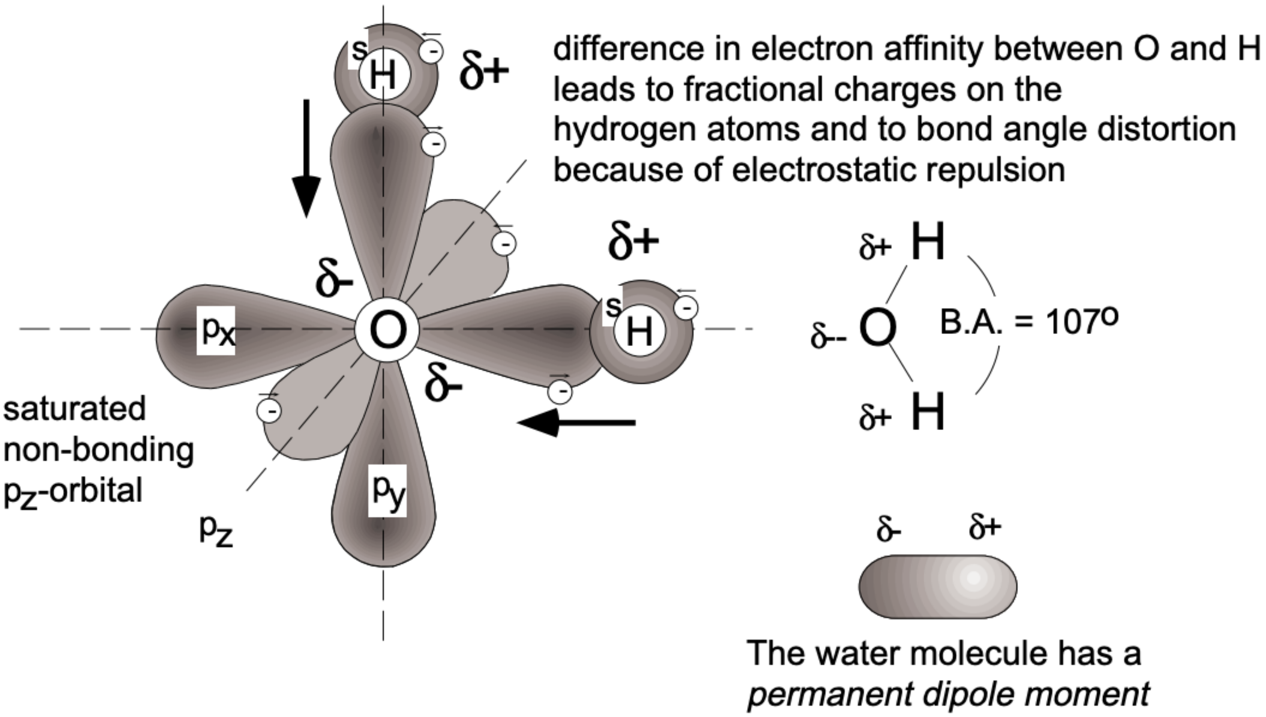
ionic bonding for: $\Delta x > 1.7$; covalent bonding for: $\Delta x < 1.7$

The fractional ionicity of polar covalent bonding as listed in the P/T is obtained by the relationship:

$$\%\ \text{ionic bonding} = \left(1 - \mathrm{e}^{-0.25(\mathrm{x_A} - \mathrm{x_B})^2}\right) \times 100$$

1.2.4.3: Bonding In Polyatomic Molecules

In the formation of covalent bonds between atoms in polyatomic molecules, the conditions that atomic orbitals distort so that maximum overlap may be achieved when bonding occurs produces more extensive changes of orbital geometry than is the case with diatomic molecules. It will be remembered that the changes which result in a σ bond formation in diatomic molecules are a distortion of the s orbitals or p lobes so that strongest bond formation results from the maximum overlap between the two joined nuclei. For polyatomic molecules extensive alterations in the spatial disposition of atomic orbitals do occur, and very often the unique orbital geometry of the original atomic orbitals is completely lost (fig. 7). It is sometimes convenient to view these alterations as occurring in each atom prior to bonding by a process involving the mixing, or *hybridization*, of atomic orbitals.



difference in electron affinity between O and H leads to fractional charges on the hydrogen atoms and to bond angle distortion because of electrostatic repulsion

saturated non-bonding pz-orbital

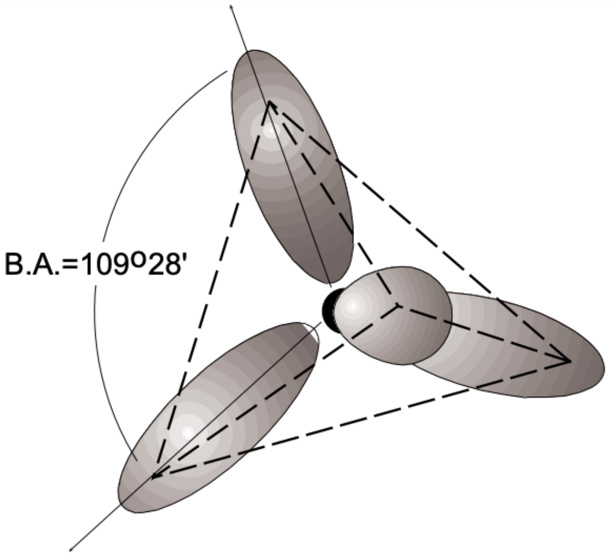
The water molecule has a *permanent dipole moment*

1.2.4.4: Bonding Involving Carbon

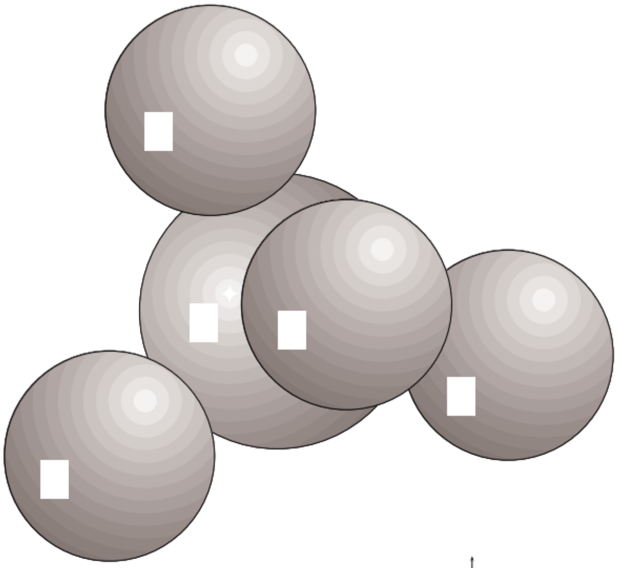
In methane (CH_4) the four outer, or valence, electrons of carbon are shared with the electrons of hydrogen; there is spin-pairing (resulting in bond formation) between each individual hydrogen electron and one of the carbon valence electrons. The noble gas structure is thus attained by each nucleus: the carbon nucleus "sees" eight outer electrons and each H nucleus "sees" two electrons. Consider now the orbitals which are involved in more detail. Each hydrogen has one spherical valence orbital (the 1s orbital) containing one electron, and covalent bond formation results from its distortion, overlap with the valence orbitals of carbon and spin-pairing.

According to the Aufbau principle and Hund's rule, in its ground state carbon has two electrons in the filled K shell and four electrons in the L shell: two 2 s electrons and two $2p$ electrons in singly occupied orbitals which are capable of covalent bond formation. This configuration provides, in principle, only two orbitals $(2p_x, 2p_y)$ for covalent bond formation. However, with two covalencies carbon will not yield the desirable octet configuration. Such a configuration can be obtained if one of the two 2s electrons is "promoted" into the empty $2p_z$ orbital since this process results in four singly occupied orbitals - all of which, being singly occupied, are capable of bond formation. The dissimilar singly occupied orbitals can assume (and therefore will assume) upon bond formation a lower energy configuration involving a process called hybridization whereby the four orbitals (of two different types) hybridize into four identical orbitals of maximum equal spacing from each other (fig. 8). Thus the hybridized orbitals (sp^3 hybrids) are lobes emanating from the carbon atom into the corners of a tetrahedron, forming bond angles of $109^\circ 28'$. sp^3 hybridization is characteristic for carbon; however, other types of hybridization, sp^2 and sp, are encountered in other elements as well. Boron, for example, will tend to promote one of its two 2s electrons into a $2p$ state and, by hybridization, form three equivalent sp^3 orbitals which assume planar orientation with band angles of 120°. Beryllium forms sp hybrid orbitals of linear orientation (the bond angle is 180°). All hybrid orbitals are capable of σ bond formation.

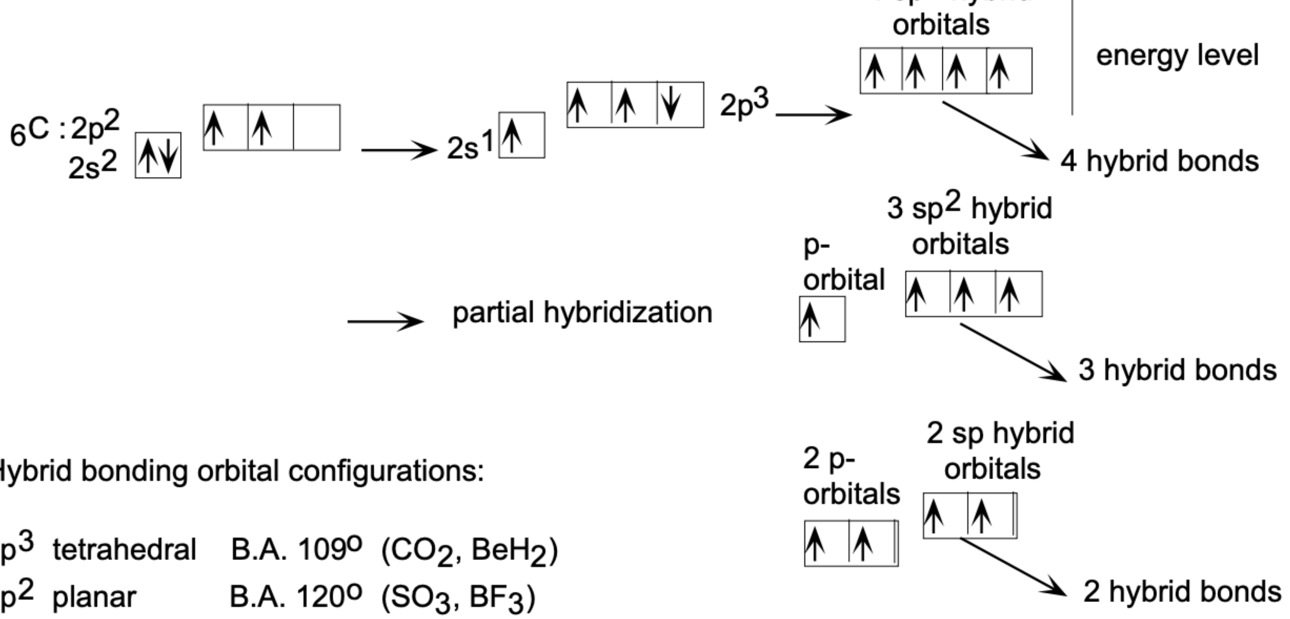
The great diversity of carbon compounds (it forms more compounds than all the rest of the elements in the Periodic Table) can be attributed to the hybridization capability of the carbon orbitals $(\mathrm{sp}^3, \mathrm{sp}^2$ and sp$)$. As a consequence, carbon forms not only axisymmetric σ bonds (through axial orbital overlap), but also π bonds (through lateral orbital overlap). In the compound ethane $(H_2C=CH_2)$, the interactive carbon atoms undergo sp^2 hybridization for a σ bond by overlap of two sp^2 hybrid orbitals and form, in addition, a π bond by lateral overlap of the remaining non-hybridized p orbitals. (Double bonds involve one σ and one π bond.) In acetylene $(HC\equiv CH)$, we find sp hybridization and, by axial overlap, σ bond formation as well as lateral overlap of the remaining non-hybridized p_x and p_y orbitals which form two π bonds (fig. 9).



CH$_4$ formed by 4 molecular orbitals (σ-bonds) based on overlap of sp^3 and s atomic orbitals

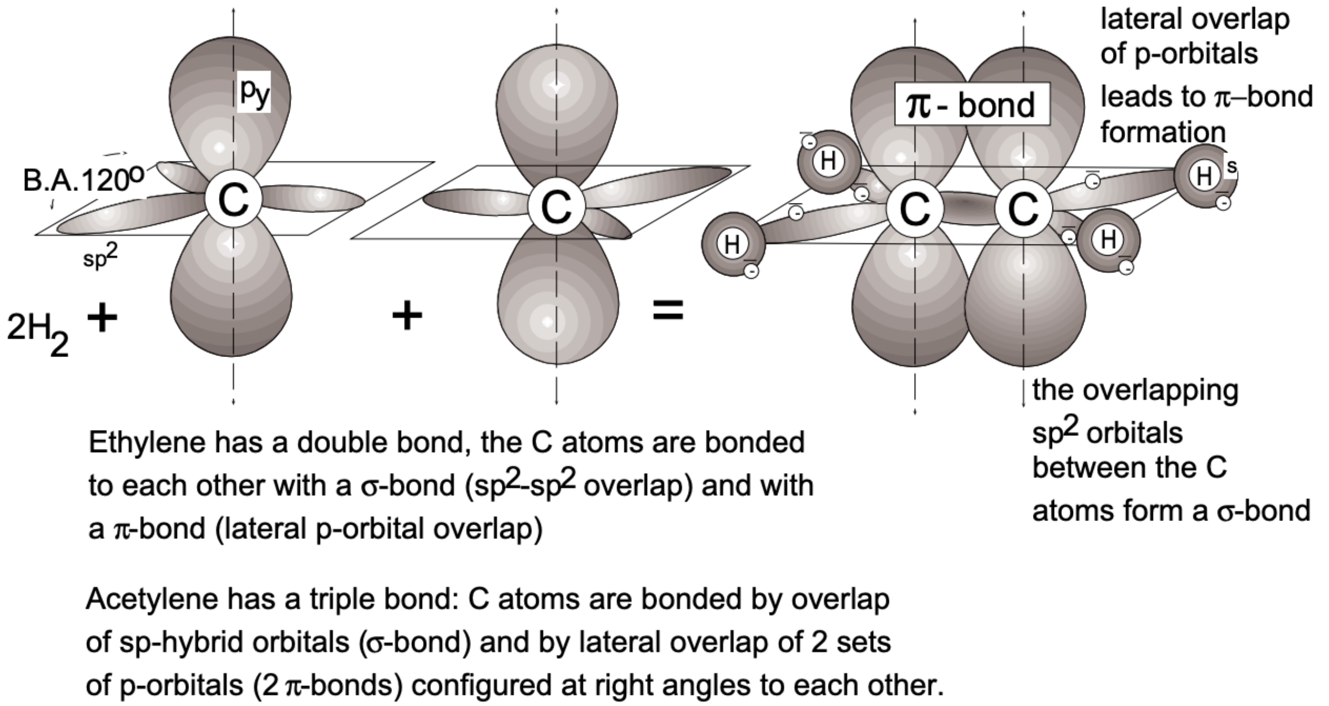


Octet formation in the carbon valence shell can be achieved by sp^3 hybridization which leads to 4 equivalent bonding orbitals spaced tetrahedrally at 109°28'



Hybrid bonding orbital configurations:

sp^3	tetrahedral	B.A. 109°	(CO_2, BeH_2)
sp^2	planar	B.A. 120°	(SO_3, BF_3)
sp	linear	B.A. 180°	(BeH_2, CO_2)



Ethylene has a double bond, the C atoms are bonded to each other with a σ-bond (sp^2-sp^2 overlap) and with a π-bond (lateral p-orbital overlap)

Acetylene has a triple bond: C atoms are bonded by overlap of sp-hybrid orbitals (σ-bond) and by lateral overlap of 2 sets of p-orbitals (2 π-bonds) configured at right angles to each other.

Figure 9 Double and Triple Bonds

1.2.5: METALLIC BONDING

The stability of both covalent and metallic bonds may be regarded as arising from the potential energy lowering experienced by valence electrons under the influence of more than one nucleus. In metals, where the valence electrons are not as tightly bound to their ion cores, we cannot expect the formation of strong electron-pair bonds. The bond energies of known diatomic molecules of metallic elements are, in fact, smaller than those consisting of nonmetallic elements: $104\ \mathrm{kJ}/$ mole for Hg_2. Only diatomic molecules of the semi-metals have relatively high binding energies ($385\ \mathrm{kJ}/\mathrm{mole}$ for As_2, $293\ \mathrm{kJ}/\mathrm{mole}$ for Sb_2 and $163\ \mathrm{kJ}/$ mole for Bi_2). These values reflect multiple bonding. Much greater stability is possible in larger aggregates of atoms such as bulk metals.

The known properties of metals, such as low electrical resistance and malleability, support the conceptual view that the valence electrons in metals never remain near any particular atom very long, but drift in a random manner through the lattice of ion cores. We may therefore visualize metals as a lattice of ion cores being held together by a gas of free electrons.

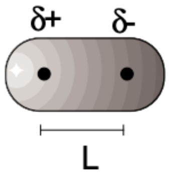
(Bonding in metallic systems is discussed in more detail in LN-3.)

1.2.6: SECONDARY (van der WAALS) BONDING

Primary bonding (ionic, covalent and metallic) is strong and the energies involved range from about 100 to 1000 kJ/mole. In contrast, secondary bonding is weak, involving energies ranging from about 0.1 to 10 kJ/mole. While this type of bonding, also referred to as “residual”, is weak, it is essential in the functioning of our environment. Coke would likely be gaseous and not a bubbly, refreshing brew were it not for secondary bonding, nor would catalytic converters function.

The energy difference between the liquid and vapor states of a given system is given by the heat of vaporization, i.e. the heat required to convert a given liquid into a vapor (normally) at the boiling point temperature at 1 atm pressure. The energy difference is due to intermolecular attraction between molecules at close distance of separation. This phenomenon of attraction through secondary bonding can best be considered between a single pair of molecules, but recognizing that the forces are of longer range. Four types of intermolecular forces can be identified.

1. Dipole-Dipole Interaction: Molecules with permanent dipoles (such as water, alcohol and other organic compounds with functional groups) exert a net attractive force on each other as a result of varying degrees of alignment of oppositely charged portions of the molecules (fig. 10). For two polar molecules with a dipole moment of (μ) separated by a distance of (r), the energy of attraction can be quantified as:



Schematic presentation of a dipole, exhibiting a Dipole-moment (μ) which is given by:

$$\mu = L.\partial q$$

where L is the distance of separation of the fractional electronic charges ∂q+ and ∂q- (in abbreviated form given as δ+ and δ–). In molecules the dipole moment is given by the vector sum of the polar bonds. Thus, because of molecular geometry (symmetry), molecules such as CCl_4 exhibit no dipole-moment.

:

Dipole-Dipole Interaction:

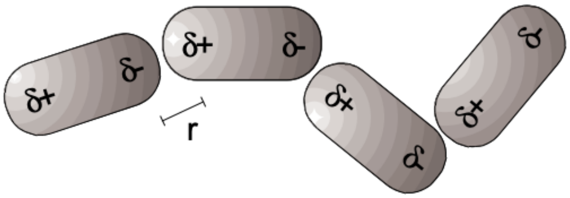


Figure 10

$$E_{Dipole-Dipole} = -\frac{2}{3}\frac{\mu^4}{Dr^6} \times \frac{1}{kT}$$

where μ is the dipole moment, r is the distance of approach of the oppositely charged molecular portions, k is the Boltzmann constant (see P/T) and T is the absolute temperature in K.

The molar energies of attraction associated with dipole-dipole interaction range from 0 to about $10\ \mathrm{kJ}/$ mole. These forces are primarily responsible for the liquid state (at room temperature) of most polar organic molecules; they are a contributing factor for H_2O to be liquid at room temperature, and are responsible for alcohol being a liquid.

2. Dipole-Induced Dipole Interaction: A dipole in one molecule can interact with and polarize the electrons of a neighboring non-polar molecule, thus generating an induced dipole which will experience an attractive force with the polarizing, polar dipole (fig. 11). P. Debye showed that in a molecule with a "polarizability" of (α) the attractive potential arising from dipole-induced dipole interaction is given as:

$$E_{\text{Dipole-Induceddipole}} = -\frac{2\alpha\mu^2}{Dr^6}$$

Dipole-Induced Dipole Interaction:

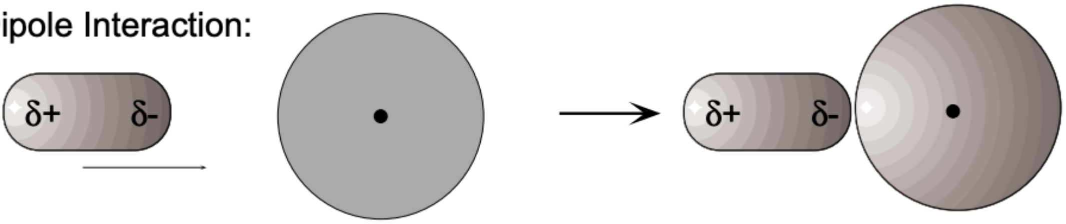


Figure 11

Induced dipole interaction is important in aqueous solutions and very effective during adsorption of inert molecules on active solid substrates.

3. London Dispersion Forces: It is a well-known fact that all substances, including rare gases and hydrogen, assume liquid state at finite temperature, an indication of the existence of attractive interatomic and intermolecular forces, even in the absence of permanent dipole systems. The origin of this force has been proposed by F. London in 1930. Accordingly, orbiting electrons will at any instance generate a "temporary dipole", the configuration of which changes as the electrons move. Since all atoms of a given system similarly experience temporary instantaneous dipole moments, their effect is expected to be cancelled because of the statistically random orientation of dipoles. It is evident that, should the dipoles be synchronized in a given assembly of atoms, then a net attractive force would result (fig. 12). But since such an attractive force constitutes a lowering of the energy of a given system, synchronization can and will take place because all systems will attempt to assume minimum energy configuration. The London dispersion force can be formulated as:

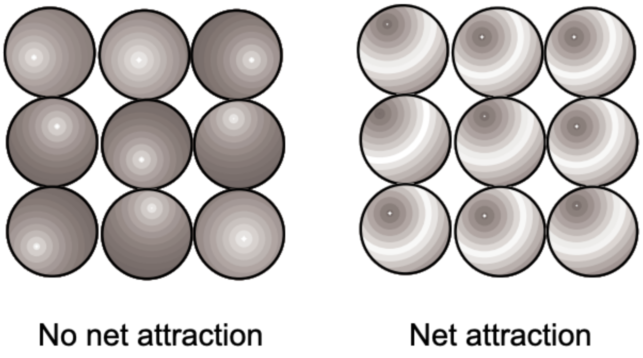
$$\mathrm{E}_{\text{London}} = -\mathrm{K}\frac{\alpha^2}{\mathrm{r}^6}$$

The attractive London forces are small, as manifested by the very low boiling points of the smaller rare gases, of hydrogen and nitrogen.

4. Hydrogen Bonding: The short and long range dipole interactions calculated from molecular dipole moments are inadequate in explaining a multitude of phenomena in organic as well as some inorganic systems. L. Pauling studied such phenomena and concluded the existence of highly specific attractive interaction between hydrogen that is acidic (carries a fractional positive charge) and the elements O, F, N and, to a lesser extent, S in both organic and inorganic molecules. This interaction, which can as yet not be formulated, is referred to as *hydrogen bonding*; its magnitude, ranging up to 40 kJ/mole, is significantly larger than that of any other secondary bonding type. Hydrogen bonding is considered instrumental in controlling most properties of water, is a key element in the structure of nucleic acid and thought to be an essential component in memory functions of the human brain.

London Dispersion (Fluctuating Dipole Interaction)

Electron motion in atoms generates fluctuating dipoles. Since the polarization is random attractions are cancelled by repulsions.



London:
Upon synchronization of electron motion inter atomic attraction will be established in an assembly of atoms.
Since this attraction constitutes a lowering of the energy of the system - attraction by synchronization will take place - as all systems attempt to assume lowest energy configuration

Figure 12

1.3: Bonding in Metals, Semiconductors and Insulators – Band Structure

1.3.1: INTRODUCTION

Characteristic properties of metals include: (1) electrical conductivity, (2) opaqueness and (3) malleability. A very simple model in which the metallic crystal is viewed as a lattice of positive ions surrounded by a "gas" of free electrons provides a crude understanding of the first and third properties. If the crystal has a gas of free electrons, it is easy to see why the application of an electric field will result in the motion of these electrons and thus for the high electrical conductivity. This model also allows one to explain the malleability of metals, as shown in fig. 1b. When a metallic crystal is subject to forces that displace one plane of atoms with respect to another, the environment of the charged species is left unchanged. In contrast, the displacement of neighboring planes in an ionic crystal as a result of a distorting force will lead to cleavage, largely because of changes in the interaction of the charged species (Figure $1.3.1, left$).

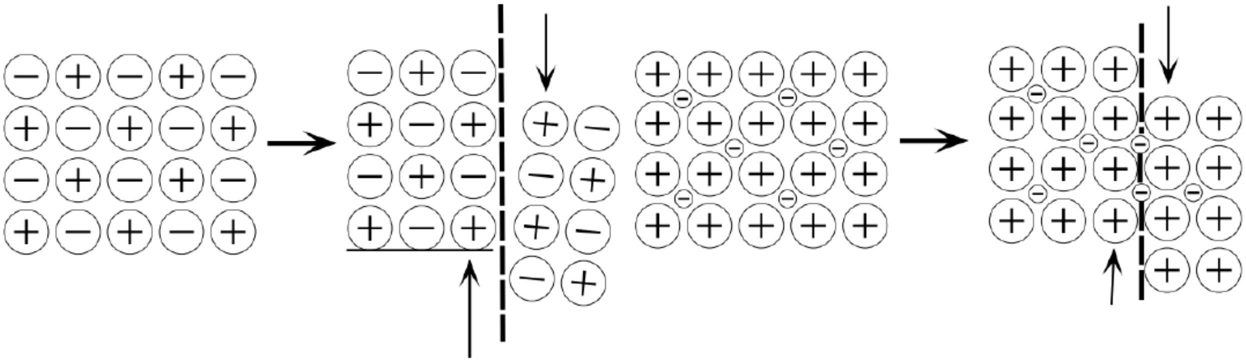


Figure $1.3.1$: Mechanical properties of ionic and metallic crystals. (left) In ionic crystals the displacement of neighboring planes by shear forces frequently results in cleavage largely because of the establishment of repulsive forces in the cleavage plane. (right) In metallic crystals the displacement of neighboring planes does not lead to charge effects; slip is a common phenomenon; metals are malleable.

The **free electron gas theory or Drude–Lorentz (D-L) theory** also explains in principle the nature of the attractive bonding forces which hold the metallic ions (the metal) together: the crystal is held together by electrostatic forces of attraction between the positively charged metal ions and the non-localized, negatively charged electrons - the electron gas. The theory in its original form assumes that the classical kinetic theory of gases is applicable to the *electron gas* ; mutual repulsion between electrons was ignored and the electrons were expected to have velocities which are temperature dependent according to a Maxwell-Boltzmann distribution law.

While the Drude-Lorentz theory of metallic bonding was considered a useful model, several shortcomings soon became apparent. The most notable failure consisted of the unexplainable discrepancy between the observed and predicted specific heats of metals (energy in the form of heat, required to increase the temperature of 1 g of a given metal by $1^{\circ}\mathrm{C}$). The D-L theory predicted much larger specific heats than are observed (because the Maxwell-Boltzmann energy distribution has no restrictions as to the number of species allowed to have exactly the same energy). [If there are restrictions as to the number of electrons with identical energy (Pauli exclusion principle!), we have to apply a different form of statistics (Fermi-Dirac statistics).]

1.3.2: ENERGY BAND THEORY BASED ON FORMATION OF MOLECULAR ORBITALS

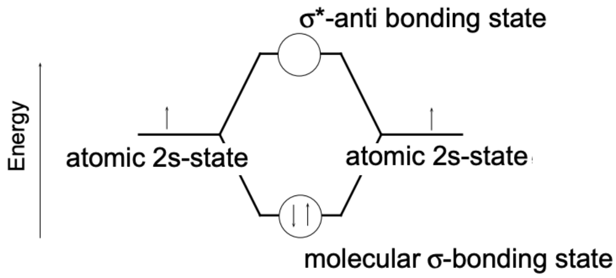
A different model, and one that is more closely related to the models of the chemical bond discussed earlier, is the *band model*. This model, proposed by Bloch before the development of the molecular-orbital approach to chemical bonding, is actually a molecular-orbital model of metallic crystals. The orbitals characteristic of the whole crystal are obtained as linear combinations of the atomic orbitals of the individual atoms.

From the large electrical conductivity of metals, it appears that at least some of the electrons can move freely through the bulk of the metal. Since even lithium with only one valence electron has eight nearest neighbors (crystallizes in a body-centered cubic lattice), it is clear that the atoms can not be bonded to each other by localized electron-pair bonds (for in that case the lithium atom, which altogether has only three electrons, would have to supply eight or even fourteen valence electrons to establish bonding with the nearest and next-to-nearest neighbor atoms). The fact that in a metal lattice one atom can simultaneously interact with a large number of others can be explained by considering that metals constitute an extreme example of *delocalized bonding*.

Conditions in metals are not as easily assessed as in organic hydrocarbon chains because metal lattices are three-dimensional structures. However, several important results from the theory of metallic bonding can be understood on a highly simplified model in which the three-dimensional lattice is replaced by a one-dimensional system. Consider the formation of a linear array of lithium atoms from individual lithium atoms:

$$\mathrm{Li} \rightarrow \mathrm{Li-Li} \rightarrow \mathrm{Li-Li-Li} \rightarrow \mathrm{Li-Li-Li-Li} \rightarrow \ldots \tag{1.3.1}$$

The first stage is the formation of a lithium molecule, $\mathrm{Li_2}$, which is comparable to the hydrogen molecule, $\mathrm{H_2}$. The two lithium atoms are bound together by a pair of valence electrons; each lithium atom supplies its 2s-electron which, through orbital overlap, forms a covalent molecular bond (fig. 2). The molecule formed occurs in lithium vapor and differs from the $\mathrm{H_2}$ molecule only by its greater interatomic distance ($\mathrm{Li-Li} = 2.67 \times 10^{-10}\ \mathrm{m}, \mathrm{H-H} = 0.75 \times 10^{-10}\ \mathrm{m}$) and smaller energy of formation. The larger separation and the consequent reduction in bond energy can be attributed to the size of the $\mathrm{Li^+}$ atomic core.



Schematic presentation of σ-bond formation in lithium, resulting from atomic orbital overlap.

Figure 2 Formation of $\mathrm{Li_2}$ molecule

In the determination of molecular orbital states by **linear combination of atomic orbitals** (LCAO) we obtain more than one solution from the Schrödinger equation. We have so far concentrated mostly on the low energy states, leading to σ or π bonds. We have largely ignored the so-called *antibonding states* which in covalent molecules have energies higher than the original energy states of the isolated reaction partners (presently Li) and, therefore, remain unoccupied (or empty) in two-atomic molecules. In any multi-atom system (such as a piece of metal), the total number of molecular orbital states (electronic states) is always the same as the total number of original atomic states (conservation of electronic states). However, not all of these states are necessarily occupied by electrons.

Consider the hypothetical linear molecule $\mathrm{Li_3}$. Since the valence electron cloud is spherical, the central lithium atom can not give preference to either of its neighbors. The three atomic valence electron clouds overlap to form one continuous distribution and two others with nodes (antibonding states), i.e., three molecular orbitals in all (Fig. 3).

As the length of the chain is increased, the number of electronic states into which the atomic $2s$ state splits also increases, *the number of states always equaling the number of atoms*. The same occurs when lithium chains are placed side-by-side or stacked on top of each other, so that finally the space lattice of the lithium crystal is obtained. It is of great significance that these electronic states have energies which are bounded by an upper and lower limiting value (see fig. 4). Within these limits the states form an *energy band* of closely spaced values (one gram of lithium contains nearly 10^{23} atoms). Similarly, energy bands can also result from overlapping p and d orbitals. The electronic states (orbitals) within an energy band are filled progressively by pairs of electrons in the same way that the orbitals of an atom were filled in accordance with the Pauli principle. This means that for lithium the electronic states of the 2s band will be exactly half-filled.

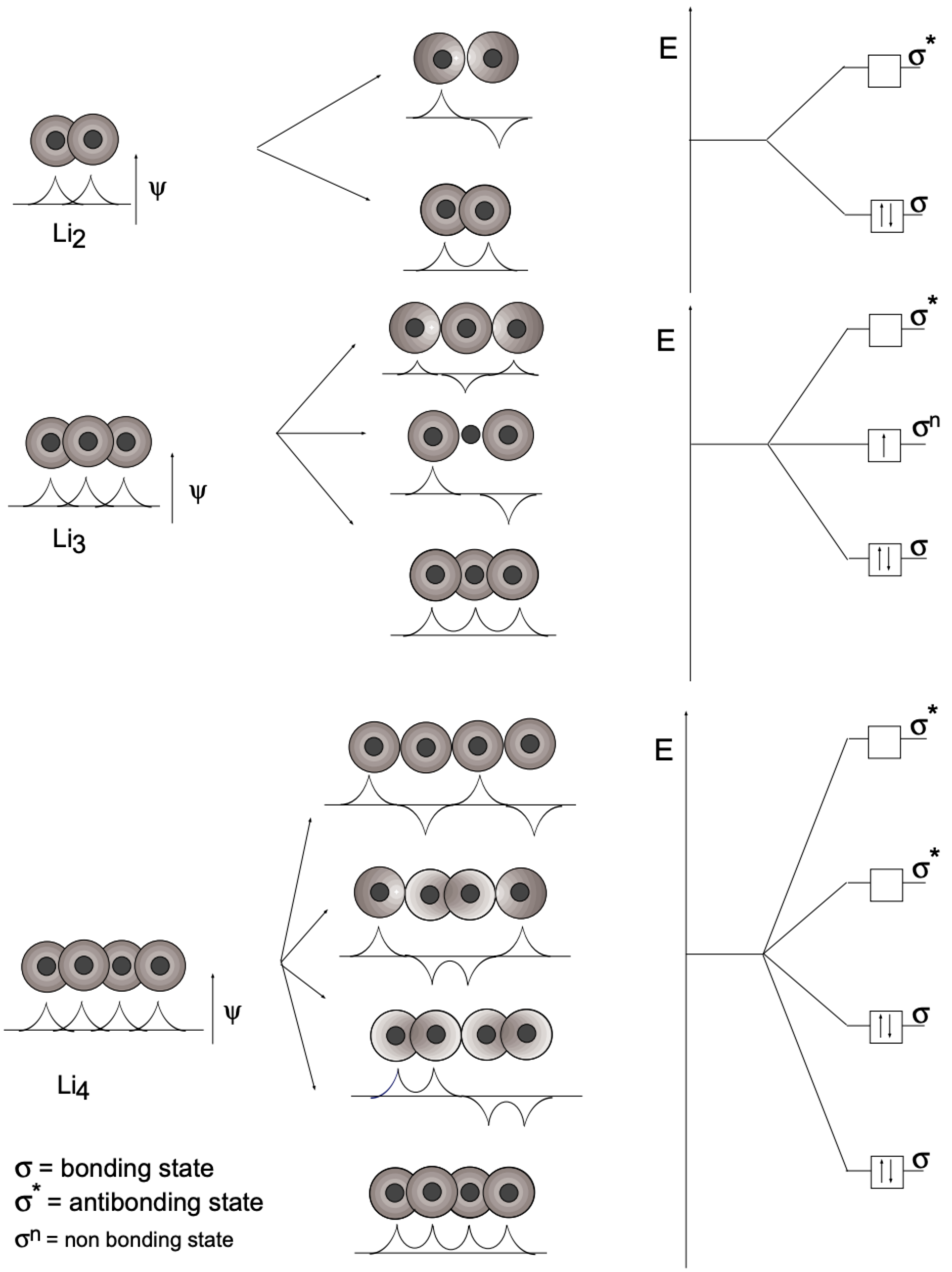


Figure 3 Formation of molecular chains of lithium atoms.

It is of interest to consider why lithium atoms or $\mathrm{Li_2}$ molecules combine to form a metal lattice. In the lithium lattice the smallest distance between neighboring atoms is 3.03×10^{-10} m, which is larger than in the $\mathrm{Li_2}$ molecule. This reflects the fact that bonds between pairs of atoms in the metal are weaker than they are in the molecule. Nevertheless, the metallic form of lithium is more stable than the molecular form because in the metal one atom has many more neighbors than in the $\mathrm{Li_2}$ molecule. As a result, the binding energy per gram atom of lithium (i.e., per 6.92 g of lithium) is 163 kJ for the metal lattice, but only 56 kJ for one mole of molecule.

> The possibility of hybridization (first advanced by L. Pauling to explain metallic bonding) is also a likely factor for the formation of metallic bonds. Thus strong bonds can be formed when the valence electron clouds become concentrated along the direction in which the bonding partners are situated. According to Pauling the situation can be described by *mesomeric* limiting formulae, just as in the theory of unsaturated carbon compounds. One reason given for hydrogen not forming a metal is its inability to hybridize.

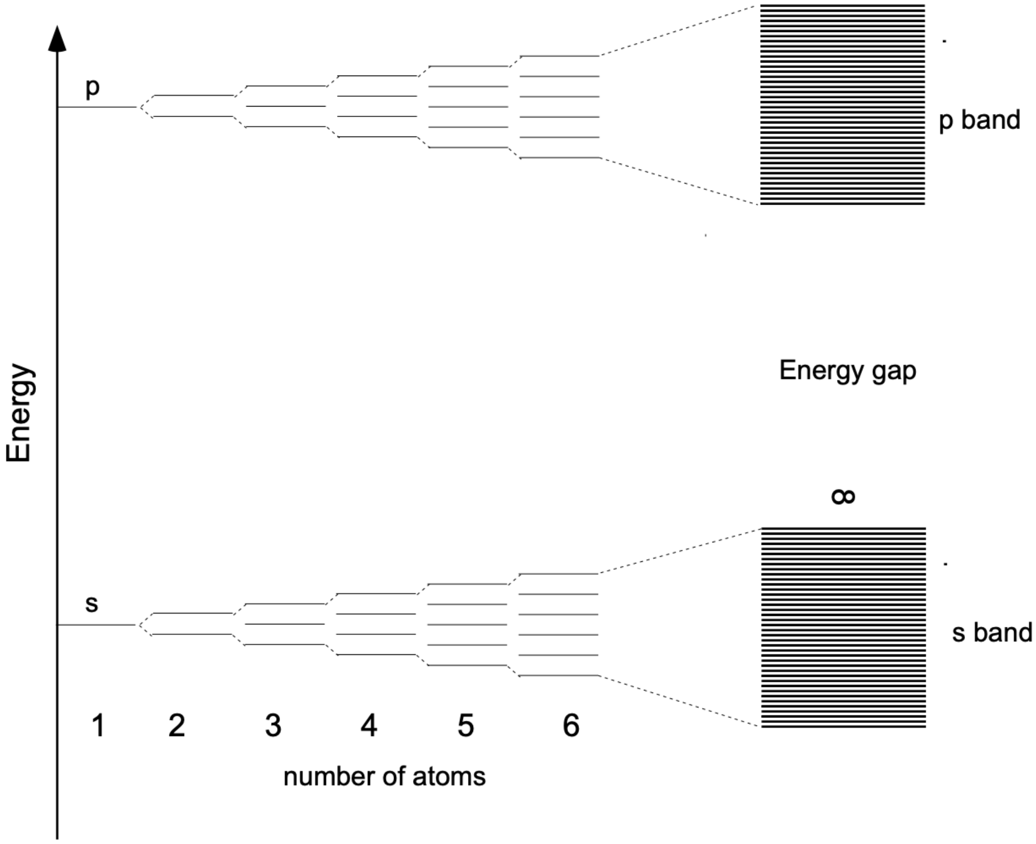


Figure 4 Formation of energy bands from energy levels of constituent atoms

The appearance of bands of allowed electron energies relates to the overlap of electron ψ functions. The width of each energy band is a function of the crystal structure because it determines the number of nearest neighbors in the crystal. Different metal atoms with the same valence, particularly elements in the same group of the periodic table, can often replace each other in arbitrary proportions without altering either the lattice type or the structure of the energy bands. This explains why such metals tend to form a complete series of *solid solutions*. Metallic alloys consist of such solid solutions or of heterogeneous mixtures of such solutions. Within certain limits, even metal atoms of different valence can be interchanged in a lattice.

1.3.2.1: Structure of Metals

According to the above considerations the band structure of Li metal can be represented as shown in fig. 5. According to previous reasoning, the 2 s band has N states ($\mathrm{N}=$ number of atoms) and accommodates $n2s$ electrons (where n is the number of electrons per atom in the 2 s state times N). Thus, this band has only half of the states filled since each state can accommodate two electrons of opposite spin (Pauli exclusion principle). In accordance with the Aufbau principle, the lowest energy states of the band are filled first and the upper states remain empty - but can readily be occupied by electrons upon thermal excitation or the application of an electric field. Since the width of the energy band is of the order of a few volts, spacings of states within the band are of the order of $\sim 10^{-20}\mathrm{eV}\left(1\mathrm{eV}=1.6\times 10^{-19}\mathrm{~J}\right)$, electrons can readily acquire the energy necessary to move into excited states, be accelerated, and move through the metal as *conducting electrons*. Partly filled bands thus constitute *conduction bands*.

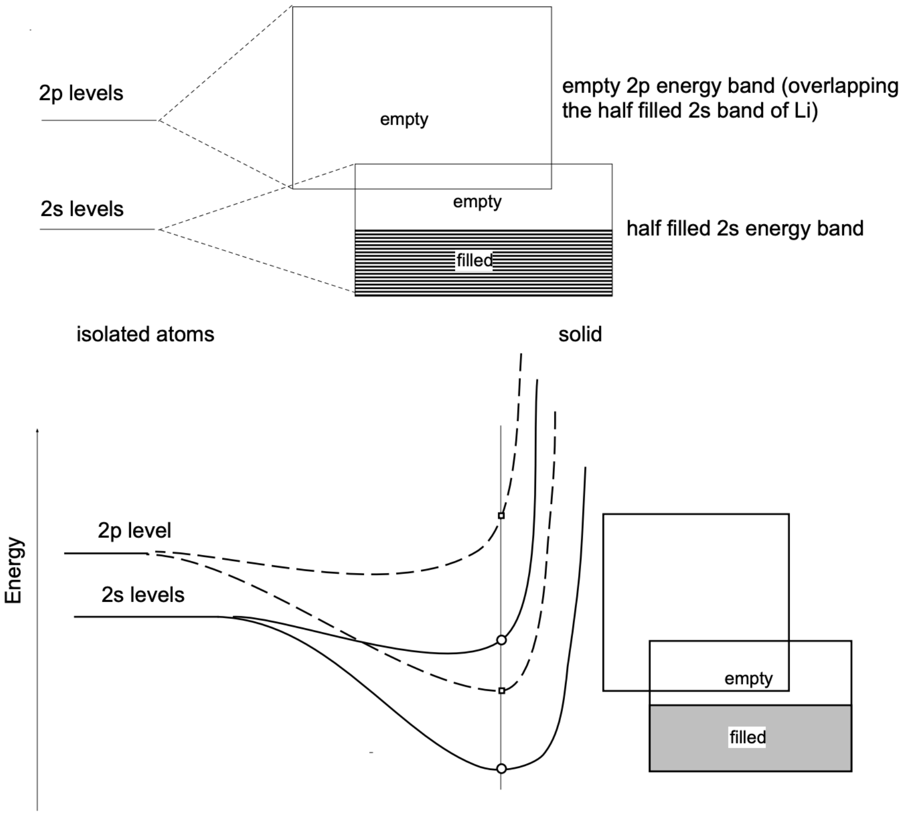


Fig. 5 Schematic energy band configuration for Li .

The conduction mechanism in Mg, for example, appears complicated by the fact that each $3s$ state of the valence shell in the atoms is doubly occupied $\left(3s^2\right)$. Thus the $3s$ band must be filled completely and no electronic conduction would in principle be expected. Electronic conduction, however, is observed because of a partial overlap of the $3s$ and the empty $3p$ bands. With this overlap, electrons can be activated into empty $3p$ states and exhibit conduction, as in the partly filled s band in Li.

1.3.2.2: Structure of Insulators and Semiconductors (Molecular Crystals)

The same band model can also account for the lack of conductivity in covalent crystals, such as diamond. In the diamond crystal, with a two-electron bond between every atom and each of its neighbors, the bonding molecular orbitals form a band at much lower energies than the energy of the atomic sp^3 hybrid orbitals, and the antibonding orbitals form a band at energies much higher than the energy of the atomic orbitals. Also, since each atom contributes four orbitals and four electrons, there are just enough electrons to fill the bonding orbitals (corresponding to an electron pair bond joining every atom to each of its neighbors) and the only vacant orbitals are those in the high energy band of antibonding orbitals (see fig. 6).

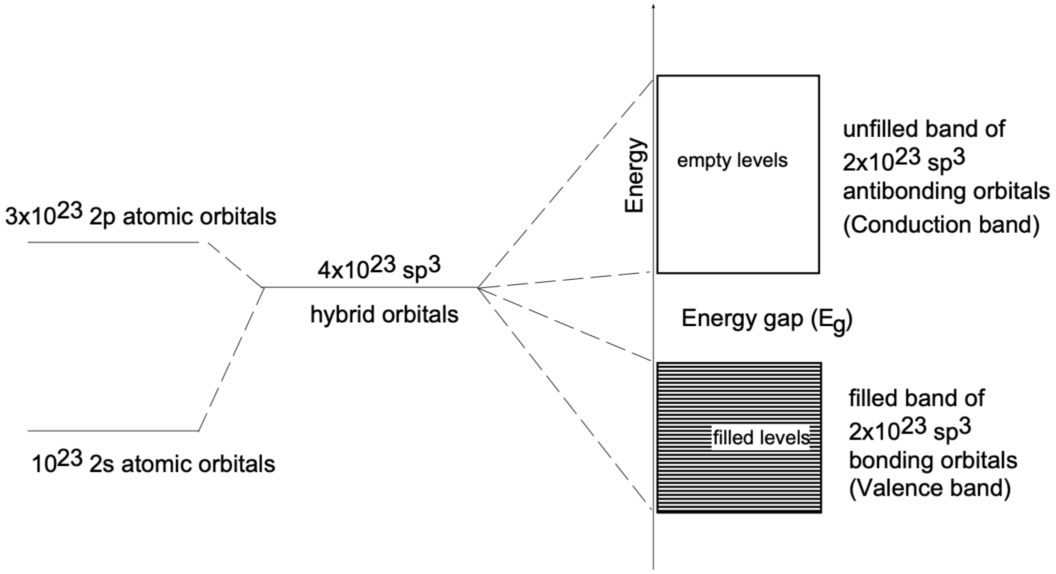


Fig. 6 Band structure of insulators and semiconductors (molecular crystals); the conditions depicted reflect a molar crystal of carbon (diamond).

Both insulators and semiconductors have the same basic band structure – the primary difference is the *width* of the forbidden energy gap $(\mathrm{E_g})$ between the valence and the conduction band.

Insulators, generically, are materials with very high resistivity (see Table I), comprising glasses, polymers, refractories, composites, liquids and gases. In the present context, an insulator is a molecular crystal, such as diamond (C) or sapphire, with a band gap (E_g) in excess of $4\mathrm{eV}$ (arbitrary value). Generally such materials will not conduct electricity since their valence band is filled and the energy required to transfer electrons from the valence band to the empty conduction band is far in excess of both the thermal energies at room temperature and the energy provided by radiation of the visible spectrum ($2\mathrm{eV}$). Therefore, insulators (in single crystal form) are normally transparent (colorless); however, if light is excessively or totally scattered at internal heterogeneities (such as grain boundaries), they may be translucent and even opaque. It should also be recognized that impurities $(\mathrm{Cr}^{3+}$ in $\mathrm{Al_2O_3})$ or particular point defects (color centers) may impart a color to the transparent insulator crystals. The color arises because of partial absorption of white light and selective transmission of the other portions of the visible spectrum.

Semiconductors: The conventional semiconductors, silicon (Si) and germanium (Ge), have a band gap $(\mathrm{E_g})$ of 1.1 and $0.7\mathrm{eV}$ respectively and therefore absorb visible radiation; they are opaque (fig. 7). Considering the statistical nature of the thermal energy distribution in the solid matrix (Maxwell-Boltzmann), a significant number of electrons in the valence band will, at room temperature, acquire sufficient energy to cross the existing energy gap and thus provide for *semiconductivity*. The conductivity will therefore increase with temperature, contrary to metallic systems, until electron scattering effects, due to increased lattice vibrations (which decrease the mobility of electrons), begin to dominate.

The value of semiconductors for solid state device fabrication lies in the fact that the number and type of conducting electric charge carriers [electrons are n-type (negative), holes are p-type (positive)] can be controlled through incorporation of appropriate *dopant elements*. Thus the substitutional incorporation of Group V elements (Sb, As, P) provides for shallow donor levels in the band gap at about $0.01\mathrm{eV}$ from the conduction band. The substitutional incorporation of Group III elements (B, Al) generates *acceptor levels* in the band gap at about $0.01\mathrm{eV}$ from the valence band. The two types of impurities are almost completely ionized at room temperature and give rise to *extrinsic* n-type and p-type conductivity – the basis for the formation of *junction devices* such as diodes and transistors (fig. 8).

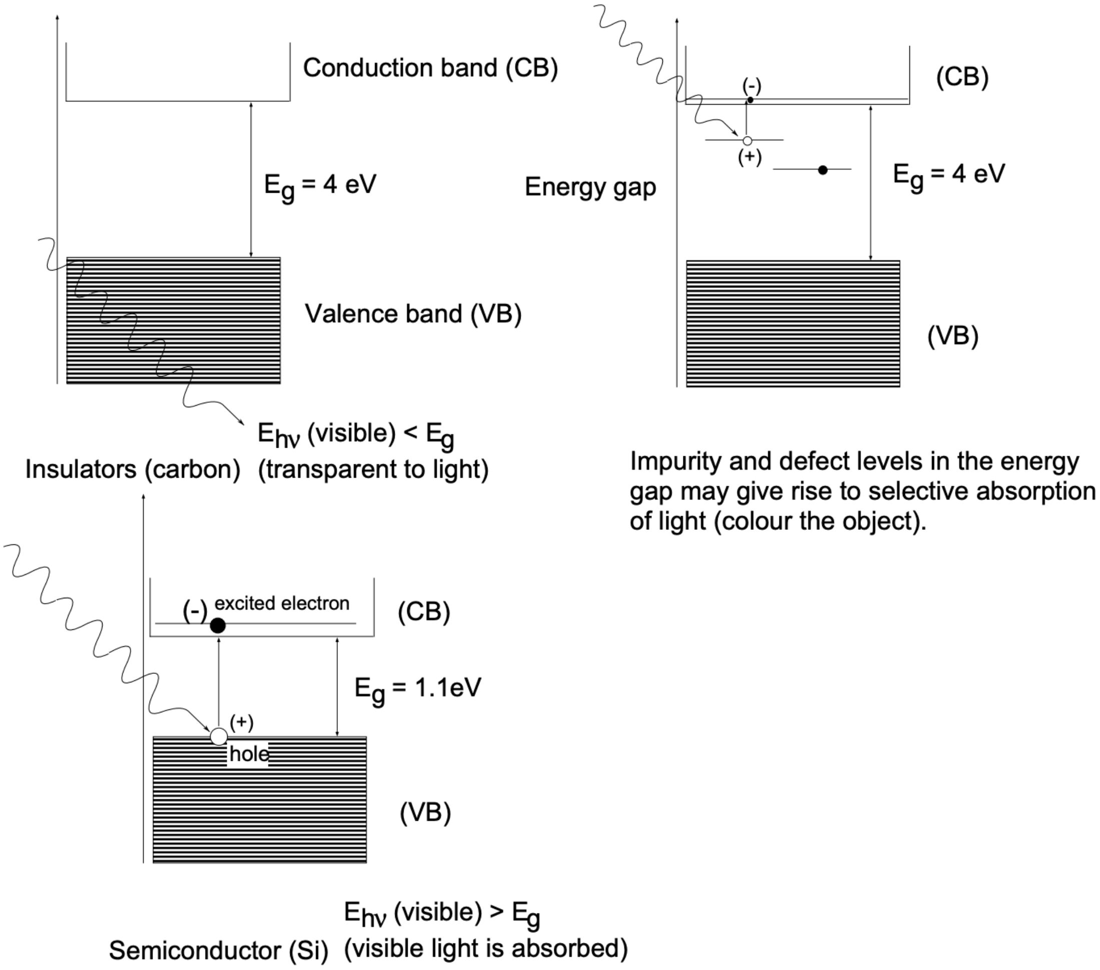


Fig. 7 Optical behavior of insulators and semiconductors

Of increasing importance are compound *III-V (adamantine) semiconductors*, such as GaAs, InSb, InP and GaP (compounds of Group III and Group V elements). Together these compounds provide eight valence electrons and, by sp^3 hybridization, are able to form a diamond-like, covalent crystal structure with semiconductor properties. These

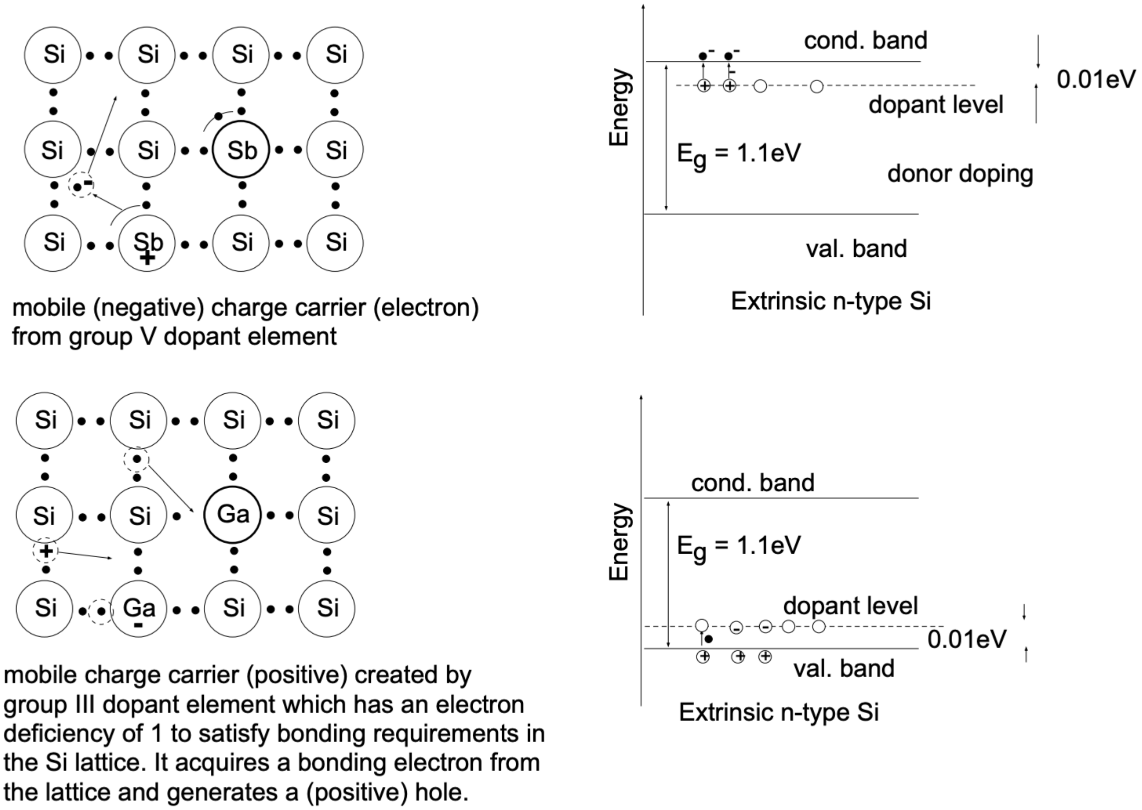


Fig. 8 Extrinsic p- and n-type semiconductors.

compounds (GaAs, for example) exhibit electron mobilities which are higher than those of silicon and, therefore, are of considerable interest for advanced device technology.

Table I. ELECTRICAL RESISTIVITIES OF METALS AND NONMETALS AT $20^\circ C^*$

Metals	Resistivity, 10^{-8} ohm–m**	Nonmetals	Resistivity, ohm–m**
Silver	1.6	Semiconductors	
Copper	1.67	Silicon	1000.0
Gold	2.3	Germanium	0.09
Aluminum	2.69	Insulators	
Magnesium	4.4	Diamond	10^{10}–10^{11}
Sodium	4.61	Quartz	1.2×10^{12}
Tungsten	5.5	Ebonite	2×10^{13}
Zinc	5.92	Sulfur	4×10^{13}
Cobalt	6.24	Mica	9×10^{13}
Nickel	6.84	Selenium	2×10^{14}
Cadmium	7.4	Paraffin wax	3×10^{16}
Iron	9.71		
Tin	12.8		
Lead	20.6		
Uranium	29		
Zirconium	41		
Manganin	44		
Titanium	55		
Lanthanum	59		
96%Iron–4%Si	62		
Cerium	78		
Nichrome	100		

*From *American Institute of Physics Handbook*, Dwight E. Gray, ed. McGraw-Hill, New York (1963), pp. 4–90; 9–38.

**Note the different units in the two columns

APPENDIX

Approximate Energy Values for Some Events and Reactions

Solar Energy Emission	$\sim 10^{30}$ kJ/ day
Convertible Solar Energy on Earth	$\sim 10^{18}$ kJ/ year
Energy Consumption on Earth	$\sim 8 \times 10^{17}$ kJ/ year
Super-Nova Explosion	$\sim 10^{39}$ kJ
100 Mega-Ton H-Bomb Explosion	$\sim 10^{15}$ kJ
Atlas Blast-Off	$\sim 10^{8}$ kJ
Lethal X-Ray Dose	~ 1 kJ
25¢ Piece Falling from Pocket	$\sim 10^{-4}$ kJ
Bee's Wing Beat	$\sim 10^{-6}$ kJ
Moonlight/Face/Second	$\sim 10^{-8}$ kJ

1.4: The Nature of Crystalline Solids

In an assembly of atoms or molecules a solid phase is formed whenever the interatomic (intermolecular) attractive forces significantly exceed the disruptive thermal forces and thus restrict the mobility of atoms, forcing them into more-or-less fixed positions. From energy considerations it is evident (as discussed in LN-2) that in such solids the atoms or molecules will always attempt to assume highly ordered structures which are characterized by *symmetry*. Depending on the nature of the acting interatomic forces, all solids may be subdivided into:

a. Ionic solids (NaCl)
b. Covalent solids (Diamond)
c. Metallic solids (Fe, Ni, etc.)
d. Van der Waals solids (ice, solid He)

Solids as we encounter them in nature may or may not reflect the internally ordered arrangement in their appearance. We find, for example, well-formed quartz crystals, garnets, diamonds and snowflakes which are all characterized by flat bounding planes which intersect at characteristic angles. On the other hand, we also observe rounded stones and man-made cast solid objects with no external evidence of internal order (fig. 1).

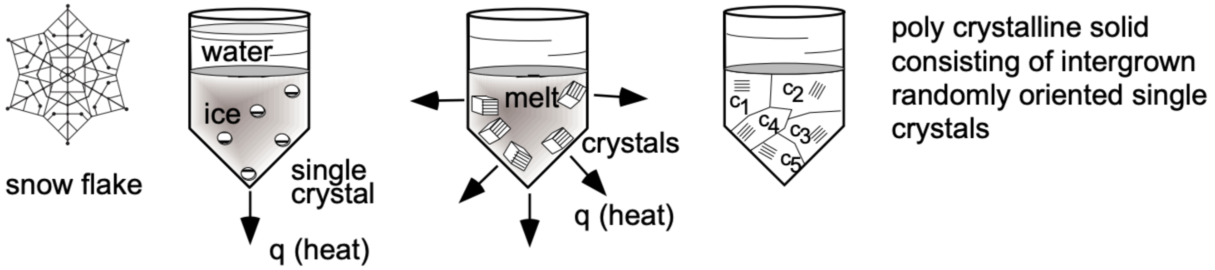


Figure 1 Crystals, internal order and external appearance

To understand the external appearance of the solid state it is necessary to consider the formation of solids from different *phases*. Solids, for example, are formed upon cooling of liquids (melts) - by freezing or solidification; this solidification process normally proceeds in total confinement and the resulting “cast” structure will have an external appearance which reflects in detail the confining geometry (and not the internal order). Moreover, depending on solidification conditions, the solid body may be either a *single crystal* or *polycrystalline*. Polycrystalline solids (in excess of 95% of the solid state encountered) may be thought of as an assembly of microscopic single crystals with random orientation held together like a maze structure by the interwoven irregular shapes of the individual crystals.

A typical example of an "unconfined" phase transformation is the formation of snowflakes where the external boundaries of the solid have assumed *crystalline* appearance, reflecting in detail the internally ordered molecular (H_2O) arrangement. Another unconfined formation of a solid is precipitation from solution (sugar crystals, $CuSO_4$ and the like). Similarly, the formation of crystals from the vapor phase leads to bodies which externally reflect elements of internal order.

1.4.1: CRYSTAL STRUCTURE

From the earlier discussion it should be apparent that, when strong interatomic forces exist, atoms tend to pack closely together - the closeness of packing being particularly pronounced in the solid state. In this case atoms can be regarded as hard spheres and the problem of close packing can be treated as one in which the whole assembly has a tendency toward efficient packing. A little thought or a few simple experiments with ping-pong balls quickly convince us that regular arrangements of the spheres generally lead to more compact assemblies than irregular arrangements (fig. 2). The same principle applies to arrangement of atoms in the solid state. Where strong attractive forces are exerted we find that the atoms or molecules concerned arrange themselves in a regular three-dimensional pattern. It is this regularity which is the basis of crystallinity in materials: i.e., *a crystal structure is nothing more than an orderly array of atoms or molecules*. This definition of a crystal is distinct from the popular concept based on observation of external symmetry of crystals, often seen during the study of elementary chemistry, in which some crystals appear cubic, others needle-shaped and so on. The regular external shape is obtained only when the conditions of crystallization are favorable to development of flat, geometric faces. In most instances, particularly with metals, these conditions are absent, and the crystals have irregular surfaces even though the internal arrangement is perfectly geometric.

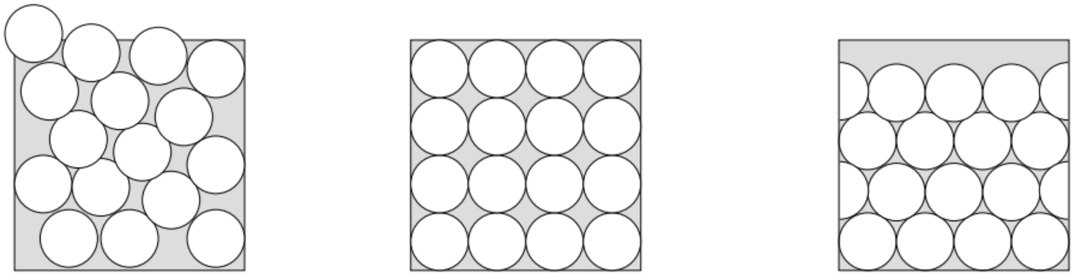


Figure 2 The packing density of ordered systems.

Atomic arrays in crystals are conveniently described with respect to a three-dimensional net of straight lines. Consider a lattice of lines, as in fig. 3, dividing space into equal-sized prisms which stand side-by-side with all faces in contact, thereby filling all space and leaving no voids. The intersections of these lines are points of a **space lattice**, i.e., a *geometrical abstraction* which is useful as a reference in describing and correlating symmetry of actual crystals. These lattice points are of fundamental importance in describing crystals for they may be the positions occupied by individual atoms in crystals or they may be points about which several atoms are clustered. Since prisms of many different shapes can be drawn through the points of a space lattice to partition it into cells, the manner in which the network of reference lines is drawn is arbitrary. It is not necessary that the lines be drawn so that atoms lie only at corners of unit prisms. In fact, it is more convenient to describe some crystals with respect to prisms in which atoms lie at prism centers or at the centers of prism faces as well as at prism corners.

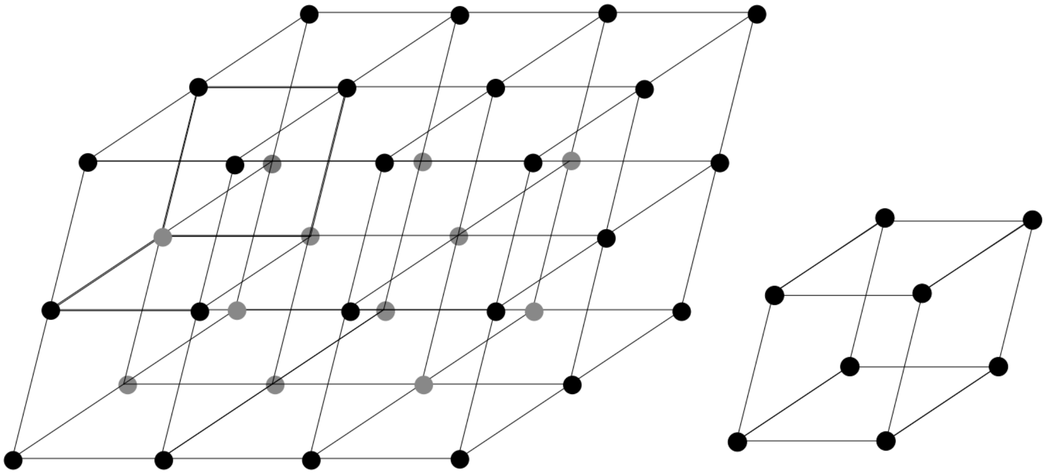


Figure 3 The space lattice

An important characteristic of a space lattice is that every point has identical surroundings: the grouping of lattice points about any given point is identical to the grouping about any other point in the lattice. In other words, if we could move about in the lattice, we would not be able to distinguish one point from another because rows and planes near each point would be identical. If we were to wander among the atoms of a solid metal or chemical compound, we would find the view from any lattice point exactly the same as that from any other.

There are fourteen space lattices (fig. 4). That is, no more than fourteen ways can be found in which points can be arranged in space so that each point has identical surroundings. Of course, there are many more than fourteen ways in which atoms can be arranged in actual crystals; thus there are a great number of crystal *structures*. Too often the term “lattice” is loosely used as a synonym for “structure”, an incorrect practice which is frequently confusing. The distinction can be clearly seen if we remember that a space lattice is an array of points in space. It is a geometrical abstraction which is useful only as a reference in describing and correlating symmetry of actual crystals. A crystal structure, however, is the arrangement of atoms or molecules which actually exists in a crystal. It is a dynamic, rather than a static, arrangement and is subject to many imperfections. Although any crystal structure has an inherent symmetry which corresponds to one of the fourteen space lattices, one, two or several atoms or molecules in the crystal structure may be associated with each point of the space lattice. This symmetry can be maintained with an infinite number of different actual arrangements of atoms - making possible an endless number of crystal structures.

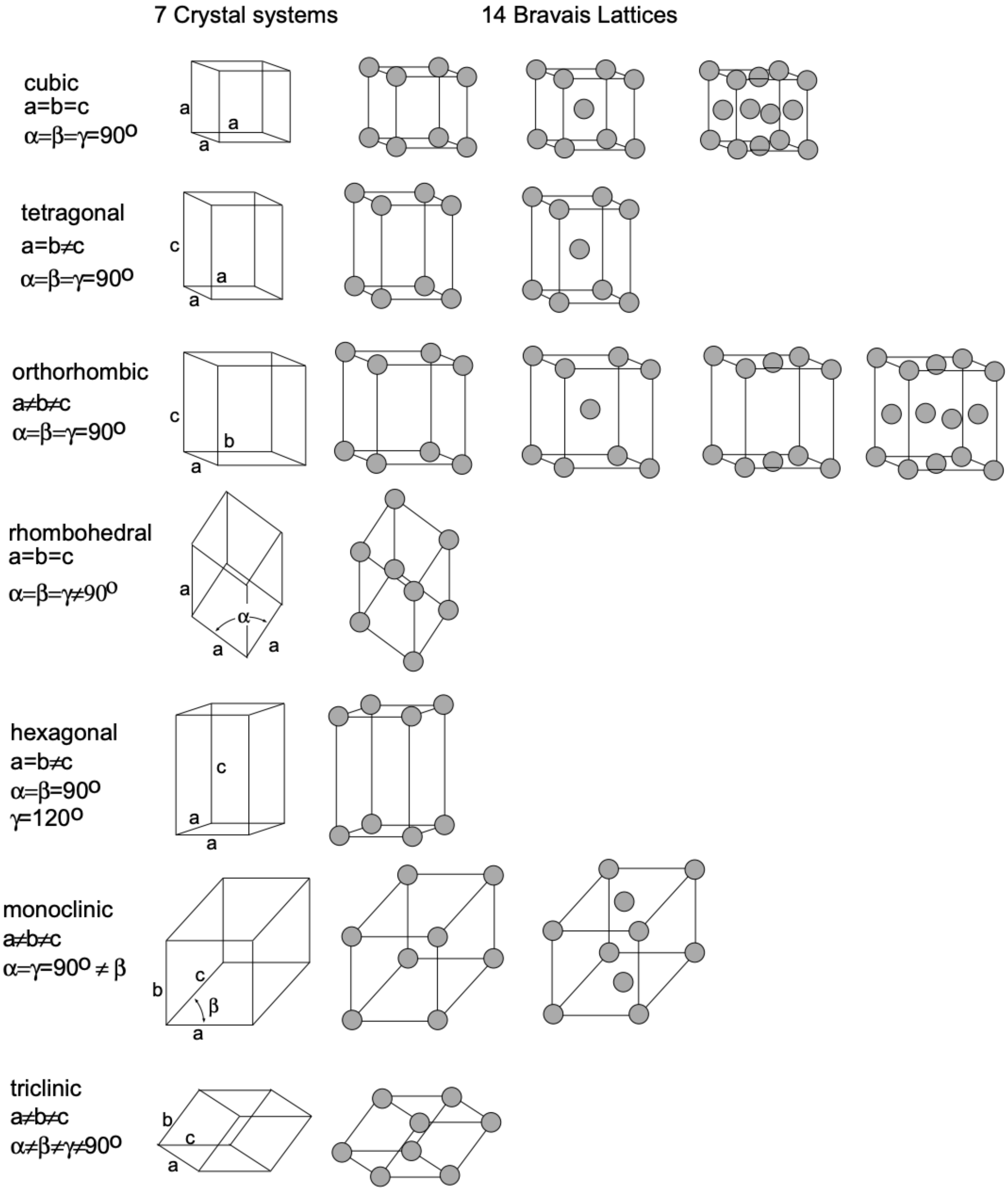


Figure 4 The 7 crystal systems and the 14 Bravais lattices

To specify a given arrangement of points in a space lattice, it is customary to identify a unit cell with a set of coordinate axes, chosen to have an origin at one of the lattice points (fig. 5). In a cubic lattice, for example, we choose three axes of equal length that are mutually perpendicular and form three edges of a cube. Each space lattice has some convenient set of axes, but they are not necessarily equal in length or orthogonal. Seven different systems of axes are used in crystallography, each possessing certain characteristics as to equality of angles and equality of lengths. These seven crystal systems are tabulated in Table I (to be considered in conjunction with fig. 4).

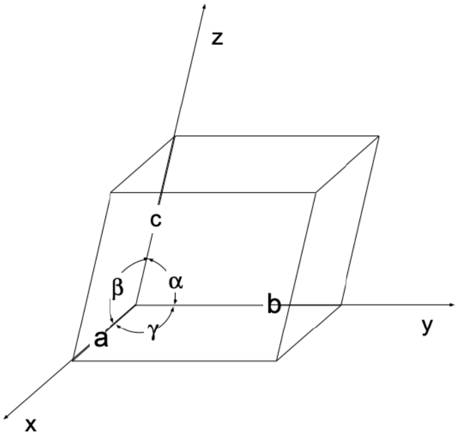


Figure 5 Specification of Unit Cell parameters

Table I. The Seven Crystal Systems

System	Parameters	Interaxial Angles
	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Triclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = \gamma$
Orthorhombic	$a = b \neq c$	$\alpha = \beta = \gamma$
Tetragonal	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$
Hexagonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Rhombohedral	$a = ch$	

The network of lines through the points of a space lattice (fig. 3) divides it into *unit cells* (see also fig. 4). Each unit cell in a space lattice is identical in size, shape and orientation to every other unit cell. It is the building block from which the crystal is constructed by repetition in three dimensions. The unit cells of the fourteen space lattices are shown in fig. 4. All crystal structures are based on these fourteen arrangements.

The body-centered cubic, face-centered cubic and hexagonal lattices are common and of prime importance in metals. Some of the metals associated with nuclear applications, such as uranium and plutonium, have crystal structures which are more complicated than these three relatively simple types. In general, crystalline ceramics also are more complex.

1.4.2: CELLS VS PRIMITIVE CELLS

In the literature we often find reference to **unit cells** and to **primitive cells**. The primitive cell may be defined as a geometrical shape which, when repeated indefinitely in three dimensions, will fill all space and is the equivalent of one atom. The unit cell differs from the primitive cell in that it is not restricted to being the equivalent of one atom. In some cases the two coincide. For instance, in fig. 4 all fourteen space lattices are shown by their unit cells. Of these fourteen, only seven (which are those?) are also primitive cells.

Primitive cells are drawn with lattice points at all corners, and each primitive cell contains the equivalent of one atom. For instance, a simple cubic unit cell has an atom at each corner. However, at any of these given corners, this atom must be shared with seven other identical cubes which fill the volume surrounding this point. Thus there is effectively only 1/8 of the atom which can be assigned to that particular unit cell. Since there are eight corners in a cube, there is the equivalent of one atom, and thus the primitive cell and unit cell coincide.

Continuing, consider the *body-centered cubic* (BCC) lattice. In this case there is one atom at the center of the cube and one atom contributed by the eight corners. This cell, then, has two atoms and, to avoid confusion, should be termed a unit cell. In the *face-centered cubic* lattice there are six face atoms, but each face atom is shared by two cells. Consequently, each face contributes 1/2 an atom. The faces thus contribute three atoms and the corners one, for a total of four atoms in the unit cell. The face-centered cubic structure (FCC) can also be considered as four interpenetrating simple cubic cells.

In the study of crystals the primitive cell has limited use because the unit cell more clearly demonstrates the symmetrical features of a lattice. In other words, the unit cell can usually be visualized readily whereas the primitive cell cannot. For example, the cubic nature of the face-centered cubic lattice is immediately apparent in the unit cell, but it is not nearly so obvious in the rhombohedral primitive cell.

1.4.3: PACKING OF ATOMS

A crystal structure is a regular array of atoms arranged on one of the fourteen space lattices. The least complicated crystal structures are those having a single atom at each lattice point. Polonium has the simplest structure, being simple cubic. In normal metals, the atoms (or positive ions) are held together by a cloud of free electrons so that each atom tends to be attracted equally and indiscriminately to all its geometrically nearest neighbors by the free electrons passing between them. This condition fosters the formation of closely packed structures of the types which can be demonstrated by efficiently packing uniformly-sized spheres into a given volume.

You can gain a better grasp of packing by conducting an experiment as follows. Assume we have a quantity of small spheres which we are required to efficiently pack into a box (a ‘two-dimensional’ approach can be made using a handful of pennies). After some shuffling, it is obvious that the closest possible packing is obtained when the spheres are in contact and their centers occupy positions which correspond to the apices of equilateral triangles (fig. 6). It is also evident that there are two sets of triangles – one set with vertices pointing away from the observer (points up) and the other set with vertices pointing toward the observer (points down).

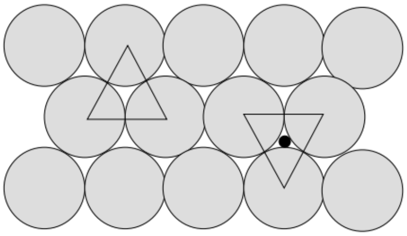


Figure 6 Close packed atomic arrangements

When a second layer is added, there is closest-packing if the spheres in this new layer rest in the hollows formed by the spheres of the first layer. The centers of the spheres in the second layer will lie above the centers of the points-up triangles or above the centers of the points-down triangles, but not both simultaneously. Which set is used is immaterial. For our discussion, however, assume the second layer is centered on the points-up triangles.

When we start adding a third layer, the spheres will again rest in the hollows formed by the spheres in the second layer. And again we have the option of placing the third layer on the points-up or on the points-down triangles. If we center the third layer on the points-down triangles, we find the third layer is directly above the first layer. If additional layers are added using an alternate stacking sequence (i.e., alternately centering the layers on the points-up and the points-down triangles), the sequence can be written as ABABABAB. . . This arrangement of spheres, translated to an arrangement of atoms, is the hexagonal close-packed (HCP) structure - very important, but not discussed in detail here.

Many elements having covalent bonding form arrangements in which the coordination number is (8–N), where N is the number of valence electrons. What, then, is the coordination number of the HCP structure just demonstrated? The geometry of the structure shows that any one atom has twelve equidistant neighbors. It is apparent that if, in any layer, a given sphere is placed in the adjoining layer, it fits in the hollow formed by three spheres and consequently is tangent to three spheres in the adjoining layer. Thus any given atom in the HCP structure is tangent to twelve other atoms – six in its own layer and three each in two adjoining layers.

When the third layer of spheres was added in the above discussion, we assumed this layer was centered on the points-down triangles of the second layer. What happens if the centers of the points-up triangles of the second layer are used instead? The distribution of spheres in the third layer is the same as in the first two layers, but does not lie directly above either of these two layers. If a fourth layer is added, centered on the points-up triangles of the third layer, we find the fourth layer is directly above the first layer and duplicates it completely. The stacking sequence for this structure can be written as ABCABCABC. . . This arrangement has the same density of packing and the same coordination number as the HCP structure. However, it is the face-centered cubic (FCC) structure.

The HCP and FCC crystal structures have the same density of packing and the same coordination number. Therefore we might expect the behavior of the two HCP and FCC structures to be very much alike with regard to physical and mechanical properties. This, however, in most instances is not the case.

The maximum density of packing is found only in the HCP and FCC crystal structures. Why the metallic bond does not always produce one or the other of these two densest arrangements of atoms is as yet subject of intensive studies. The BCC unit cell contains two atoms, and the coordination number is eight. There is partial compensation for this in the fact that there are six next-nearest neighbors at distances only slightly greater than that of the eight nearest neighbors. Some characteristics of cubic structures are given in Table II.

An interesting example of the type of crystal structure obtained in covalently bonded elements which obey the (8–N) coordination number rule (where N is the number of valence electrons) is the diamond structure. This structure is found in carbon, germanium, silicon, and tin at low temperatures and in certain compounds. Each atom has four nearest neighbors – a configuration that is variously called diamond cubic, body-centered tetrahedral or tetrahedral cubic.

TABLE II. Characteristics of Cubic Lattices

	Simple	Body-Centered	Face-Centered
Unit Cell Volume	a^3	a^3	a^3
Lattice Points Per Cell	1	2	4
Nearest Neighbor Distance	a	$\frac{a\sqrt{3}}{2}$	$\frac{a}{\sqrt{2}}$
Number of Nearest Neighbors	6	8	12
Second Nearest Neighbor Distance	$a\sqrt{2}$	a	a
Number of Second Neighbors	12	6	6

Many compounds crystallize in variations of cubic forms. Rock salt (NaCl), for example, is typical of many oxides, fluorides, chlorides, hydrides and carbides. It is sometimes considered as simple cubic with alternate Na and Cl atoms on the cube corners. Actually the structure is two interpenetrating FCC lattices – one of Na and the other of Cl – and the corner of one is located at point 1/2, 0, 0 of the other.

Many other oxides, fluorides and some intermetallic compounds have the fluorite $(\mathrm{CaF_2})$ structure. This is FCC with Ca at the cube corners and face centers and F at all quarter points along the cube diagonals.

1.4.4: LATTICE PLANES AND DIRECTIONS

It is desirable to have a system of notation for planes within a crystal or space lattice such that the system specifies orientation without giving position in space. *Miller indices* are used for this purpose. These indices are based on the intercepts of a plane with the three crystal axes - i.e., the three edges of the unit cell. The intercepts are measured in terms of the edge lengths or dimensions of the unit cell which are the unit distances from the origin along the three axes. For instance, the plane that cuts the x-axis at a distance from the origin equal to one-half the x-dimension of the cell is said to have an x-intercept equal to $1/2$, and if it cuts the y-axis at $1/2$ the y-dimension of the cell, the y-intercept is $1/2$, regardless of the relative magnitudes of the x - and y-dimensions. If a plane is parallel to an axis, it intercepts the axis at infinity.

To determine Miller indices (hkl) of a plane, we take the following steps:

1. Find the intercepts on the three axes in multiples or fractions of the edge lengths along each axis.
2. Determine the reciprocals of these numbers.
3. Reduce the reciprocals to the three smallest integers having the same ratio as the reciprocals.
4. Enclose these three integral numbers in parentheses, e.g., (hkl).

A cube has six equivalent faces. If we have a definite orientation and wish to discuss one specific plane of these six, it is possible to specify this plane by using the proper Miller indices. Parentheses are used around the Miller indices to signify a specific plane. On the other hand, it is often advantageous to talk about planes of a “form” – i.e., a family of equivalent planes such as the six faces of a cube. To do this it is customary to use the Miller indices, but to enclose them in curly brackets (braces). Thus the set of cube faces can be represented as $\{100\}$ in which

$$\{100\} = (100) + (010) + (001) + (\overline{100}) + (0\bar{1}0) + (00\bar{1})$$

This notation thus provides a shorthand scheme to avoid writing the indices for all six cube faces.

The utility of the scheme is even more evident in the case of the (110) planes – i.e., the dodecahedral planes (in a cubic system), where

$$\begin{aligned}\{110\} = &(110)+(101)+(011)+(\bar{1}10)+(\bar{1}01)+(0\bar{1}1)\\ &+(1\bar{1}0)+(10\bar{1})+(01\bar{1})+(\overline{110})+(\bar{1}0\bar{1})+(0\overline{11})\end{aligned}$$

The equivalent form for the orthorhombic system is

$$\begin{aligned}\{110\} &= (110)+(\overline{110})+(1\bar{1}0)+(\overline{110})\\ \{101\} &= (101)+(\bar{1}01)+(10\bar{1})+(\bar{1}0\bar{1})\\ \{011\} &= (011)+(0\bar{1}1)+(01\bar{1})+(0\overline{11})\end{aligned}$$

The octahedral planes for the cube are

$$\begin{aligned}\{111\} = &(111)+(\overline{1111})+(1\bar{1}1)+(11\bar{1})\\ &+(\overline{111})+(\overline{111\bar{1}})+(1\overline{11})+(\overline{111})\end{aligned}$$

Direction indices are defined in a different manner. A line is constructed through the origin of the crystal axis in the direction under consideration and the coordinates of a point on the line are determined in multiples of lattice parameters of the unit cell. The indices of the direction are taken as the smallest integers proportional to these coordinates and are closed in square brackets. For example, suppose the coordinates are $x = 3a, y = b$ and $z = c/2$, then the smallest integers proportional to these three numbers are 6, 2 and 1 and the line has a [621] direction. As further examples, the x-axis has direction indices [100], the y-axis [010] and the z-axis [001]. A face diagonal of the xy face of the unit cell has direction indices [110], and a body diagonal of the cell has direction indices [111]. Negative indices occur if any of the coordinates are negative. For example, the $-y$ axis has indices [010]. A full set of equivalent directions, i.e., directions of a form, are indicated by carets: $\langle uvw \rangle$.

1.5: X-rays and X-ray Diffraction

1.5.1: HISTORICAL INTRODUCTION

X-rays were discovered during the summer of 1895 by Wilhelm Röntgen at the University of Würtzburg (Germany). Röntgen was interested in the *cathode rays* (beams of electrons) developed in discharge tubes, but it is not clear exactly which aspects of cathode rays he intended to study. By chance he noticed that a fluorescent screen $\left(\mathrm{ZnS}+\mathrm{Mn}^{++}\right)$ lying on a table some distance from the discharge tube emitted a flash of light each time an electrical discharge was passed through the tube. Realizing that he had come upon something completely new, he devoted his energies to investigating the properties of the unknown ray " X " which produced this effect. The announcement of this discovery appeared in December 1895 as a concise ten page publication.

The announcement of the discovery of X-rays was received with great interest by the public. Röntgen himself prepared the first photographs of the bones in a living hand, and use of the radiation was quickly adopted in medicine. In the succeeding fifteen years, however, very few fundamental insights were gained into the nature of X-radiation. There was some indication that the rays were waves, but the evidence was not clear-cut and could be interpreted in several ways. Then, at the University of Munich in 1912, Max von Laue performed one of the most significant experiments of modern physics. At his suggestion, Paul Knipping (who had just completed a doctoral thesis with Röntgen) and Walter Friedrich (a newly appointed assistant to Sommerfeld) directed a beam of X-rays at a crystal of copper sulfate and attempted to record the scattered beams on a photographic plate. The first experiment was unsuccessful. The result of a second experiment was successful. They observed the presence of spots produced by diffracted X-ray beams grouped around a larger central spot where the incident X-ray beam struck the film. This experiment demonstrated conclusively that X-radiation consisted of waves and, further, that the crystals were composed of atoms arranged on a *space lattice*.

1.5.2: ORIGIN OF X-RAY SPECTRA

The interpretation of X–ray spectra according to the Bohr theory (LN-1) of electronic levels was first (and correctly) proposed by W. Kossel in 1920: the electrons in an atom are arranged in shells (K, L, M, N, corresponding to n = 1, 2, 3, 4, ..., etc.). Theory predicts that the energy differences between successive shells increase with decreasing n and that the electron transition from n = 2 to n = 1 results in the emission of very energetic (short wavelength) radiation (fig. 1), while outer shell transitions (say, from $n=5$ to $n=4$) yield low energy radiation (long wavelength). For hydrogen, you recall, the wave number of the emitted radiation associated with a particular electron transition is given by the Rydberg equation:

$$\bar{v}=\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right) R$$

For "hydrogen-like" atoms with the atomic number Z (containing one electron only) the corresponding Rydberg equation becomes:

$$\bar{v}=\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right) R Z^2$$

From this relationship it is apparent that the energy difference associated with electron transitions increases strongly with the atomic number and that the wavelength of radiation emitted during such transitions moves with increasing Z from the $10^{-7}\ \mathrm{m}$ range to the $10^{-10}\ \mathrm{m}$ range (radiation now defined as X-rays).

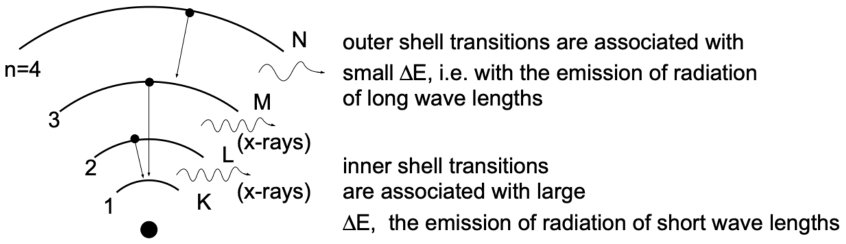


Figure 1 X-rays are generated by inner shell electron transitions

To bring about such inner shell transitions requires the generation of an *electron vacancy*: an electron must be removed, for example from the K shell $(\mathrm{n}=1)$, of an atom. Such a vacancy is conveniently produced in an X-ray tube by an electron beam (generated by a heated filament which is made a cathode) impinging, after being subjected to an accelerating potential of several kV, into a target material made anode (fig. 2). The impinging electrons will transfer part of their energy to electrons of the target material and result in electronic excitation. If the energy of the arriving electrons is high enough, some may knock out a K shell electron in the target and thus generate a vacancy. [It should be clear that a $\mathrm{K} \rightarrow \mathrm{L}$ excitation cannot take place since the L shell is filled: excitation must involve $(n=1) \rightarrow (n=\infty)$.] When such a vacancy is generated, it can readily be filled by an electron from the L shell or the M shell of the same atom. These internal electron transitions give rise to the emission of "characteristic" X-radiation which, because of its short wavelength, has extremely high "penetrating" power.

> Since an electron beam is used to generate X-rays, the X-ray tube has to be evacuated: to dissipate the energy flux arriving at the target, the anode support (onto which the target is mounted) is water-cooled.

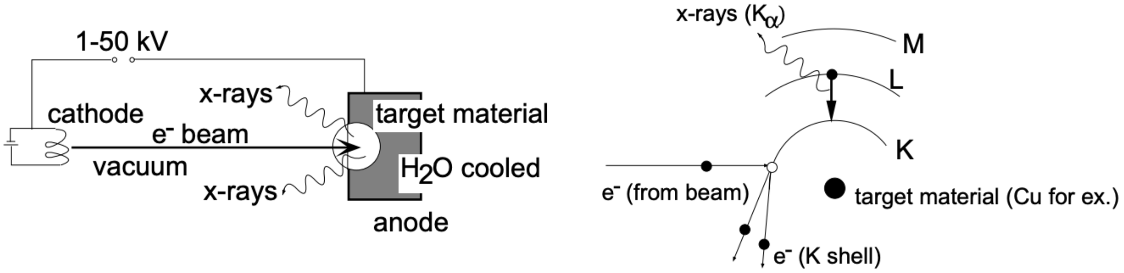


Figure 2 Generation of x-rays

Under standard operating conditions, the characteristic radiation emitted by the target comprises two sharp lines, referred to as K_α and K_β lines (fig. 3). They are associated, respectively, with electron transitions from $n=2$ to $n=1$ and from $n=3$ to $n=1$.

Emitted X-ray spectra were extensively studied by H.G.J. Moseley who established the relationship between the wavelength of characteristic radiation and the atomic number Z of the radiation emitting target material (fig. 4). Experimentally he found that the K_α lines for various target materials (elements) exhibit the relationship:

$$\lambda K_\alpha \propto \frac{1}{Z^2} \quad (\bar{v} K_\alpha \propto Z^2)$$

Moseley's empirical relationship (which reflects a behavior in agreement with the Rydberg equation) can be quantified. While the energy levels associated with outer electron transitions are significantly affected by the "screening" effect of inner electrons (which is variable and cannot as yet be determined from first principles), the conditions associated with X-ray generation are simple. Very generally, the screening effect of the innermost electrons on the nuclear charge is accounted for in an effective nuclear charge $(Z-\sigma)$ and the Rydberg equation assumes the form:

$$\bar{v}=\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right) R(Z-\sigma)^2$$

where $\sigma=$ screening effect

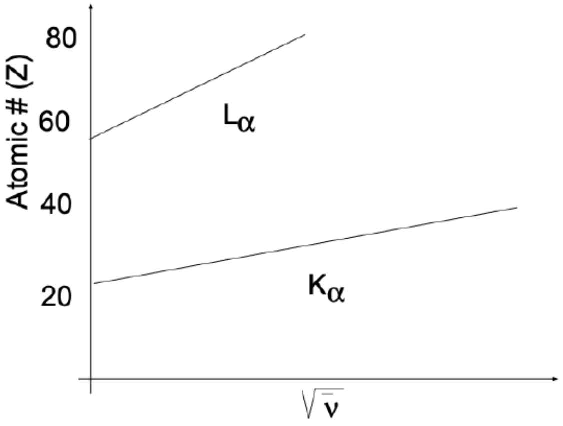
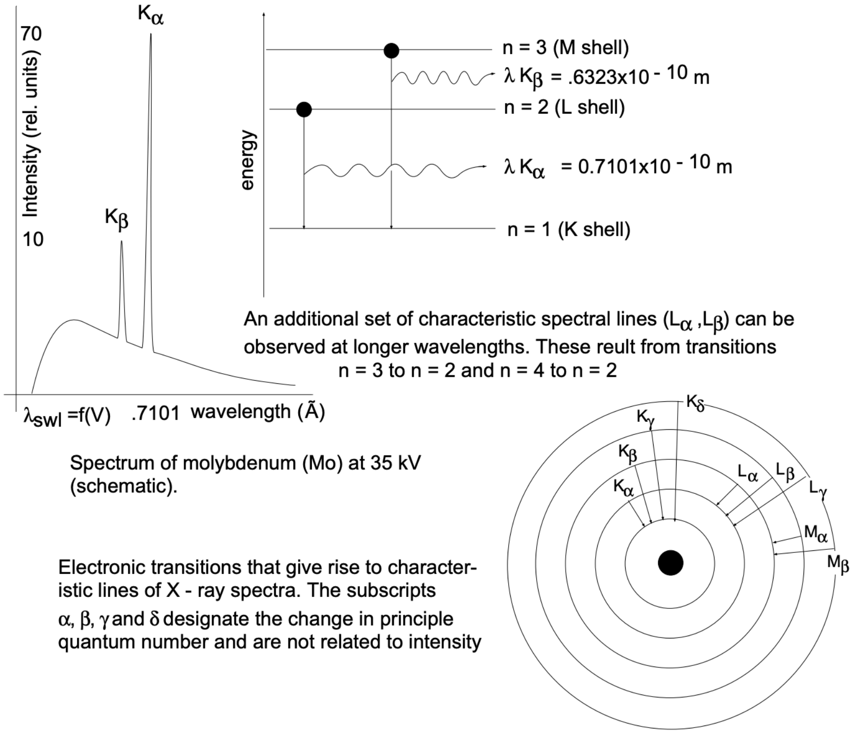


Figure 4 Moseley relationship for K_α and L_α radiation

Considering the transition $n_2 \rightarrow n_1$, screening of the full nuclear charge is only provided by the one electron remaining in the K shell. Thus it is possible to use the v modified Rydberg equation, taking $\sigma = 1$. Accordingly, we have:

$$\bar{v}K_{\alpha} = \left(\frac{1}{2^2} - \frac{1}{1^2}\right) R(Z-1)^2 = -\frac{3}{4} R(Z-1)^2$$

where: $\mathrm{R} =$ Rydberg constant and $\mathrm{Z} =$ atomic number of the target material. [The minus sign (-) only reflects radiative energy given off by the system.]



An additional set of characteristic spectral lines (L_α ,L_β) can be observed at longer wavelengths. These reult from transitions n = 3 to n = 2 and n = 4 to n = 2

Spectrum of molybdenum (Mo) at 35 kV (schematic).

Electronic transitions that give rise to characteristic lines of X - ray spectra. The subscripts α, β, γ and δ designate the change in principle quantum number and are not related to intensity

Figure 3 Electronic transitions giving rise to characteristic X- ray spectra.

Similarly, for the characteristic L_α series of spectral lines ($n = 3$ to $n = 2$) we find, after removal of one L electron, that the screening of the electrons in the K shell and the remaining electrons in the L shell reduces the nuclear charge by 7.4 (empirical value).

$$\overline{\mathrm{v}}\mathrm{L}_{\alpha} = \left(\frac{1}{3^2} - \frac{1}{2^2}\right) \mathrm{R}(\mathrm{Z}-7.4)^2 = -\frac{5}{36} \mathrm{R}(\mathrm{Z}-7.4)^2$$

A second look at the X-ray spectrum of a Mo target, obtained with an electron accelerating potential of $35\mathrm{kV}$ (fig. 5), shows that the characteristic radiation $(\mathrm{K}_\alpha, \mathrm{K}_\beta)$ appears superimposed on a continuous spectrum (continuously varying λ) of lower and varying intensity. This continuous spectrum is referred to as **bremsstrahlung** (*braking radiation*) and has the following origin. Electrons, impinging on the target material, may lose their energy by transferring it to orbiting electrons, as discussed above; in many instances, however, the electrons may come into the proximity of the force fields of *target nuclei* and, in doing so, will be "slowed down" or decelerated to a varying degree,

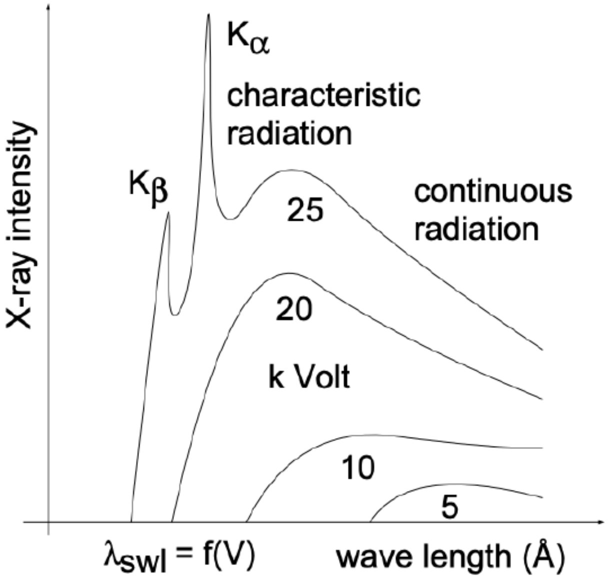
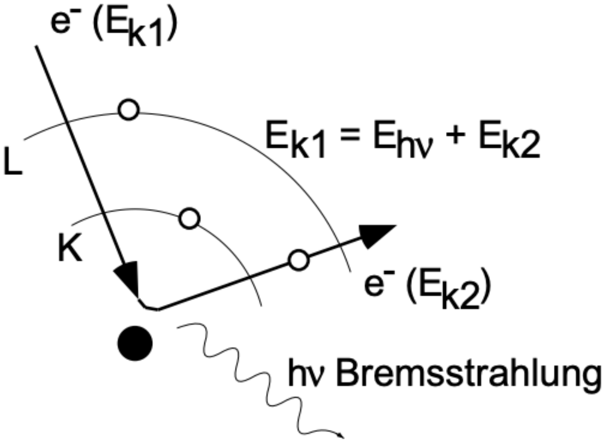


Figure 5 X-ray spectrum of Mo target as a function of applied Voltage.

ranging from imperceptible deceleration to total arrest. The energy lost in this slowing down process is emitted in the form of radiation (braking radiation, or bremsstrahlung). This energy conversion, as indicated, can range from partial to complete (fig. 6). The



$$\boxed{\text{for } E_{k2} = 0,\ E_{(h\nu)max} = E_{k1} = \lambda_{SWL} = h\nu = eV\ ;\ \lambda_{swl} = hc/eV}$$

Figure 6 Origin of Bremsstrahlung; the continuous part of the X-ray spectrum

incident electrons have an energy of $\mathrm{e} \cdot \mathrm{V}$ (electronic charge times accelerating Voltage) in the form of kinetic energy $\left(\mathrm{mv}^2/2\right)$, and their total energy conversion gives rise to a *Shortest Wavelength* (SWL) - the cut-off of the continuous spectrum for decreasing values of λ (fig. 5). Analytically, we have:

$$\mathrm{eV} = \mathrm{h}v_{\max} = \mathrm{h}\frac{\mathrm{c}}{\lambda_{\mathrm{SWL}}} \quad ; \quad \lambda_{\mathrm{SWL}} = \frac{\mathrm{hc}}{\mathrm{eV}}$$

From this relationship it is evident that the cut-off of the continuous spectrum toward decreasing λ''s $\left(\lambda_{\mathrm{SWL}}\right)$ is controlled by the accelerating potential (fig. 5).

1.5.3: “FINE STRUCTURE” OF CHARACTERISTIC X-RAYS

It is customary to consider the characteristic X-ray spectral lines as discrete lines $\left(\mathrm{K}_\alpha, K_\beta, L_\alpha, L_\beta\right.$, etc.). In reality, they are not discrete since the electron shells involved in the associated electron transitions have energy *sublevels* (s, p, d orbitals). These sublevels give rise to a "fine structure" insofar as the K_α lines are doublets composed of $\mathrm{K}_{\alpha 1}$ and $\mathrm{K}_{\alpha 2}$ lines. Similarly, L_α, L_β, etc., exhibit a fine structure.

These considerations suggest that X-ray spectra contain information concerning the energetics of electronic states. Obviously, analysis of X-rays emitted from a target of unknown composition can be used for a quantitative chemical analysis. [This approach is taken routinely in advanced scanning electron microscopy (SEM) where X-rays, generated by the focused electron-beam, are analyzed in an appropriate spectrometer.]

In fundamental studies it is also of interest to analyze soft (long λ) X-ray spectra. For example, take the generation of X-rays in sodium (Na). By generating an electron vacancy in the K shell, a series of K_α and K_β lines will result. The cascading electron generates vacancies in the $2p$ level, which in turn can be filled by electrons entering from the 3s level (generation of "soft" X-rays). If the X-rays are generated in a Na vapor, the $3s \rightarrow 2p$ transition will yield a sharp line; on the other hand, if X-rays are analyzed in sodium metal, the same transition results in the emission of a continuous broad band, about 30Å in width. This finding confirms the existence of an *energy band* (discussed earlier).

An analysis of the width and intensity distribution of the X-ray band provides experimental data concerning the energy band width and the energy state density distribution within the energy band (fig. 7).

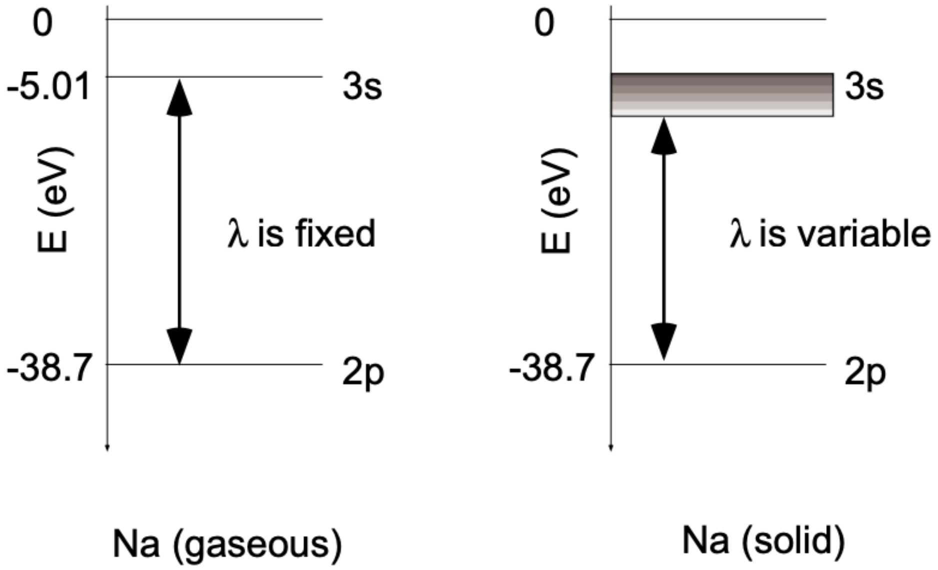


Figure 7 Soft X-rays from 3s - 2p transitions in solid Na and Na vapor

1.5.4: X-RAYS FOR STRUCTURAL ANALYSIS

The extensive use of X-rays for the analysis of atomic structural arrangements is based on the fact that waves undergo a phenomenon called *diffraction* when interacting with systems (diffracting centers) which are spaced at distances of the same order of magnitude as the wavelength of the particular radiation considered. X-ray diffraction in crystalline solids takes place because the atomic spacings are in the $10^{-10}\ \mathrm{m}$ range, as are the wavelengths of X-rays.

1.5.5: DIFFRACTION AND BRAGG'S LAW

The atomic structure of crystalline solids is commonly determined using one of several different X-ray diffraction techniques. Complementary structure information can also be obtained through electron and neutron diffraction. In all instances, the radiation used must have wavelengths in the range of 0.1 to 10Å because the resolution (or smallest object separation distance) to which any radiation can yield useful information is about equal to the wavelength of the radiation, and the average distance between adjacent atoms in solids is about $10^{-10}\ \mathrm{m}(1\text{Å})$. Since there is no convenient way to focus X-rays with lenses and to magnify images, we do not attempt to look directly at atoms. Rather, we consider the interference effects of X-rays when scattered by the atoms, comprising a crystal lattice. This is analogous to studying the structure of an optical diffraction grating by examining the interference pattern produced when we shine visible light on the grating. (The spacing of lines on a grating is about 0.5 to 1 μm and the wavelength of visible radiation ranges from 0.4 to 0.8 μm.) In the optical grating the ruled lines act as scattering centers, whereas in a crystal it is the atoms (more correctly, the electrons about the atom) which scatter the incident radiation.

The geometrical conditions which must be satisfied for diffraction to occur in a crystal were first established by Bragg. He considered a monochromatic (single wavelength) beam of X-rays with coherent radiation (X-rays of common wave front) to be incident on a crystal, as shown in fig. 8. Moreover, he established that the atoms which constitute the actual scattering centers can be represented by sets of parallel planes (in which the atoms are located) which act as mirrors and "reflect" the X-rays. In cubic systems the spacing of these planes, $\mathrm{d_{(hkl)}}$ $\mathrm{(see\ LN-4)}$, is related to the lattice constant (a):

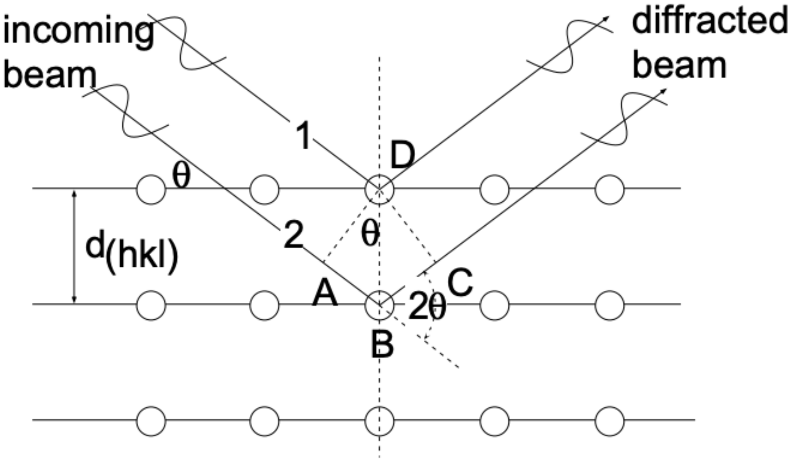


Figure 8 Bragg's law, assuming the planes of atoms behave as reflecting planes.

$$\mathrm{d_{(hkl)}} = \frac{\mathrm{a}}{\sqrt{\mathrm{h^2 + k^2 + I^2}}} \tag{1}$$

For constructive interference of the scattered X-rays (the appearance of a diffraction peak) it is required that the beams, scattered on successive planes, be "in phase" (have again a common wave front) after they leave the surface of the crystal. In terms of the beams labeled 1 and 2 in fig. 8 this requires that the distance $\overline{\mathrm{AB}} + \overline{\mathrm{BC}}$ be equal to an integral number of wavelengths (λ) of the indicent radiation. Accordingly:

$$\overline{\mathrm{AB}} + \overline{\mathrm{BC}} = \mathrm{n}\lambda \quad (\mathrm{n} = 1, 2, 3, \ldots)$$

Since $\overline{\mathrm{AB}} = \overline{\mathrm{BC}}$ and $\sin\theta = \frac{\overline{AB}}{d_{(hk)}}\left[\overline{AB} = d_{(hk)}\sin\theta\right]$:

$$\mathrm{n}\lambda = 2\ \mathrm{d_{(hkl)}}\sin\theta \tag{2}$$

This relation is referred to as *Bragg's Law* and describes the angular position of the diffracted beam in terms of λ and $d_{(hkl)}$. In most instances of interest we deal with first order diffraction $(n = 1)$ and, accordingly, Bragg's law is:

$$\lambda = 2d_{(hkl)}\sin\theta$$

[We are able to make $n = 1$ because we can always interpret a diffraction peak for $n = 2, 3, \ldots$ as diffraction from (nh $nknl$) planes - i.e., from planes with one-nth the interplanar spacing of $d_{(\mathrm{hkl})}\cdot]$.

If we consider fig. 8 as representative for a "diffractometer" set-up (fig. 11), we have a collimated beam of X-rays impinging on a (100) set of planes and at 2θ to the incident beam a detector which registers the intensity of radiation. For a glancing incident beam (small θ) the detector will register only background radiation. As θ increases to a value for which $2d\sin\theta = \lambda$, the detector will register high intensity radiation - we have a diffraction peak. From the above it is evident that the diffraction angle (θ) increases as the interplanar spacing, $\mathrm{d_{(hkl)}}$, decreases.

The diffraction experiment as presently considered is intended to provide quantitative information on the volume (the lattice constant a) and shape characteristics (SC, BCC, FCC) of the unit cell. The intensity of diffraction peaks depends on the phase relationships between the radiation scattered by all the atoms in the unit cell. As a result, it happens quite often that the intensity of a particular peak, whose presence is predicted by Bragg's law, is zero. (This is because Bragg's law deals not with atom positions, but only with the size and shape of the unit cell.) For example, consider the intensity of the (100) diffraction peak of a crystal which has a BCC unit cell. The phase relationships show that the X-rays scattered at the top and bottom faces of the unit cell, (100) planes, interfere constructively, but are 180° out of phase with the X-rays scattered by the atom at the center of the unit cell. The resultant intensity is therefore zero. The rules which govern the presence of particular diffraction peaks in the different cubic Bravais lattices (SC, BCC and FCC) are given in Table I.

TABLE I. *Selection Rules for Diffraction Peaks in Cubic Systems*

Bravais Lattice	Reflections Present	Reflections Absent
Simple Cubic	All	None
Body-Centered Cubic	$(\mathrm{h}+\mathrm{k}+\mathrm{l}) = $ even	$(\mathrm{h}+\mathrm{k}+\mathrm{l}) = $ odd
Face-Centered Cubic	h, k, l unmixed (either all odd or all even)	h, k, l mixed

The rules given are strictly true only for unit cells where a single atom is associated with each lattice point. (Unit cells with more than one atom per lattice point may have their atoms arranged in positions such that reflections cancel. For example, diamond has an FCC Bravais lattice with two atoms per lattice point. All reflections present in diamond have unmixed indices, but reflections such as {200}, {222} and {420} are missing. The fact that all reflections present have unmixed indices indicates that the Bravais lattice is FCC – the extra missing reflections give additional information as to the exact atom arrangement.)

A hypothetical diffraction experiment: A material is known to be of simple cubic structure; determine a, the lattice constant, by X-ray diffraction. In theory, the question may be answered by placing the crystal into a diffractometer, rotating it into all possible positions relative to the incident X-ray beam and recording all diffracting 2θ values. From the above we know that the smallest observed θ value must correspond to diffraction on $\{100\}$ planes and also that $d_{(100)} = a$. We may now use Bragg's equation to determine a, the lattice constant:

$$\lambda = 2d\sin\theta = 2a\sin\theta$$

$$a = \frac{\lambda}{2\sin\theta}$$

There are two simplifying assumptions in this problem: (1) we know the system is SC and (2) we are able, through rotation, to bring all planes present into diffraction conditions.

1.5.6: EXPERIMENTAL APPROACHES TO X-RAY DIFFRACTION

In the context of this course we are interested in making use of X-ray diffraction for the purpose of (a) identifying (cubic) crystal systems, (b) determining the lattice constant, a, and (c) identifying particular planes or meaningful orientations. The possible approaches can, in principle, be identified through an examination of Bragg's law. The Bragg condition for particular $\mathrm{d}_{(\mathrm{hkl})}$ values can be satisfied by adjusting either one of two experimental variables: (a) λ, the wavelength of the X-ray beam used, or (b) θ, the orientation of the crystal planes relative to the incident X-rays.

(a) Fixed θ. Variable λ: One means of satisfying Bragg's law is to irradiate a stationary single crystal (θ fixed for all planes within the crystal) with an X-ray beam of "white" radiation, which contains the characteristic and continuous spectrum produced by an X-ray tube. (For λ variable we have the simultaneous exposure of a crystal to a range of λ values). Each set of planes will reflect (diffract) the particular λ which satisfies the Bragg condition for the fixed θ. The diffracted beams may conveniently be recorded with a Polaroid camera or, alternately, with an electronic imaging device. It is possible to analyze either the transmitted or the back-reflected X-rays. This experimental procedure is referred to as the **Laue technique** (fig. 9); it is mostly conducted in the back-reflection mode. Note that the approach taken makes it possible to determine the values of θ for each reflection, but not the corresponding λ. Therefore, the technique cannot be used, for example, to determine lattice constants. However, it is very valuable if particular planes or crystal orientations are to be identified.

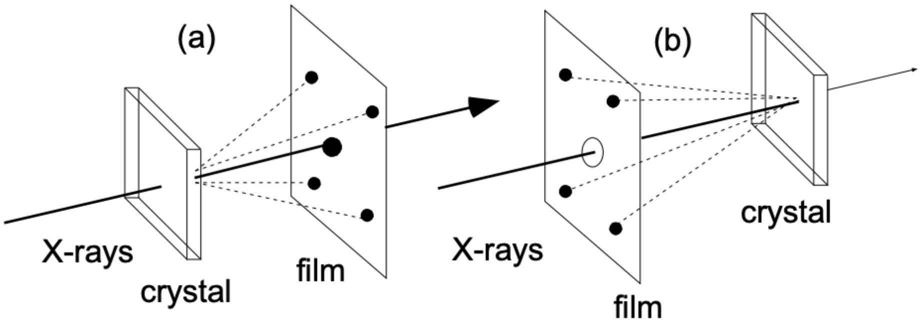


Figure 9: Laue diffraction in (a) transmission and (b) back-reflection mode.
Long

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(b)Fixed λ (Monochromatic X-Rays), Variable θ: The basic prerequisite for this approach is the availability of a monochromatic X-radiation of known wavelength (λ). Such radiation can be conveniently obtained by using a crystal (i.e., its diffracting property) as a filter or monochromator (fig. 10). Filter action is achieved by positioning the crystal in such a way that the unfiltered radiation emitted by the X-ray tube becomes incident at an angle, θ, on a set of low index planes which satisfy Bragg's law for the highest intensity radiation (K_α) emitted. The condition of a fixed λ and variable θ is experimentally used in two techniques. Using a **diffractometer** (fig. 11), we place a sample (ground to a powder) into the center of a rotating stage and expose it to a monochromatic X-ray beam. The sample is rotated into diffraction condition and the diffraction angle determined.

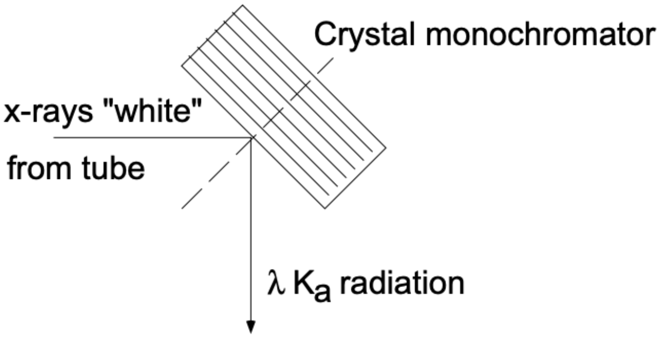

Figure 10 Isolation of monochromatic radiation from target radiation

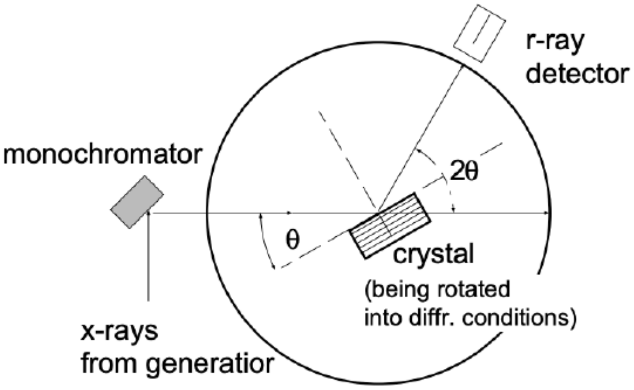

Figure 11 X-ray Diffractometer setup.

In the **Debye-Scherrer method** (fig.12) the sample is ground to a powder and placed (in an ampoule) into the center of a Debye-Scherrer camera. Exposed to monochromatic X-rays, in this way a large number of diffracted cone-shaped beams are generated such that the semiangles of the cones measure 2θ, or twice the Bragg angle for the particular diffracting crystallographic planes. The reason diffracted beams are cone-shaped is that the planes in question (within the multitude of randomly oriented grains) give rise to diffraction for any orientation around the incident beam as long as the incident beam forms the appropriate Bragg angle with these planes – thus there is a rotational symmetry of the diffracted beams about the direction of the incident beam. Those planes with the largest interplanar spacing have the smallest Bragg angle, θ.

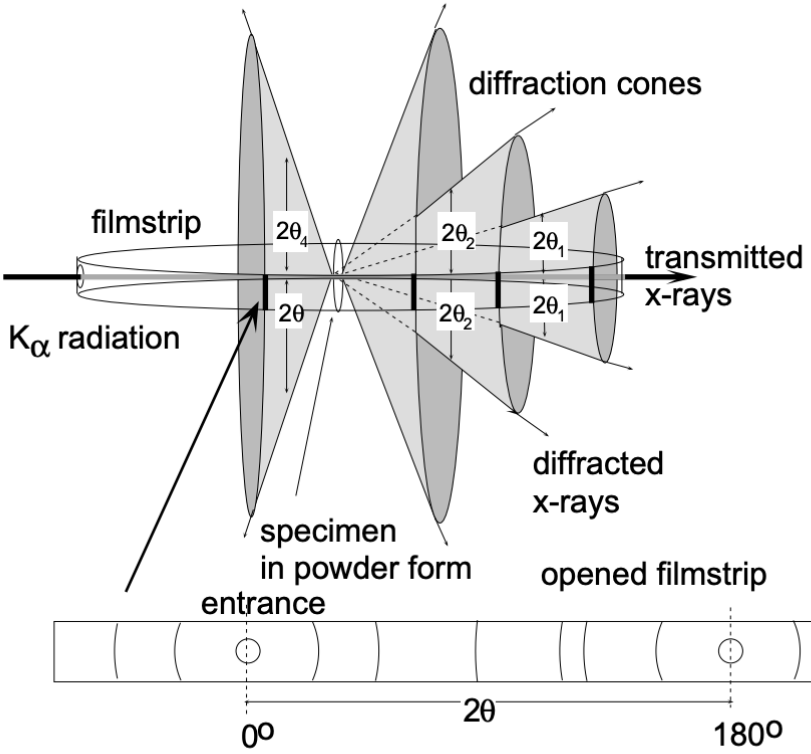

Figure 12 Debye-Scherrer powder diffraction setup and analysis

In a Debye-Scherrer arrangement, after exposing a powder of a crystalline material to monochromatic X-rays, the developed film strip will exhibit diffraction patterns such as indicated in fig. 12. Each diffraction peak (dark line) on the film strip corresponds to constructive interference at planes of a particular interplanar spacing $\left[\mathrm{d}_{(\mathrm{hkl})}\right]$. The problem now consists of "indexing" the individual lines - i.e., determining the Miller indices (hkl) for the diffraction lines:

$$\text{Bragg:}\quad \lambda = 2\,\mathrm{d}_{(\mathrm{hkl})}\sin\theta \qquad ;\mathrm{d}_{(\mathrm{hkl})} = \frac{\mathrm{a}}{\sqrt{\mathrm{h}^2+\mathrm{k}^2+\mathrm{l}^2}}$$

$$\lambda^2 = 4\,\mathrm{d}^2_{(\mathrm{hkl})}\sin^2\theta \qquad ;\mathrm{d}^2_{(\mathrm{hkl})} = \frac{\mathrm{a}^2}{\left(\mathrm{h}^2+\mathrm{k}^2+\mathrm{l}^2\right)}$$

Substitution and rearrangement of above yields:

$$\frac{\sin^2\theta}{\left(h^2+k^2+|^2\right)} = \frac{\lambda^2}{4a^2} = \text{const.}$$

Accordingly, we find that for all lines (θ values) of a given pattern, the relationship

$$\frac{\sin^2\theta_1}{\left(h^2+k^2+|^2\right)_1} = \frac{\sin^2\theta_2}{\left(h^2+k^2+\mathrm{I}^2\right)_2} = \frac{\sin^2\theta_3}{\left(h^2+k^2+\mathrm{I}^2\right)_3} = \text{const.}$$

holds. Since the sum $\left(h^2+k^2+l^2\right)$ is always integral and $\lambda^2/4a^2$ is a constant, the problem of indexing the pattern of a cubic system is one of finding a set of integers $\left(h^2+k^2+l^2\right)$ which will yield a constant quotient when divided one by one into the observed $\sin^2\theta$ values. (Certain integers such as $7, 15, 23$, etc. are impossible because they cannot be formed by the sum of three squared integers.)

Indexing in step-by-step sequence is thus performed as follows: θ values of the lines are obtained from the geometric relationship of the unrolled film strip. Between the exit hole of the X-ray beam $(2\theta=0^{\circ})$ and the entrance hole $(2\theta=180^{\circ})$ the angular relationship is linear (fig. 12). The increasing θ values for successive lines are indexed $\theta_1, \theta_2, \theta_3$, etc., and $\sin^2\theta$ is determined for each. If the system is simple cubic we know that all planes present will lead to diffraction and the successive lines (increasing θ) result from diffraction on planes with decreasing interplanar spacing: (100), (110), (111), (200), (210), (211), (220), etc. From equation (3) above we recognize:

$$\frac{\sin^2\theta_1}{1}=\frac{\sin^2\theta_2}{2}=\frac{\sin^2\theta_3}{3}=\frac{\sin^2\theta_4}{4}=\frac{\sin^2\theta_5}{5}=\text{const.}$$

If the system is BCC, however, we know from the selection rules that only planes for which $(h+k+l)=$ even will reflect. Thus:

$$\frac{\sin^2\theta_1}{2}=\frac{\sin^2\theta_2}{4}=\frac{\sin^2\theta_3}{6}=\frac{\sin^2\theta_4}{8}\text{ etc. }=\text{const.}$$

[SC can be differentiated from BCC through the fact that no sum of three squared integers can yield 7, but 14 can be obtained from planes (321)].

For FCC systems, the selection rules indicate reflections on planes with unmixed h,k,l indices:

$$\frac{\sin^2\theta_1}{3}=\frac{\sin^2\theta_2}{4}=\frac{\sin^2\theta_3}{8}==\text{const.}$$

After proper indexing, the constant is obtained:

$$\frac{\sin^2\theta}{(h^2+k^2+L^2)}=\text{const.}$$

and the particular Bravais lattice is identified. The lattice constant of the unit cell is subsequently obtained, knowing the wavelength of the incident radiation:

$$\begin{gathered}\frac{\sin^2\theta}{\left(\mathrm{h}^2+\mathrm{k}^2+\mathrm{I}^2\right)}=\text{const.}=\frac{\lambda^2}{4\mathrm{a}^2}\\ a^2=\frac{\lambda^2}{4\sin^2\theta}\left(h^2+k^2+1^2\right)\\ a=\frac{\lambda}{2\sin\theta}\sqrt{\left(h^2+k^2+1^2\right)}\end{gathered}$$

1.6: The Imperfect Solid State

1.6.1: INTRODUCTION

Real crystals are never perfect: they always contain a considerable density of defects and imperfections that affect their physical, chemical, mechanical and electronic properties. The existence of defects also plays an important role in various technological processes and phenomena such as annealing, precipitation, diffusion, sintering, oxidation and others. It should be noted that defects do not necessarily have adverse effects on the properties of materials. There are many situations in which a judicious control of the types and amounts of imperfections can bring about specific characteristics desired in a system. This can be achieved by proper processing techniques. In fact, “defect engineering” is emerging as an important activity.

All defects and imperfections can be conveniently considered under four main divisions: *point defects*, *line defects* or dislocations, *planar defects* or interfacial or grain boundary defects, and *volume defects*. We can also add here *macroscopic* or *bulk defects* such as pores, cracks and foreign inclusions that are introduced during production and processing of the solid state. Point defects are inherent to the equilibrium state and thus determined by temperature, pressure and composition of a given system. The presence and concentration of other defects, however, depend on the way the solid was originally formed and subsequently processed.

Briefly consider the effects of *imperfections* or crystal defects on a few important properties of solids. The electrical behavior of semiconductors, for example, is largely controlled by crystal imperfections. The conductivity of silicon can thus be altered in type (n or p) and by over eight orders of magnitude through the addition of minute amounts of electrically active dopant elements. In this case, each atom of dopant, substitutionally incorporated, represents a point defect in the silicon lattice. The fact that such small amounts of impurity atoms can significantly alter the electrical properties of semiconductors is responsible for the development of the transistor and has opened up the entire field of solid state device technology. Practically none of the semiconducting properties that led to these engineering accomplishments are found in a “perfect” crystal. They are properties peculiar to the defective solid state.

The existence of dislocations (line defects) in crystals provides a mechanism by which permanent change of shape or mechanical deformation can occur. A crystalline solid free of dislocations is brittle and practically useless as an engineering material. While the existence of dislocations in crystals insures ductility (ability to deform), the theoretical strength of crystalline solids is drastically reduced by their presence.

We should recognize that dislocations play a central role in the determination of such important properties as strength and ductility. In fact, virtually all mechanical properties of crystalline solids are to a significant extent controlled by the behavior of line imperfections.

The ability of a ferromagnetic material (such as iron, nickel or iron oxide) to be magnetized and demagnetized depends in large part on the presence of two-dimensional imperfections known as *Bloch walls*. These interfaces are boundaries between two regions of the crystal which have a different magnetic state. As magnetization occurs, these defects migrate and by their motion provide the material with a net magnetic moment. Without the existence of Bloch walls all ferromagnetic materials would be permanent magnets. In fact, electromagnets would not exist if it were not for this type of defect.

The presence of surface defects such as cracks causes brittle materials like glass to break at small applied stresses. This fact is familiar to anyone who has broken a glass tube by first filing a small notch (or crack) into the surface. Removal of cracks from the surface of glass either by etching in hydrofluoric acid or by flame polishing almost always raises the fracture strength. For example, glass in the absence of any surface cracks has a fracture strength of $\sim 10^{10}\mathrm{Newton}/\mathrm{m}^2$ (as opposed to real glass which has a fracture strength of $\sim 0^7$ Newton $/\mathrm{m}^2$).

1.6.2: POINT DEFECTS

1.6.2.1: Formation of Point Defects

An incontrovertible law of nature states: “Nothing is perfect”. This law applies to humans as well as to the inorganic world of crystalline solids and can be formulated as the 2nd law of thermodynamics:

$$\mathrm{F}=\mathrm{H}-\mathrm{TS} \tag{1}$$

where F is the free energy of a given system, H is the heat content or enthalpy and TS is the entropy, or disorder, term. If a reaction takes place at a temperature T, we find the change in $\mathrm{F}(\Delta\mathrm{F})$ related to a change in $\mathrm{H}(\Delta\mathrm{H})$, the heat content, and possibly also a change in TS ($T\Delta S$). Such is the case when defects are formed in a perfect solid: The energy distribution in a solid (Maxwell-Boltzmann) suggests that a number of individual atoms may acquire enough thermal energy to be displaced from the equilibrium lattice site into an interstitial position. This process of point defect formation requires energy and leads to lattice strain which constitutes, as discussed earlier, an increase in the heat content of the system (ΔH is positive and increases linearly with the number of defects formed). The departure from perfection by the generation of defects leads to disorder (ΔS is positive). The magnitude of disorder generated (ΔS) is very large during the initial step from perfection to slight disarray, but the increase in disorder (with a given number of defects generated) decreases as the overall disorder increases.

Correspondingly the term $T\Delta S$ drops rapidly at the beginning and then flattens out. The net result (fig. 1), free energy, exhibits a minimum for a certain number of defects in the

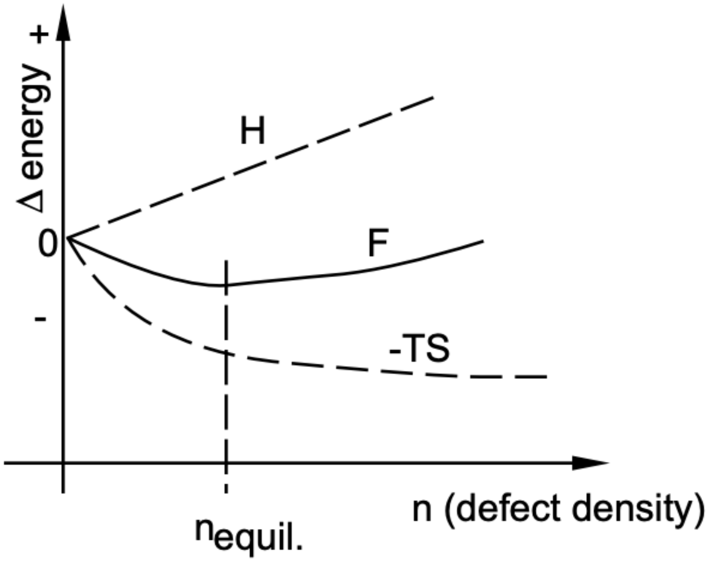

Figure 1 Thermodynamics of point defect formation

solid [equilibrium defect density = f (temperature)]; the F_{minimum} suggests also that the transition from perfection to equilibrium defect structure is spontaneous: it occurs naturally!

While the detailed mechanisms for the formation of atomic vacancies in solids are still the subject of extensive research, the associated equilibrium energetics are clear: calculations of the thermal energy of atoms in a lattice show that the average vibrational energy of lattice atoms is much less than 1eV (the approximate energy change associated with vacancy formation, i.e., the least amount of energy required to form a vacancy) at room temperature. Therefore a lattice atom will only acquire the energy $\Delta \mathrm{H}_{\mathrm{d}}$, the energy required to form the defect, upon the occurrence of a large energy fluctuation. Since the relative probability of an atom having an energy $\Delta \mathrm{H}_d$ or more in excess of the ground state energy is $e^{-\Delta H_d/kT}$, the probability that an atomic site is vacant varies in the same way. In a (molar) crystal containing N atomic sites, the number n_{d} of vacant sites is, therefore,

$$\mathrm{n}_{\mathrm{d}} = \mathrm{ANe}^{-\Delta \mathrm{H}_{\mathrm{d}}/\mathrm{kT}} \tag{2}$$

where

- n_{d} is the number of defects (in equilibrium at T)
- N is the total number of atomic sites per mole
- $\Delta \mathrm{H}_{\mathrm{d}}$ is the energy necessary to form the defect
- T is the absolute temperature (K)
- k is the Boltzmann constant
- A is a proportionality constant

1.6.2.2: Point Defects in “Pure” Metallic Systems

Point defects in “pure” crystalline metals are defects of atomic dimensions, such as impurity atoms, the absence of a matrix atom and/or the presence of a matrix atom in the wrong place. Some of these point defects are shown in fig. 2. An impurity atom that occupies a normal lattice site is called a *substitutional impurity atom* and an impurity atom found in the interstice between matrix atoms is called an *interstitial impurity atom*. Whether a foreign atom will occupy a substitutional or interstitial site depends largely on the size of the atom relative to the size of the site. Small atoms are usually interstitial impurities, while larger atoms are usually substitutional impurities.

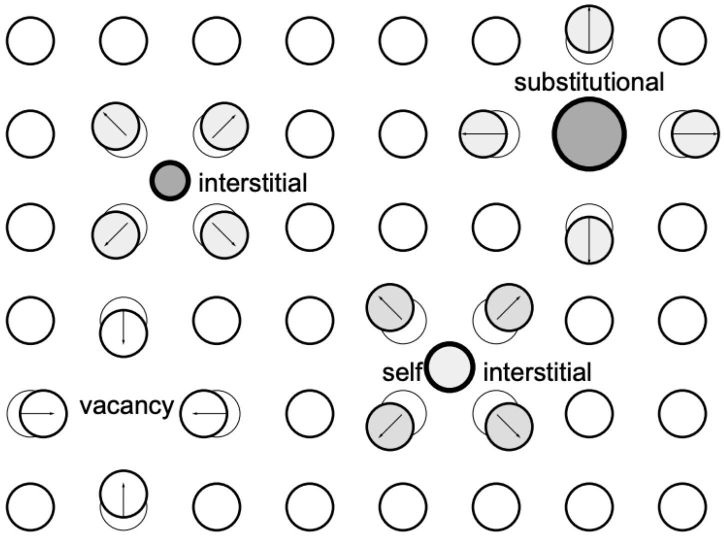

Figure 2 Point defects in crystalline solids

A *vacancy* is an atom site, normally occupied in the perfect crystal, from which an atom is missing. Often the term “vacancy” is used to denote a so-called *Schottky defect*, which is formed when an atom or an ion leaves a normal lattice site and repositions itself in a lattice site on the surface of the crystal. This may be the result of atomic rearrangement in an existing crystal at a high temperature when atomic mobility is high because of increased thermal vibrations. A vacancy may also originate in the process of crystallization as a result of local disturbances during the growth of new atomic planes on the crystal surface. Vacancies are point defects of a size nearly equal to the size of the original (occupied) site; the energy of the formation of a vacancy is relatively low - usually less than 1 eV.

The number of vacancies at equilibrium at each temperature in a crystal can be determined from eq. (2), in which ΔH_d is the energy necessary to take an atom from a regular site of the crystal and place it on the surface for a Schottky-type defect. When a solid is heated a new higher equilibrium concentration of vacancies is established, usually first at crystal surfaces and then in the vicinity of dislocations and grain boundaries which provide sites for the atoms which have left their normal lattice site. Vacancies gradually spread throughout the crystal (from the surfaces into the bulk). On cooling the vacancy concentration is lowered by "diffusion of vacancies" to grain boundaries or dislocations, which act as sinks. In both cases, the new equilibrium vacancy concentration is established only after a finite amount of time. The rate at which vacancies move from point to point in the lattice decreases exponentially with decreasing temperature. Thus, on very rapid cooling (quenching) from a high temperature near the melting point most of the vacancies do not have time to diffuse to sinks and are said to be "frozen in". This gives a considerably greater ("non-equilibrium") concentration of vacancies in quenched specimens than that indicated by the thermal equilibrium value.

The concentration of vacant lattice sites in pure materials is very small at low temperatures - about one vacancy every 10^8 atom sites - and increases with increasing temperature to about one vacancy every 10^3 sites at the melting temperature. Vacancies are important because they control the rate of matrix (or substitutional) atom diffusion - i.e., atoms are able to move around in a crystalline solid primarily because of the presence of vacancies. (The mechanism by which they move is the same as that associated with moving a car in a filled parking lot to the exit). This is shown schematically in fig. 3. *Self-interstitials* are generally not encountered in close-packed

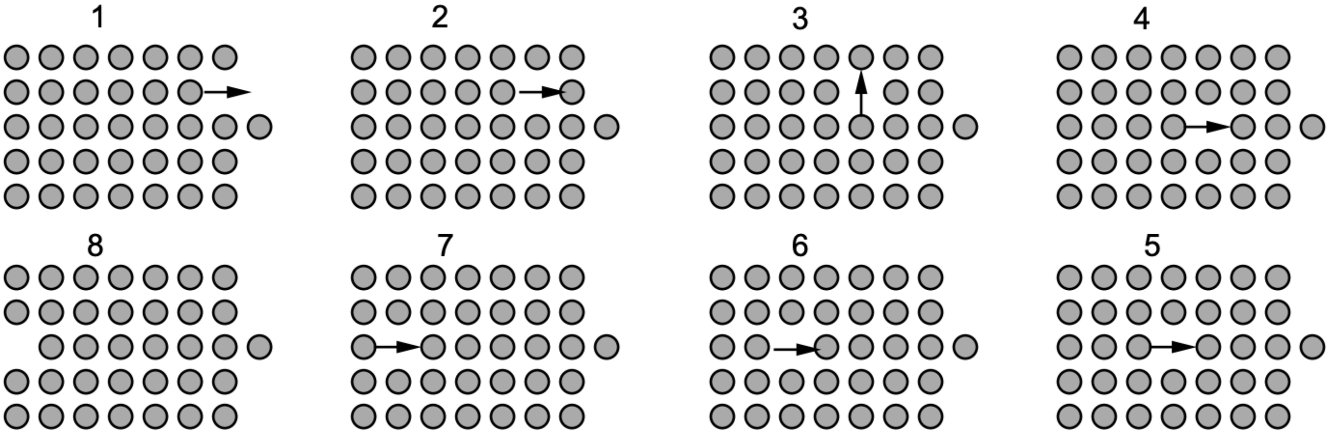

Figure 3 Dynamics of vacancy movements in a close packed solid

metallic systems, but may be introduced by irradiation. For example, high-energy neutrons from atomic fission can knock metal atoms from their regular sites into interstitial sites, creating vacancy-interstitial pairs.

1.6.2.3: Point Defects in Ionic Solids

Point defects in ionic structures differ from those found in pure elements because of the charge neutrality requirement. For example, in a pure monovalent ionic material a cation vacancy must have associated with it either a cation interstitial or an anion vacancy to maintain charge neutrality. Similar requirements hold for anion vacancies. A vacancy pair defect (migration of a cation and an anion to the surface) is usually called a *Schottky imperfection*, and a vacancy-interstitial pair defect is referred to as a *Frenkel imperfection* (an anion or cation has left its lattice position, which becomes a vacancy, and has moved to an interstitial position). These two types of imperfections are shown in fig. 4. Self-interstitials are much more common in ionic structures than in pure elements because many ionic compounds have relatively large interstitial sites available. That is, there are often interstitial sites in the unit cell that have nearly the

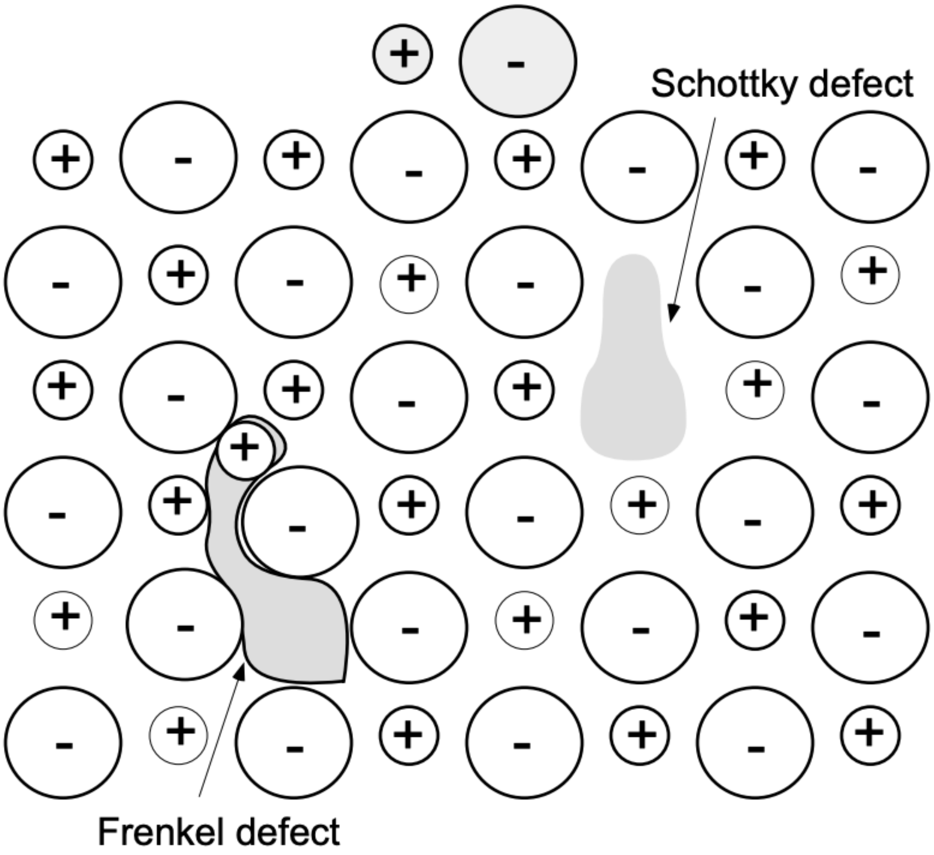

Figure 4 Point defects in ionic solids

same surroundings as normal atom sites. (For example, in BeO the Be atoms fill only one-half the available tetrahedral sites, leaving four possible cation interstitial sites per unit cell. Thus a Be atom could go from a regular lattice site to an almost equivalent interstitial site with little distortion of the lattice.)

Foreign atoms in ionic crystals produce defects that also must maintain charge neutrality. For example, in NaCl a monovalent cation, such as lithium, may simply replace one of the sodium ions as a substitutional impurity. But a divalent cation, such as calcium, replacing a sodium ion must be accompanied by either a cation vacancy or an anion interstitial if charge neutrality is to be maintained. Correspondingly, monovalent impurity cations in a divalent structure (e.g., Na in MgO) must be accompanied by an appropriate number of cation interstitials or anion vacancies.

1.6.2.4: Point Defects in Covalently Bonded Solids

Substitutional impurities in covalently bonded materials can create a unique imperfection in the electronic structure if the impurity atom is from a group in the periodic table other than the matrix atoms. For example, you already considered Group V and Group III elements in a Group IV matrix, such as As or B in Si.

When foreign atoms are incorporated into a crystal structure, whether in substitutional or interstitial sites, we say that the resulting phase is a *solid solution* of the matrix material (solvent) and the foreign atoms (solute). The term “solid solution”, however, is not restricted to the low solute contents of doped semiconductor systems; there are many solid solutions, such as metallic alloys, that comprise a wide composition range.

1.6.3: LINE DEFECTS

Line imperfections, or *dislocations*, in crystalline solids are defects that produce lattice distortions centered about a line. A dislocation is simply the edge of an extra inserted fractional plane of atoms (fig. 5). Normally the symbol $\perp$ is used to represent a *positive*

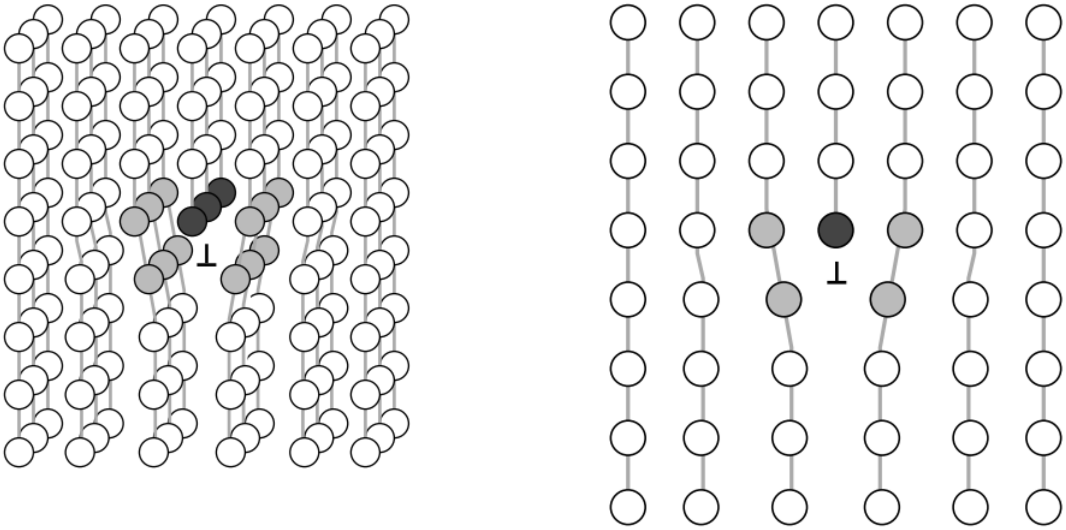

Figure 5 Schematic presentation of a dislocation; the last row of atoms (dark) in the inserted fractional plane

dislocation (extra fractional plane) and ⊤ is used to represent a *negative dislocation* (missing fractional plane).

The importance of dislocations is readily demonstrated in the deformation of crystalline materials. The plane in which a dislocation moves through the lattice is called a *slip plane*. With an applied shear stress the dislocation moves, atomic row by atomic row, and one part of the crystal is displaced relative to the other. When the dislocation has passed through the crystal, the portion of the crystal above the *slip plane* has shifted one atomic distance relative to the portion below the slip plane. In other words, the motion of the dislocation has caused the crystal to change its shape - to be permanently deformed (fig. 6).

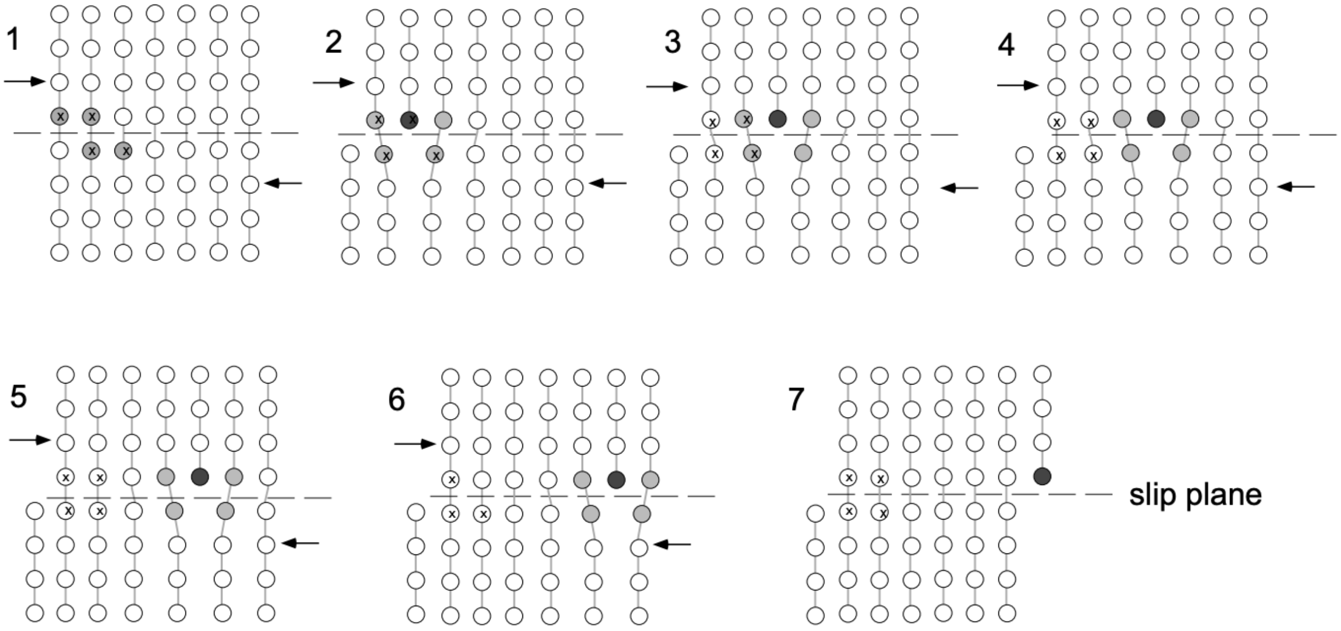

Figure 6 Plastic deformation of crystalline solid by slip associated with stress induced motion of dislocation

Please note: on either side of the dislocation the crystal lattice is essentially perfect, but in the immediate vicinity of the dislocation the lattice is severely distorted. For a positive edge dislocation, the presence of the extra half plane causes the atoms above the slip plane to be put in compression, while those below the slip plane are put in tension. Consequently, the edge dislocation will have a stress field around it that is compressive above the slip plane and tensile below the slip plane.

Plastic Deformation By Slip:

When single crystals of metal (or semiconductor) are pulled in tension, they will begin to deform (elongate) plastically at relatively low stress levels, and “blocks” of the crystals slide over one another because of dislocation motion. Simultaneously, so-called *slip lines* appear on their surface. It is found that deformation by slip occurs most easily on planes with high atomic density and with large interplanar spacing, while the direction of slip is in all instances an atomically "close-packed direction". For FCC structures we therefore observe as the primary slip system {111} planes in direction, while in BCC structures the primary slip occurs on {110} planes in directions. (It should be noted that an alternate deformation mechanism is "deformation twinning", presently not to be considered.)

Dislocation Climb:

Climb is the name given to the motion of dislocations when the extra "half" plane is extended farther into a crystal or partially withdrawn from it. Clearly, the climb process is not a motion of the plane, but rather its growth or shrinking as a result of the addition of atoms or "vacancies" respectively from the environment of the dislocation (fig. 7).

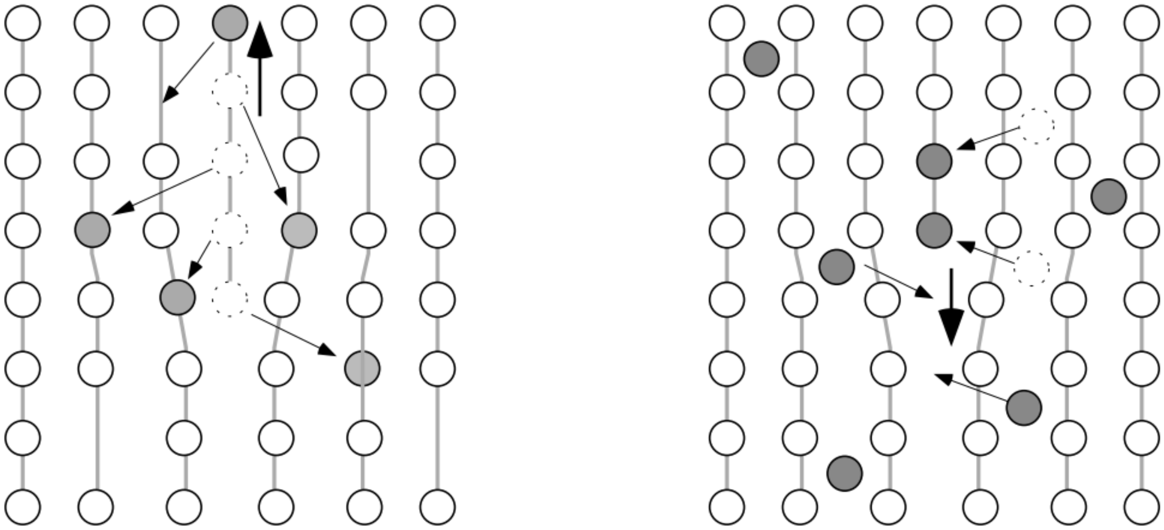

Figure 7 Dislocation climb by (a) loss of atoms to surrounding vacancies and (b) incorporation of interstitial atoms.

Multiplication of Dislocations:

Since during slip each dislocation leaves the matrix, macroscopic deformation could not take place given normal dislocation densities in the range of $10^6 - 10^8/\mathrm{cm}^3$. Examination of the deformed crystals indicates that multiplication of dislocations takes place during deformation. While there are a multitude of multiplication mechanisms, the one most extensively studied is the Frank-Read Source (not to be discussed in detail).

Dislocation Interactions:

The relative ease with which dislocations move across a solid matrix can be attributed to the severe displacements of atoms in the core of dislocations. If these local stresses are reduced, the mobility of dislocations - and thus the ease of slip - is reduced. It is found that impurities in the vicinity of dislocation cores tend to reduce the local distortion energy of the dislocations and thus stabilize the system against slip. In many systems impurities are intentionally added (e.g., solid solution hardening) to increase the strength of materials. Similarly, micro-precipitates tend to impede dislocation motion (e.g., precipitation hardening).

1.6.4: INTERFACIAL IMPERFECTIONS

The several different types of interfacial, or planar imperfections, in solids can be grouped into the following categories:

1. Interfaces between solids and gases, which are called *free surfaces;*
2. Interfaces between regions where there is a change in the electronic structure, but no change in the periodicity of atom arrangement, known as *domain boundaries;*
3. Interfaces between two crystals or grains of the same phase where there is an orientation difference in the atom arrangement across the interface; these interfaces are called *grain boundaries;*
4. Interfaces between different phases, called *phase boundaries*, where there is generally a change of chemical composition and atom arrangement across the interface.

Grain boundaries are peculiar to crystalline solids, while free surfaces, domain boundaries and phase boundaries are found in both crystalline and amorphous solids.

1.6.4.1: Free Surfaces

Because of their finite size, all solid materials have free surfaces. The arrangement of atoms at a free surface differs slightly from the interior structure because the surface atoms do not have neighboring atoms on one side. Usually the atoms near the surface have the same crystal structure but a slightly larger lattice parameter than the interior atoms.

Perhaps the most important aspect of free surfaces is the *surface energy* (γ) associated with surfaces of any solid. The source of this surface energy may be seen by considering the surroundings of atoms on the surface and in the interior of a solid. To bring an atom from the interior to the surface, we must either break or distort some bonds - thereby increasing the energy. The surface energy is defined as the increase in energy per unit area of new surface formed. In crystalline solids, the surface energy depends on the crystallographic orientation of the surface - those surfaces that are planes of densest atomic packing are also the planes of lowest surface energy. This is because atoms on these surfaces have fewer of their bonds broken or, equivalently, have a larger number of nearest neighbors within the plane of the surface. Typical values of surface energies of solids range from about 10^{-1} to $1\ \mathrm{J/m^2}$. Generally, the stronger the bonding in the crystal, the higher the surface energy.

Surface energies can be reduced by the adsorption of foreign atoms or molecules from the surrounding atmosphere. For example, in mica the surface energy of freshly cleaved material in a vacuum is much higher than the surface energy of the same surface cleaved in air. In this instance, oxygen is adsorbed from the air to partially satisfy the broken bonds at the surface. Impurity atom adsorption makes it almost impossible to maintain atomically clean surfaces. As a result, surface properties such as electron emission, rates of evaporation and rates of chemical reactions are extremely dependent on the presence of any adsorbed impurities. These properties will be different if the measurements are made under conditions giving different surface adsorption.

1.6.4.2: Grain Boundaries

Grain boundaries separate regions of different crystallographic orientation. The simplest form of a grain boundary is an interface composed of a parallel array of edge dislocations. This particular type of boundary is called a tilt boundary because the misorientation is in the form of a simple tilt about an axis, parallel to the dislocations. Tilt boundaries are referred to as low-angle boundaries because the angle of misorientation is generally less than 10°.

When a grain boundary has a misorientation greater than 10° or 15°, it is no longer practical to think of the boundary as being made up of dislocations because the spacing of the dislocations would be so small that they would lose their individual identity. The grain boundary represents a region a few atomic diameters wide where there is a transition in atomic periodicity between adjacent crystals or grains.

Grain boundaries have an interfacial energy because of the disruption in atomic periodicity in the vicinity of the boundary and the broken bonds that exist across the interface. The interfacial energy of grain boundaries is generally less than that of a free surface because the atoms in a grain boundary are surrounded on all sides by other atoms and have only a few broken or distorted bonds.

Solids with grain boundaries are referred to as *polycrystalline*, since the structure is composed of many crystals - each with a different crystallographic orientation. In the case of iron the grain boundary structure can be revealed by preferential chemical attack (*etching*) at the grain boundaries, while the grain structure in polyethylene is revealed by the use of polarized light. The grain structure is usually specified by giving average grain diameter or by using a scheme developed by the American Society for Testing and Materials (ASTM). In the ASTM procedure the grain size is specified by a “grain size number” (n) where

$$N = 2^{n-1} \tag{1.6.1}$$

with N equal to the number of grains per square inch when the sample is viewed at 100X magnification. For example, at a magnification of $X = 100$, a material with grain size number 8 will show 128 grains per inch ^{2} - this material in effect has (at $X = 1$) 1.28×10^6 grains per square inch. If the grains are approximately square in cross section, this corresponds to an average grain dimension of $8.8 \times 10^{-4}\mathrm{in}^*$.

In polycrystalline samples the individual grains usually have a random crystallographic orientation with respect to one another, and the grain structure is referred to as *randomly oriented*. In some instances, however, the grains all have the same orientation to within a few degrees. In this instance the material is said to have a *preferred orientation* or *texture*.

1.6.4.3: Phase Boundaries

A *phase* is defined as a *homogeneous, physically distinct and mechanically separable portion of the material with a given chemical composition and structure*. Phases may be substitutional or interstitial solid solutions, ordered alloys or compounds, amorphous substances or even pure elements; a crystalline phase in the solid state may be either polycrystalline or exist as a single crystal.

Solids composed of more than one element may - and often do - consist of a number of phases. For example, a dentist's drill, something painfully familiar to all of us, consists of a mixture of small single crystals of tungsten carbide surrounded by a matrix of cobalt. Here the cobalt forms a continuous phase. Polyphase materials such as the dentist's drill are generally referred to as *composite materials*. Composite materials have great importance in the engineering world because they have many attractive properties that set them apart from single-phase materials. For example, the dentist's drill has good abrasive characteristics (due to the hard carbide particles) and good toughness and impact resistance (due to the continuous cobalt matrix). Neither the tungsten carbide nor the cobalt has both abrasion resistance and impact resistance, yet the proper combination of the two phases yields a composite structure with the desired properties.

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ASTM has as yet not issued specifications in SI units!

The nature of the interface separating various phases is very much like a grain boundary. Boundaries between two phases of different chemical composition and different crystal structure are similar to grain boundaries, while boundaries between different phases with similar crystal structures and crystallographic orientations may be analogous to low-angle grain boundaries in both energy and structure.

The concept of a solid consisting of a continuous phase and a discontinuous phase (or phases) leads to a simple classification of the various types of composite materials. Table 1 gives this classification, which is based on the structure (whether amorphous or crystalline) of the continuous and discontinuous phases.

TABLE 1

Classification of Composite or Multiphase Materials

Continuous Phase	Discontinuous Phase (or Phases)	Examples
Crystalline	Crystalline	All metallic systems such as cast iron, steel, soft solder, etc.; most natural rocks such as granite and marble.
Crystalline	Amorphous	None of practical significance.
Amorphous	Crystalline	Most man-made ceramics such as building bricks and electrical insulator porcelain, concrete, partially crystalline polymers, some polymer-crystalline particle composites.
Amorphous	Amorphous	Fiberglass, asphalt, wood, hydrated cement, other gels.

1.7: Glasses

1.7.1: INTRODUCTION

When a liquid phase is cooled to below its freezing temperature, it usually transforms into a crystalline solid, i.e. it crystallizes. Some liquids, because of complex molecular configuration or slow molecular transport, do not “crystallize” (assume an ordered configuration) upon being cooled to low temperatures, but instead form a rigid disordered network, known as glass, which is very similar in structure to that of the liquid. Most metals and alkali halides crystallize easily upon cooling through the freezing temperature because the structural rearrangement from the liquid to the crystalline state is simple and bonding is nondirectional. At temperatures just above the freezing temperature, most metals and molten salts have fluidities approximately equivalent to that of water at room temperature. Thus, the required structural rearrangements can take place relatively easily.

In contrast, many inorganic silicates form glasses upon cooling because the fluidity at and even above the freezing temperature is very low. This glass formation is related to the high silicon-oxygen single-bond energies and the directional bonding requirements imposed by sp^3 hybridization of silicon. The disordered liquid cannot flow easily and thus cannot undergo the rearrangements required for crystallization. Moreover, the fluidity decreases very rapidly as the temperature is lowered. [For large organic and polymeric liquids, crystallization is difficult because of their chain lengths. In polymer systems the intermolecular bonding (Van der Waals) is weak and expected to permit individual molecules to readily slide past one another. Thus, it is the "difficult" structural rearrangement required for crystallization that induces glass formation in these systems.]

The fluidity of liquids (the reciprocal of the viscosity) is a measure of their ability to flow. In turn, the viscosity (η) (fig. 1) is a measure of their resistance to flow.

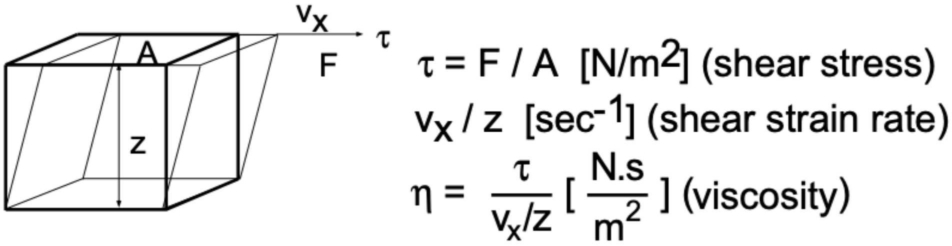


Figure 1 Dimensional analysis of viscosity

Viscosity is formulated as the ratio of an applied shear stress to the resultant shear-strain rate - its dimensions are Newton seconds per meter^2. Liquid flow, involving the motion of molecules past one another, requires the breaking and making of new bonds. Thus the fluidity, like chemical reactions and diffusion in solids (to be discussed later) is expected to exhibit an exponential temperature dependence and may be modelled as:

$$\frac{1}{\eta} \propto e^{-}\left(\frac{\text{Bond Energy}}{kT}\right) \tag{1.7.1}$$

It is noteworthy that inorganic glasses occur in nature as do organic glasses (such as the sap from trees) whereas metallic glasses do not occur naturally and have been manufactured only within the last two decades. The major obstacle to achieving metallic glasses was our inability to cool metallic melts to room temperature at rates high enough so that ordering (and thus crystallization) is prevented.

The *glass transition* point, T_g, (temperature at which a supercooled liquid becomes a glass) is for glasses what the melting point, T_m, is for crystalline solids. Characteristic for almost all glass-forming materials is that at T_g a change in the temperature dependence of the density $(\Delta V/\Delta T)$ takes place [where the viscosity is in the range 10^4 to $10^6 \mathrm{Ns/m^2}$ (the viscosity of H_2O is $1.5 \times 10^{-3} \mathrm{Ns/m^2}$, or about nine orders of magnitude less)]. At higher temperatures (lower viscosities) the structural units are able to reorganize themselves quickly as a quasi-equilibrium liquid. At temperatures below T_g reorganization among the structural units virtually ceases and the resulting rigid material is referred to as a glass. The experimental value obtained for T_g depends on the time scale of the experiment. On slow cooling, for example, the structural units have more time to reorganize and, thus, T_g is lower (fig. 2).

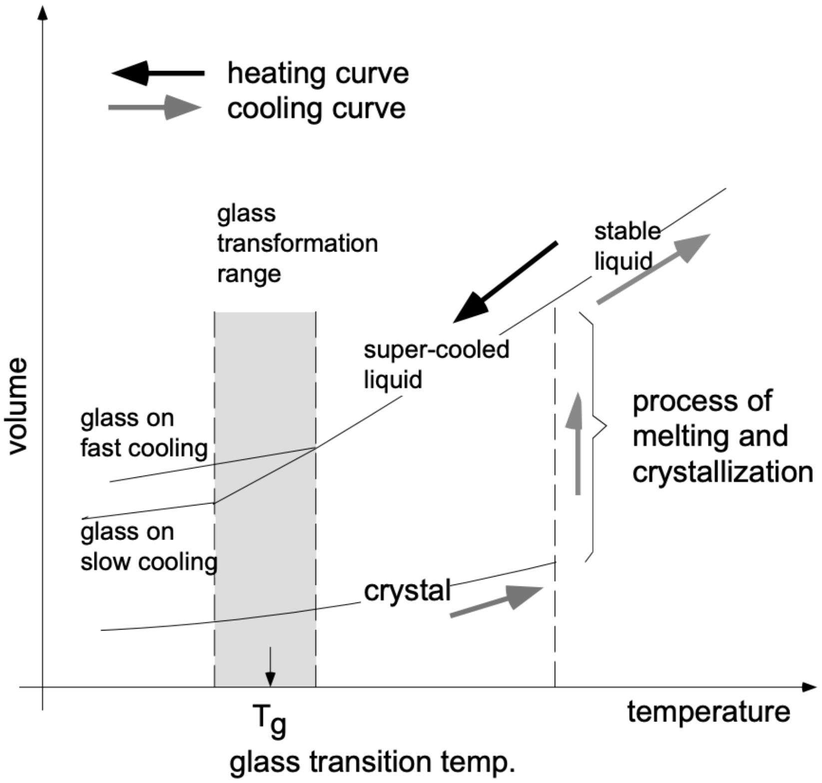


Figure 2 Volume changes associated with heating and cooling in systems susceptible to glass formation.

1.7.2: METALLIC GLASSES

The existence of metallic glasses shows the generality of the glass-forming process. In addition, the physical picture in this case is especially simple. Even with the highest presently attainable cooling rates (up to $10^{7\circ}\mathrm{C/s}$), no "pure" metal has yet been obtained in a glassy state. However, if the liquid is an alloy of two (or more) metals whose atoms differ greatly in size, the crystallization process is more difficult and can be prevented in many instances by extremely rapid cooling of the melt $\left(10^{6\circ}\mathrm{C/sec}\right)$. The two experimental techniques for rapid cooling are (1) propelling a liquid drop at high velocity and "splatting" it against a cooled copper surface, (2) flattening a liquid drop between a piston and an anvil or between two rolls and (3) "spinning" the melt by transferring it in a continuous mode onto a rapidly rotating, cooled wheel (fig. 3). X-ray patterns of the solidified alloys are similar to those of liquid metals - this and other evidence suggest that they are "amorphous", that their structure is that of a glass.

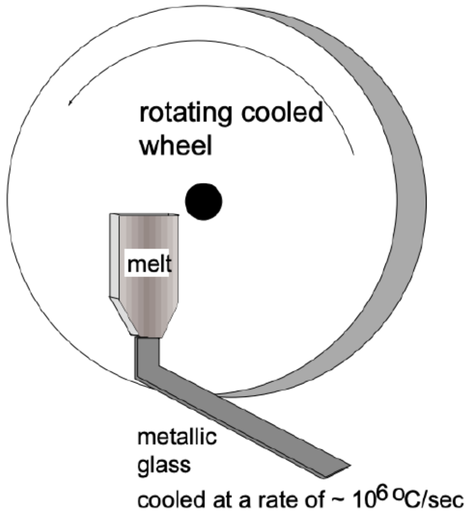


Figure 3 Production of metalic glass by melt spinning

Another method for preparing metallic glasses is by vacuum deposition onto a substrate cooled to approximately 80K. Again, pure metals crystallize under these conditions, but suitable alloys form glasses, some of which are stable when brought to room temperature. An example is the silver-copper system in which the two solid metals have only about eight percent solubility in each other. If a melt containing 50 wt.$\%$ silver and 50 wt.$\%$ copper is slowly cooled, two crystalline phases are produced. When this same alloy is obtained by vacuum deposition, a metastable metallic glass is formed. Initially the glass has metallic electrical conductivity comparable to that of the liquid alloy. When the glass is heated for $1/2$ hour at $380\ \mathrm{K}$, it converts to a crystalline, metastable face-centered cubic solid solution. Only on heating at about $500\ \mathrm{K}$ does the equilibrium, two-phase structure form. Many pure nonmetallic elements, however, such as S, Se, Ge and Si, form a stable glass under suitable conditions.

1.7.3: THE GLASSY STATE

The properties and chemical composition of the glass used for optical purposes differ greatly from those of the glass used for baking dishes. Likewise, the glass used for window panes differs from the glass used for artwork or optical purposes. However, (most) inorganic glasses have one thing in common: they are ceramic materials (compounds that contain metallic and non-metallic elements, most often oxygen) with the amorphous structure of a frozen liquid.

Quartz glass is not crystalline at room temperature because the rearrangement of interatomic bonds between Si and O required for the establishment of order is impeded: the viscosity of glass is so high at room temperature that millions of years would be required for it to crystallize (see above). Hence, glass can be viewed as a perfectly rigid "liquid", being exceptional in that its extraordinarily high viscosity slows down its flow properties even on an expanded time scale.

Upon cooling of liquid “glass” we observe that $\Delta V/\Delta T$ (the contraction with lowering of T) changes. This may be seen by following the three basic steps in the production of glass: (1) the melting of quartz sand (minute crystals of silica), (2) the shaping of the glass while in a viscous state and (3) the controlled cooling of the shaped article. The $\mathrm{SiO_4}$ tetrahedra in the sand (crystals) are arranged in an ordered pattern (fig. 4), but in the molten state the crystal matrix breaks up into strings and rings of tetrahedra in irregular patterns (fig. 5). Because the temperature is very high, the groupings continually break up and reform, making the mass fluid.

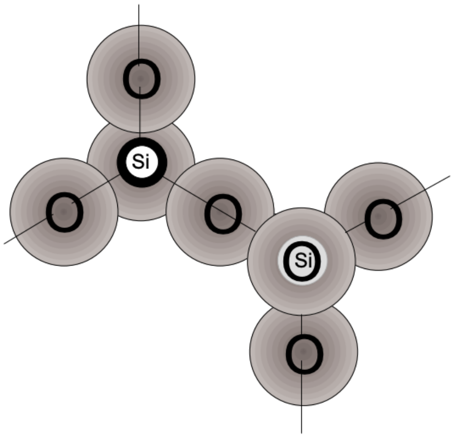


Figure 4 Basic Si - O - Si - units as established with sp^3 hybridization of Si

Upon cooling of molten $\mathrm{SiO_2}$ the tetrahedra form larger groupings and the glass becomes more viscous, permitting it to be shaped by blowing, rolling, pressing, etc. With continuing cooling, larger groupings of tetrahedra form as their kinetic energy decreases. These two phenomena are responsible for the increase in viscosity and the shrinkage that takes place during the cooling period. Beyond the glass transformation temperature changes in configuration of the tetrahedra virtually cease because the glass, to all intents and purposes, has lost its fluidity.

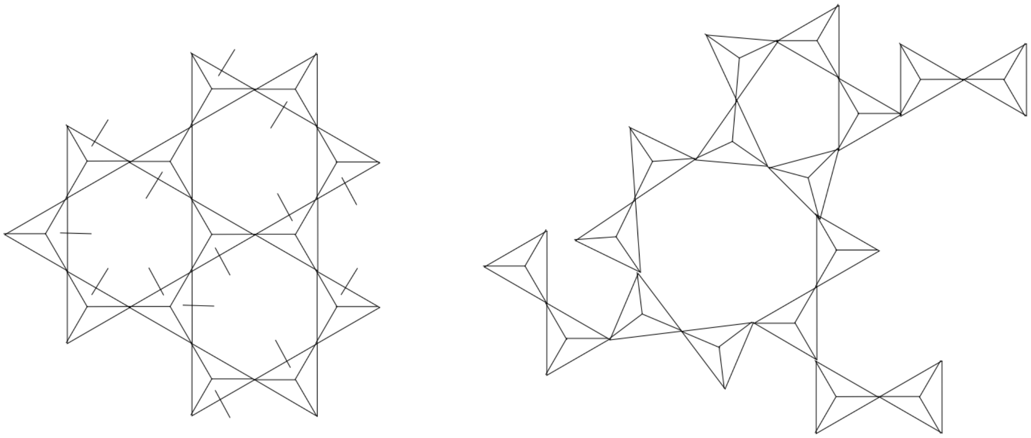


Figure 5 Two-dimensional view of tetrahedra as in silicondioxide structures: (a) in crystalline, ordered structures and (b) in disordered glassy (amorphous) structures.

1.7.4: OXIDE GLASSES

The bonding forces responsible for the formation of network structure in crystalline SiO_2 produce similar networks in glasses of other oxides such as B_2O_3 and P_2O_5 which are thus also considered as primary *network formers* (the present discussion will be limited to silica glasses). If an oxide, such as Na_2O, is added to silica glass, a bond in the network is broken and the relatively mobile sodium ion becomes a part of the structure (fig. 6). Examples of such *network modifiers* are N_2O, K_2O, Li_2O, CaO, MgO and PbO.

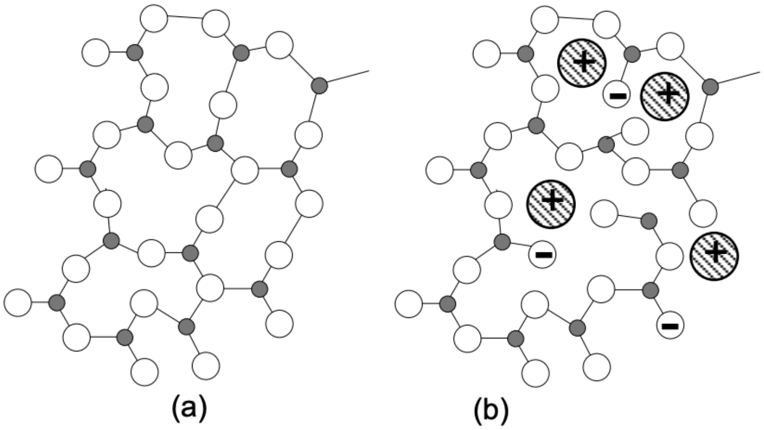


Figure 6 Schematic glass networks; (a) SiO_2 network (b) SiO_2 network modified through addition of Na_2O.

With increase in the amount of modifier, the average number of oxygen-silicon bonds forming bridges between silicon between silicon atoms decreases as follows:

O/Si Ratio in Glass	Bridging-O-Si Bonds/Si atom
2.0	4 (fig. 7)
2.5	3
3.0	2

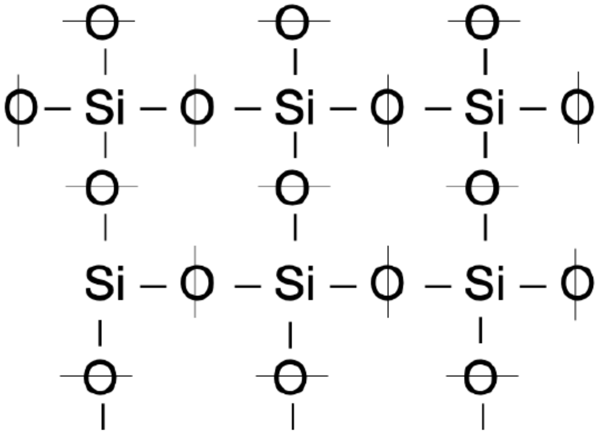


Figure 7 Schematic of SiO_2 network; the O to Si ratio is 2 : 1 as indicated by the chemical formula

Two bridging bonds per silicon atom will correspond, for example, to a linear chain structure, and any further increase in modifier would reduce the length of the chain. The principal effect of a modifier is to lower the melting and working temperature by decreasing the viscosity. An excess of modifier can make the structural units in the melt sufficiently simple and mobile that crystallization occurs in preference to the formation of a glass.

The compositions and properties of typical glasses are listed in Table 1. Soda-lime glass not only has the advantage of being made from inexpensive raw materials, but also the practical convenience of low working temperatures (fig. 8). Most glass-forming operations (pressing, drawing, etc.) begin at the temperature corresponding to the working point, but can continue while the glass cools.

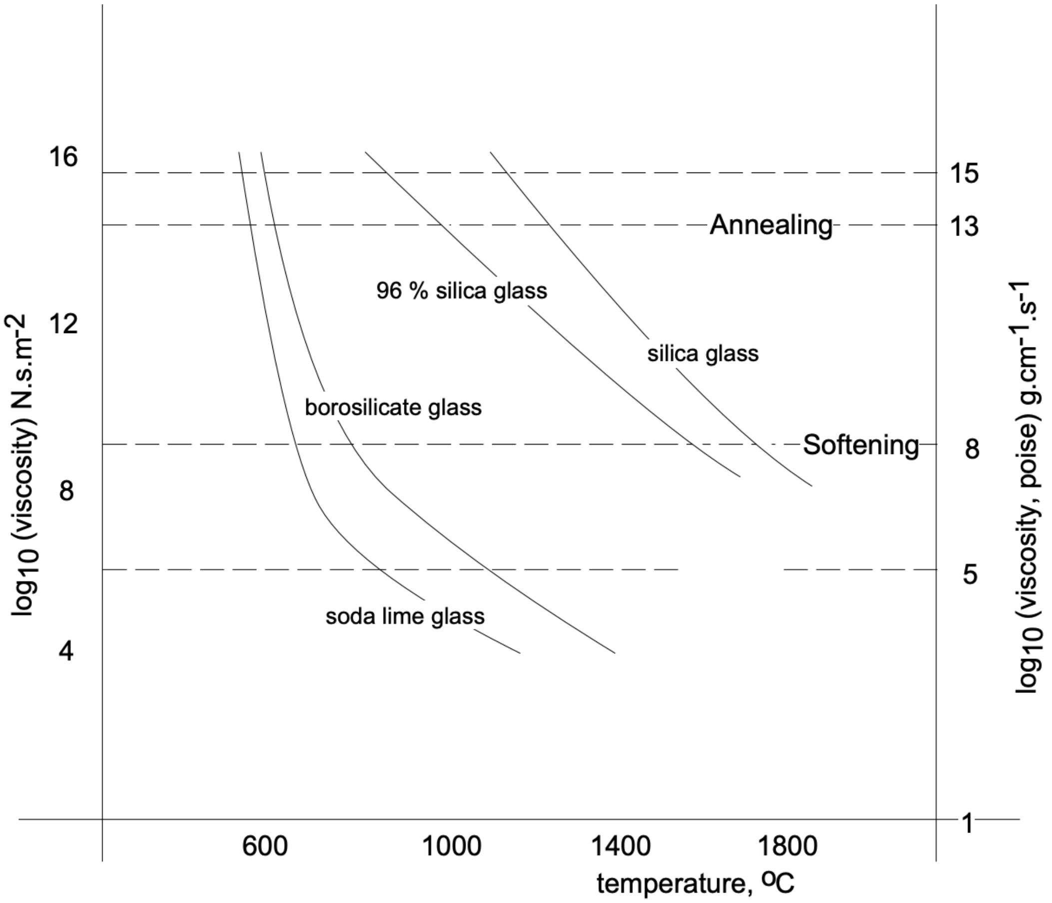


Figure 8 Important temperatures in fabrication of silicate glasses (the temperatures are related to viscosity which in turn controls workability)

1.7.5: ANNEALING OF GLASS

In order to relieve the internal stresses that may develop during glass formation, all commercial glassware is annealed (slowly cooled) immediately after shaping. This slow cooling operation is carried out in industry by placing the shaped objects on a conveyor belt which transports them first through a reheating zone and then through sections having successively lower temperatures in a furnace called the *lehr*.

TABLE 1. Typical Oxide Glasses

	Composition, w/o								
Type	SiO_2	Na_2O	K_2O	CaO	MgO	B_2O_3	Al_2O_3	Other	Properties or uses
Soda-lime	72	14		9	4		1		Window glass
Silica glass (fused quartz)	99.5+								High-temperature applications; low coefficient of expansion
96% silica glass	96.3	<0.2	<0.2			2.9	0.4		Comparable to fused quartz
Borosilicate	80.5	3.8	0.5			12.9	2.2		Resistant to heat and to chemicals
Light flint optical	54	1	8					37PbO	High index of refraction
Surface-strengthened glass	55	16	2	2		2	19	$4TiO_2$	Cookware
Glass-ceramic	56				15		20	$9TiO_2$	Radomes

The transformation of a liquid to a glass actually takes place over a range of temperatures at which the glass shrinks (thermal contraction). The glass does not undergo a change from disordered liquid structure to crystal structure as iron does at its transformation temperature; in glass, the transformation temperature is the temperature below which viscosity prevents any further configurational changes. Any contraction beyond the transformation temperature range is due only to the lower kinetic energy of the groupings.

The transformation temperature of a given "glass composition" depends on its constituents and upon the rate of cooling. Slow cooling results in a lower transformation range because the tetrahedra will have more time to rearrange (to some degree). This results in tighter packing of tetrahedra as the mass reaches its transformation range. When the glass reaches room temperature, its volume will be smaller when cooled slowly than glass melt which has been cooled rapidly. Hence, slower cooling from the melt results in a denser glass. (See fig. 2.)

Glass is thermodynamically unstable at room temperature because configuration changes (which require eons of years to come about!) would result in a lower free energy configuration. However, the changes are so slow that they may be considered negligible.

1.7.6: PROPERTIES OF GLASSES

The strong covalent bonds that exist between the atoms of inorganic glasses plus the lack of crystal structure give glass unusual characteristics. Thus, quartz glass is:

1. (a) Chemically stable;
2. (b) A poor conductor of heat and electricity;
3. (c) Inherently transparent;

4. (d) Inherently strong.

1.7.6.1: Chemical Stability

All glasses are immune to oxidation (decay) because their atoms are fully oxidized. Glass composed of 100 percent silica tetrahedra is extraordinarily inert. It resists the action of most acids (the most notable exception is hydrofluoric acid, utilized to etch glass), but it is attacked by strong alkalis. (The bottles containing liquid alkalis on a chemist’s shelf have a clouded surface.)

1.7.6.2: Conductivity

The ability of a material to conduct electricity is dependent upon the presence of electrons in the conduction band, separated in glasses by as much as 10eV from the valence band. Because the electrons in glass are tightly bonded, glass is a very poor conductor of electricity - in fact, the large energy gap makes glass an excellent insulator. Glass is also a poor conductor of heat. Thus, hot common glass may crack when cold water is poured onto it because the surface exposed to the cold water will shrink while the dimensions of the interior remain unaffected.

1.7.6.3: Strength

Glass is harder than many types of steel and is also very elastic, as evidenced by the speed and accuracy with which glass marbles rebound when they meet.

Glass has "no" crystal structure, and hence the phenomenon of slip cannot take place. This, together with the strong bonding between atoms, gives glass a very high compressive strength and a theoretical tensile strength of about $10^7 \mathrm{kN/m^2}$ (significantly higher than that of steel). (Glass fibers with an actual tensile strength of $4 \times 10^7 \mathrm{kN/m^2}$ have been produced.) Since glass has a "liquid structure" it may be considered "saturated with dislocations". [If a piece of metal has a very high dislocation density (eg., due to cold working) the dislocations interfere with each other's movements. Therefore, with increasing dislocation density a piece of metal becomes harder and stronger, but also more brittle.] Since the molecular structures in glass are unable to move, the presence of minute cracks or imperfections in glass permits stress concentrations to localize and exceed the bond strength between atoms - common glass will crack. Thus, in actual practice, the strength of glass is, by a factor of 100 to 1000, less than the theoretical strength, and glass is brittle. For example, a freshly made electric light bulb may not crack when initially dropped, but its surface becomes damaged and, after it rebounds and strikes the floor a few more times, it breaks.

The inherent high strength of fibrous glass is utilized in the fiberglass sections employed for boats and automobile bodies. Before being pressed into shape fiberglass is mixed with a synthetic resin which serves to protect the fibers from scratching. Since the fibers thus retain their high strength, fiberglass sections are very strong for their weight.

1.7.7: STRENGTHENED GLASS

The glass scientist has produced objects made of glass which can be struck with a hammer or dropped from a tall building without breaking. Two techniques are employed in strengthening glass - one physical and one chemical. Both techniques are based on the fact that, when there is the slightest imperfection (minute scratch) on the surface, glass remains extraordinarily strong in compression but becomes weak in tension. Thus the strengthening treatment consists of *prestressing* a glass object by inducing compressive strains in its exterior and thereby enabling it to counteract any tensile stresses which develop under tension.

In physical prestressing, the shaped object is heated to just below its softening point (surface flows are annealed out) and its surface is then chilled by means of a blast of air or an oil bath. Under these conditions the exterior of the glass cools and contracts immediately, but since glass is a poor conductor of heat the interior will not contract - the glass will not crack because the interior remains plastic. When the interior starts to cool, it cannot contract because the exterior has already set, but, in attempting to contract, the interior continues to draw the exterior together. A built-in compressive stress then develops in the outer layers of the glass. When a tensile stress is applied to this glass, it is counteracted by these compressive stresses. Thus the prestressed glass will not shatter until the surface compression is exceeded.

As long as its surface remains intact, prestressed glass continues to be strong and shock-resistant. However, if a deep scratch develops on the surface, the tensile stresses set up in the interior by the surface compression are released and the glass will shatter into thousands of tiny particles. Therefore prestressed articles must be cut to exact size and all holes drilled prior to prestressing. Among the many uses for this type of glass are plate-glass doors, side windows of automobiles and portholes of ships.

Ion exchange is a chemical technique for prestressing glass objects. The first step is to place the shaped object into a molten salt bath containing potassium ions, which replace the sodium ions on the surface of the glass. The potassium ions are larger than the sodium ions and, in accommodating them, the surface of the glass becomes more crowded - thus inducing compressive strains on the exterior. Glass of this type, characterized by very high strength, is useful for a great variety of applications. Its flexural strength can be as high as $10^6 \mathrm{kN/m^2}$ compared with $10^5 \mathrm{kN/m^2}$ for untreated glass.

1.7.8: DEVITRIFICATION OF GLASS

Under certain conditions glass will become "contaminated" with crystalline particles. A glass in this condition is termed *devitrified*, which is simply another way of stating that it has partially or completely crystallized. Devitrified glass, unless of the very special variety that is deliberately produced, is undesirable since the crystalline areas form large crystals and are extremely weak and brittle, as well as being translucent only. Crystalline segregations in glass are known as stones

1.7.9: RECRYSTALLIZED GLASS (GLASS CERAMICS)

Recrystallized glass, also known as polycrystalline glass, is commonly produced by adding nucleating agents to the glass batch. Subsequently the glass can be formed into a desired shape by any of the conventional glass forming processes and then be heat-treated to promote recrystallization. Recrystallized glass possesses increased impact strength, hardness and thermal shock resistance compared with conventional non-crystalline glasses. One commonplace application of a recrystallized glass is in the manufacture of the so-called refrigerator-to-oven cooking dishes.

1.7.10: COLORED GLASSES

We recognize that glass is normally colorless due to the fact that all electrons are "tightly bonded" and no electronic excitations in the energy range of the visible light spectrum are possible. Glass, however, may be made to absorb selectively in the visible spectrum (thus becoming colored) by any one of three processes:

(1) Addition of ions of transition metals. Such ions provide electronic excitation possibilities to visible light. Typical ions added are:

$\mathrm{Cr^{++}}$	blue
$\mathrm{Cr^{+++}}$	green
$\mathrm{Co^{++}}$	pink
$\mathrm{Mn^{++}}$	orange
$\mathrm{Fe^{++}}$	blue-green

(2) Addition of colloidal particles (ϕ 40 to 2000Å). These small particles, while not impeding light transmission (because of their small size) exhibit selective absorption and complementary reflection. Au particles (at $10^{-4}\ \mathrm{g/cm^3}$) give colors which vary with particle size:

Au	$\phi 4-10$ nm	pink
Au	$\phi 10-75$ nm	ruby
Au	$\phi 75-110$ nm	green
Au	$\phi 110-170$ nm	brown

(3) Addition of colored crystals. Some glasses are colored by means of crystals dispersed throughout. An example is the scarlet glass made by the early Egyptians (brought about by the addition of red copper oxide). Another example is red color from the addition of red $\mathrm{Pb_2CrO_6}$ whereas $\mathrm{Cr_2O_3}$ yields green color.

1.7.11: GLASS FIBER

Glass fiber, or fiberglass* as it is commonly known, is glass in fiber form. It is made by one of several processes, each of which involves the drawing out of the filaments from glass in the viscous state. Modern technical developments date from World War I when Germany had to find a substitute for asbestos as insulating material.

The process whereby continuous filament glass fiber is made is particularly interesting. The glass batch is melted in the glass tank furnace and the molten glass is molded into ordinary sized marbles. These marbles are fed into an electric furnace which has a platinum-alloy bushing containing many tiny holes. When the glass marbles reach the holes, the glass flows through them and is drawn down vertically, forming individual filaments. These filaments can then be twisted into a "yarn" and spun on normal textile spindles as required. About one third of an ounce of glass produces about one hundred miles of filament at a rate of about 6,000 feet per minute.

Glass wool, on the other hand, is produced by a different process. The most common technique, known as the Crown process, produces a thick matte of short glass fibers which are held together by a polymer binder. In the Crown method, a thick stream of molten glass is poured into a rapidly rotating steel dish that has tiny vents around its periphery. The glass is forced through these vents by centrifugal force, forming relatively short fibers with diameters of about 0.0007 cm. The matte is then passed through curing ovens where the binder sets and is then cut into sizes suitable for insulation.

*

Fiberglass is really a registered trade name.

1.7.12: SHEET AND PLATE GLASS PRODUCTION

The main types of flat glass produced are drawn sheet and float glass. The processes involved are highly automated.

Flat drawn glass is used for windows and other applications where accuracy of thickness and a high surface finish are not vital. In this process the molten glass is drawn up vertically from the end of a large rectangular tank furnace, the thickness of the drawn sheet being controlled principally by the size of the slot in the steel form held just above the surface of the molten glass. A steel starting dummy is used to commence the drawing action, but this is cracked off once it passes through. Once started, this process is continuous, the cooled and solidified sheet merely being cracked off in suitable lengths once it leaves the rolls.

The *float process* is the most recent advance in the production of plate glass with a high surface finish. In the float process, flat, fire-finished, stress-free glass is formed by preventing contact between the glass sheet and anything solid. The glass leaves the glass-tank in a continuous molten strip and is floated immediately onto the surface of a bath of molten tin. The tin bath is surrounded by a non-oxidizing atmosphere and, while in this atmosphere, the glass is heated sufficiently to prevent the development of internal stresses. As the glass sheet leaves the float bath chamber it enters an annealing furnace. Glass produced by the float process is free from distortion and has fire-finished surfaces that are smoother and flatter than those of normal polished plate glass.

1.8: Theory of Reaction Rates

1.8.1: 1. INTRODUCTION

We can readily understand that chemical reactions normally are preceded by collisions of atoms, ions, or molecules. However, the rate of such collisions in solids, liquids and gases is so great that all reactions would be very rapid were it only necessary for collisions to occur. “Chemical” reactions will not proceed more rapidly than molecular collisions allow, but many reactions proceed much more slowly. It is thus apparent that not every molecular collision leads to reaction. We have also seen from earlier examples that the driving force for physical as well as chemical reactions is the (free) energy change - which must be negative for reactions to occur spontaneously. However, while providing a “go/no-go” answer, this criterion alone cannot give us any information concerning the rate at which reactions occur, nor can it tell us which factors influence the reaction velocity.

Rates at which reactions occur vary considerably. For example, the nuclear reaction:

$$\mathrm{U}_{92}^{238} \rightarrow \mathrm{Th}_{90}^{234}+\alpha \qquad \text{is } 50\% \text{ completed } \left(\tau_{1/2}\right) \text{ after } 5\times 10^{9} \text{ years.}$$

$$\tau_{1/2}=5\times 10^{9}\,\text{years}$$

On the other hand, the chemical reaction:

$$\begin{array}{ll} \mathrm{SO}_4^- +\mathrm{H}^+ \rightarrow \mathrm{HSO}_4^- & \text{is } 50\% \text{ completed after about } 10^{-4} \text{ s.} \\ \tau_{1/2}=3\times 10^{-4} & \text{seconds} \end{array}$$

Reaction kinetics (rate theory) deals to a large extent with the factors which influence the reaction velocity. Take corrosion (rusting of iron), for example. We all know that it requires air and water to provoke rusting and we also know, much to our sorrow, that rusting proceeds much more rapidly near the ocean where salt is present. We also know that the rate of rusting depends strongly on the composition of iron (pure Fe and steel corrode much less rapidly than cast iron, for example). It is primarily kinetic studies which lead to the elucidation of chemical reactions and, in the case of corrosion, to the development of more corrosion resistant materials.

The principal experimental approach to the study of the reaction process involves the measurement of the rate at which a reaction proceeds and the determination of the dependence of this reaction rate on the concentrations of the reacting species and on the temperature. These factors are grouped together in the term *reaction kinetics* and the results for a given reaction are formulated in a *rate equation* which is of the general form:

Rate = k(T) x function of concentration of reactants

The quantity k(T) is called the *rate constant* and is a function only of the temperature if the term involving the reactant concentrations correctly expresses the rate dependence on concentration. Thus the experimental information on the reaction process is summarized in the rate equation by the nature of the concentration function and by the value and temperature dependence of the rate constant.

1.8.2: 2. EXPERIMENTAL METHODS IN REACTION RATE STUDIES

Since we know that chemical reactions are temperature dependent, kinetic investigations will require rigorous temperature control (thermostats). Furthermore, we have to be able to observe and investigate concentration changes of reactions and products. For this purpose it frequently is customary to interrupt a reaction (for example, by quenching - the abrupt lowering of temperature) and to make a chemical analysis. In other instances, particularly for very fast reactions, a direct measurement of concentration changes is physically impossible. In such cases it is necessary to quantitatively follow reactions indirectly, through the accompanying changes in specific physical properties such as:

(1) electrical conductivity

(2) optical absorption

(3) refractive index

(4) volume

(5) dielectric constant

as well as by other means. In the last twenty years, for example, the use of isotopes (as “tracer” elements) has become a valuable tool for the study of reaction kinetics (in slow reactions).

1.8.3: 3. CONCENTRATION DEPENDENCE OF REACTION RATES

Normally experimental data of kinetic investigations are records of concentrations of reactants and/or products as a function of time for constant temperatures (taken at various temperatures).

Theoretical expressions for reaction rates (involving concentration changes) are differential equations of the general form:

$$\frac{dc}{dt} = f\left(c_1^m, c_2^n, c_3^o \ldots\right)$$

where (c) are concentration terms which have exponents that depend on details of the reaction.

If we want to compare the theory with the experiment, it is therefore necessary to either integrate the theoretical laws or to differentiate experimental concentration vs time data.

The rate laws are of importance since they provide analytical expressions for the course of individual reactions and enable us to calculate expected yields and optimum conditions for “economic” processes.

In most instances the differential rate equation is integrated before it is applied to the experimental data. Only infrequently are slopes of concentration vs time curves taken to determine dc/dt directly (fig. 1).

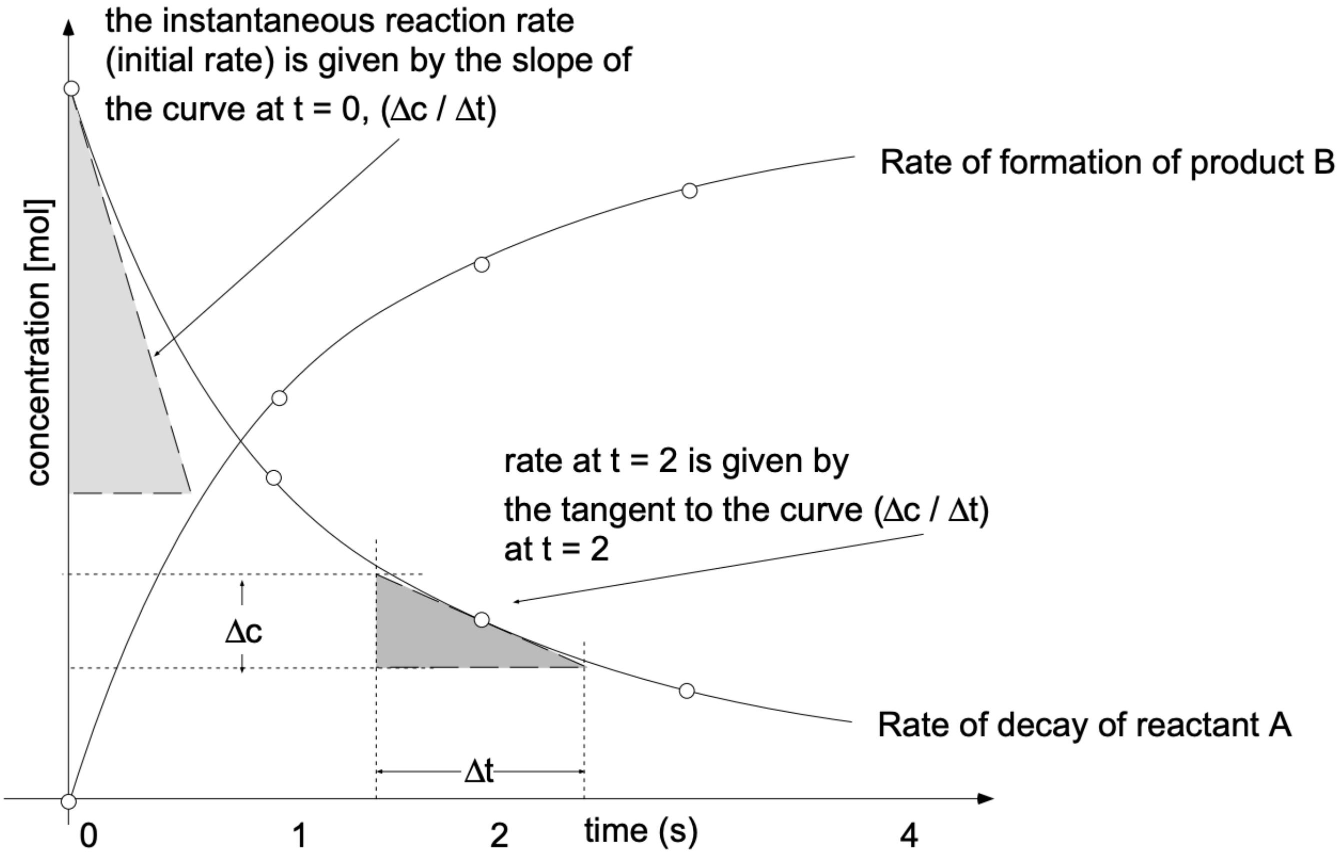


Figure 1 Variation with time of the concentration of a reactant (A) and of a product (B)

Let us look at a simple reaction, the decay of H_2O_2 to water and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

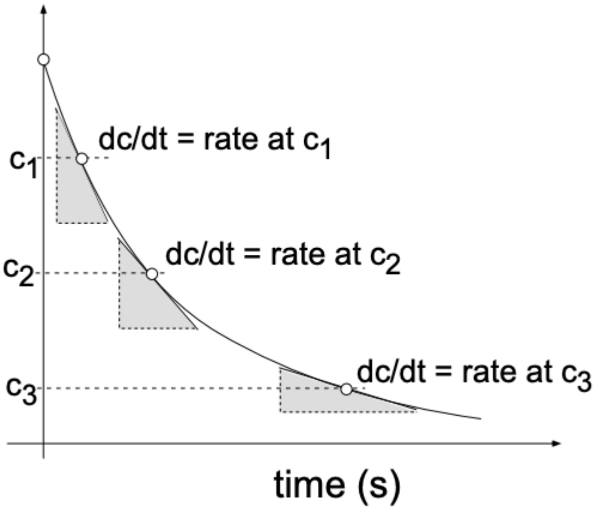


Figure 2 Decay curve (dc/dt vs. c) for H_2O_2

Experimentally we obtain a curve (such as fig. 2) by plotting the concentration of remaining H_2O_2 in moles/liter, normally written $[H_2O_2]$, as a function of time. The rate is then given by the time differential:

$$\text{Rate}\left(\frac{\text{moles}}{\text{liter}\cdot\text{s}}\right)=\frac{-d\left[H_2O_2\right]}{dt}$$

If we now determined and plotted the variation of the reaction rate, $\left[-d\left[H_2O_2\right]/(d\text{ time })\right]$, with concentration, $[H_2O_2]$, we would find a straight line (fig. 3). Thus:

$$-\frac{d\left[H_2O_2\right]}{dt}=k\left[H_2O_2\right]\text{ or generally, }-\frac{dc}{dt}=kc$$

Upon integration:

$$\int\frac{dc}{c}=-k\int dt$$

we have:

$$\ln c=-kt+\text{ const.}$$

Taking $c=c_o$ for $t=0$, we get $(\text{ const}=\ln c_o)$ and:

$$\ln c=-kt+\ln c_o$$

or:

$$c=c_oe^{-kt}\quad\text{and}\quad k=\frac{1}{t}\times\ln\frac{c_o}{c}$$

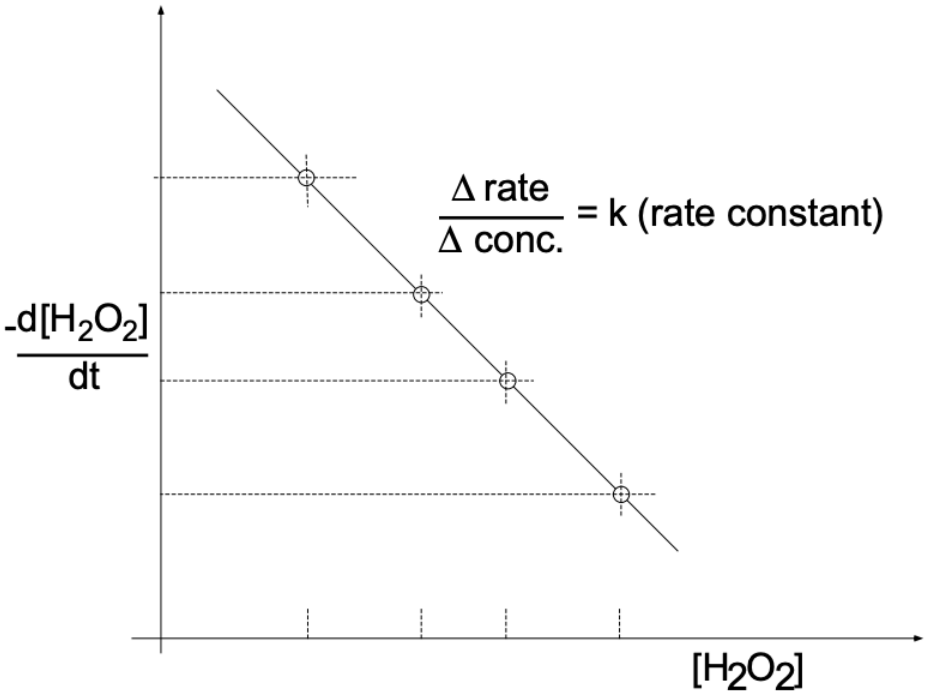


Figure 3 Concentration dependance of the rate of reaction

Alternately:

$$k=\frac{2.3}{t}\times\log\frac{c_0}{c}\quad\text{ and }\quad k=\frac{2.3}{t_2-t_1}\times\log\frac{c_1}{c_2}$$

From the above we see that for decay of $\mathrm{H_2O_2}$ a plot of $(\ln \mathrm{c})$ vs. t results in a straight line (fig. 4). This behavior is characteristic of first order reactions in which the concentration exponent (n) is "one":

$$-\frac{\mathrm{dc}}{\mathrm{dt}}=\mathrm{kc}$$

First Order Reactions: Radioactive Decay

From the relationship:

$$\mathrm{k}=\frac{2.3}{\mathrm{t_2-t_1}}\times\log\frac{\mathrm{c_1}}{\mathrm{c_2}}$$

which relates the rate constant (k) to the concentration change (Δc) for the time interval (Δt), we can show that (for first order reactions) the time required to complete a reaction to $1/2$ or $1/4$ or any fraction of the initial concentration is independent of the initial concentration of reactant present (fig. 5).

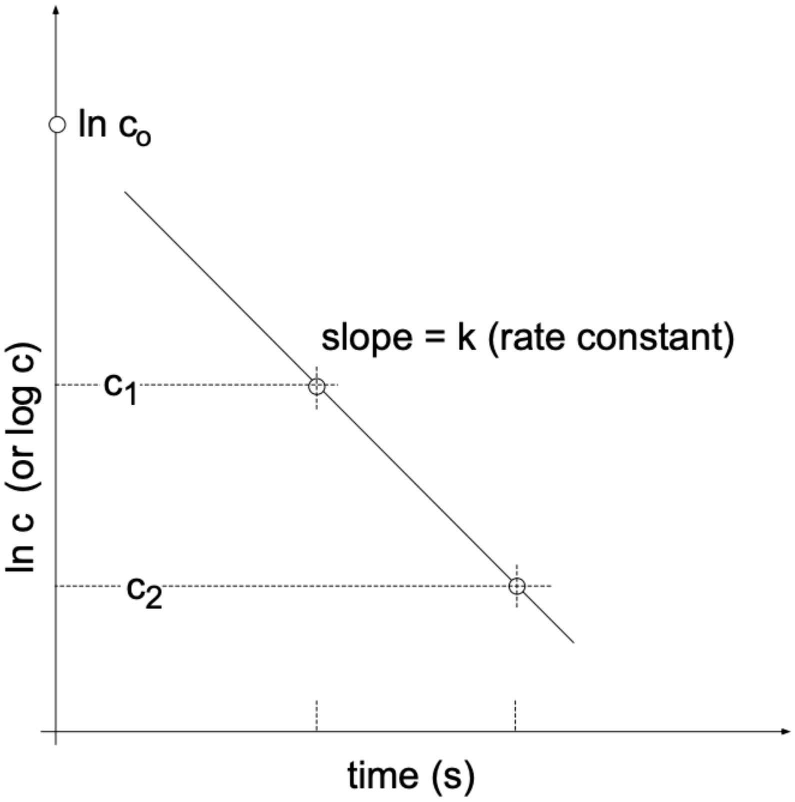


Figure 4 Plot of ln c vs. time

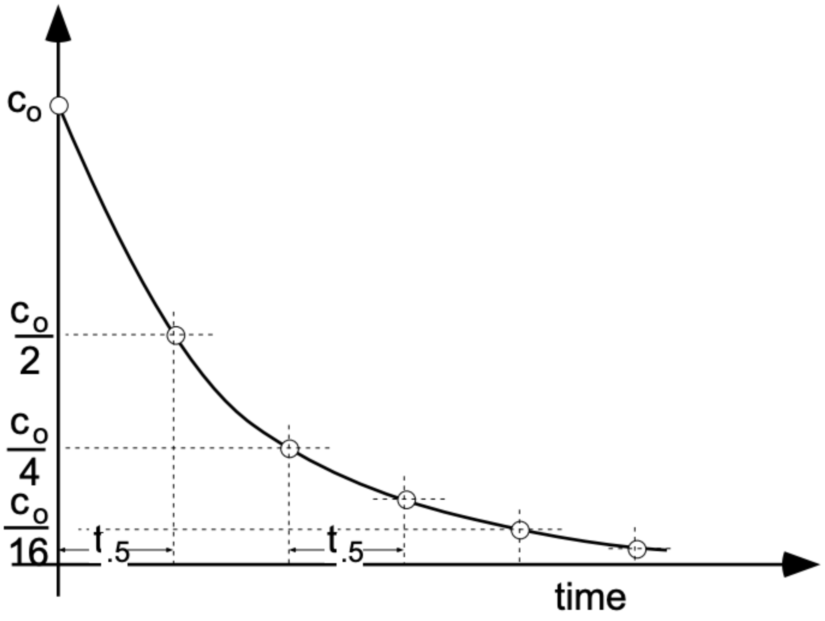


Figure 5 Concentration independent half life (t.5) of First order reactions.

When discussing radioactive decay it is customary to call the “rate constant” (k) the “decay constant”. It is furthermore customary to consider the time it takes to decrease the number of originally present species (normally called reactants) to 0.5 (by 50%). We then talk about the *half-life*. Accordingly, the above equation can be reformulated as:

$$\mathrm{k}=\frac{2.3}{\mathrm{t}_{1/2}}\times\log\frac{\mathrm{c}_1}{\frac{\mathrm{c}_1}{2}}=\frac{2.3}{\mathrm{t}_{1/2}}\times\log 2$$

or:

$$k=\frac{0.693}{t_{1/2}}$$

This means that from the half-life $\left(\mathrm{t}_{1/2}\right)$ we may obtain the decay constant (rate constant in general). Vice versa, knowing the rate constant, we can calculate the time it takes to complete 50% of the reaction (or decay).

1.8.4: 4. REACTION ORDER

Reactions of first order, such as the decay of $\mathrm{H}_2\mathrm{O}_2$ or radioactive decay, do not require molecular or atomic collisions - in principle they reflect inherent instability. A multitude of chemical reactions do involve collisions, however. For example, take the decay of HI:

$$2\mathrm{HI}\rightarrow\mathrm{H}_2+\mathrm{I}_2$$

The rate law for this reaction reflects the requirement of a collision in the concentration exponent:

$$-\frac{\mathrm{d}[\mathrm{HI}]}{\mathrm{dt}}=\mathrm{k}[\mathrm{HI}]\times[\mathrm{HI}]=k[H\mathrm{H}]^2$$

The reaction is referred to as a *second order reaction* which can readily be identified since upon integration the rate law yields:

$$\frac{1}{[\mathrm{HI}]}=\mathrm{kt}+\text{ const}$$

or, more generally:

$$\frac{1}{\mathrm{c}}=\mathrm{kt}+\text{ const}$$

A plot of $1/c$ vs t will yield a straight line.

It is interesting to note that a determination of the reaction order from experimental data supplies insight to the details of how molecules and atoms react with each other. Even though rate data involve measurements of gross numbers of molecules, their interpretation (through the reaction order) permits us to formulate the probable step (or steps) which individual molecules undergo.

1.8.5: 5. TEMPERATURE DEPENDENCE OF REACTION RATES

Although a chemical reaction may be "thermodynamically" favored (which means the free energy of the system will be lowered as a result of the reaction), reaction may nevertheless not take place. Thus, H_2 and O_2 gases can exist in intimate contact over a considerable temperature range before reaction takes place. Nevertheless, a lighted match or a platinum powder catalyst can nucleate an immediate explosive reaction. Another example with which we are familiar is glass: some glasses remain "supercooled liquids" for thousands of years at room temperature unless reheated to some definite temperature for at least some minimum period of time. Many different factors may influence the rate of a reaction - for example:

(1) Existing interatomic (or intermolecular) bonds must be broken.

(2) Atoms must be moved to and away from the reaction site.

(3) A new boundary is required wherever a new "phase" is to be nucleated.

All three steps cited require work or a supply of energy. Furthermore, all three steps are temperature dependent. At the beginning of this chapter we have stated:

$$\text{Rate}=k(T)\times\text{ function of concentration of reactants}$$

In other words: the reaction rate is proportional to the concentration of reactants. The proportionality constant k is a function of temperature $k(T)$. The temperature dependence of k (which represents the temperature dependence of the rate of a given reaction) can be studied by performing experiments (with constant concentrations) at different temperatures. From such experiments it can be seen that the value of the rate constant (k) is much greater at higher temperatures - the reactions proceed faster

In 1899 Arrhenius showed that the rate constant of reactions increased in an exponential manner with T. By an empirical procedure he found that a plot of log k versus 1/T gives a linear relation.

Remember: In all kinetic and thermodynamic calculations it is mandatory to use the "absolute temperature scale" in Kelvin (K) which is given by:

$$\mathrm{K}={}^{\circ}\mathrm{C}+273.16$$

Thus $\mathrm{OK}=-273.16\mathrm{C}$, which corresponds to the thermodynamic absolute zero temperature. Linear plots of $\log \mathrm{k}$ vs $1/\mathrm{T}$ imply the relation:

$$\ln k \propto \frac{1}{T}$$

$$k \propto e^{\mathrm{const}/\mathrm{T}}$$

In view of later deductions this empirical relation can be conveniently written as:

$$\mathrm{k}=\mathrm{Ae}^{-\mathrm{E}/\mathrm{RT}}$$

where A is a proportionality constant sometimes called the reaction constant, R is the gas constant and equals $8.31\ \mathrm{J}/$ mole K, E is the activation energy in Joules/mole and e is the base of the natural (Naperian) system of logarithms. Since $\ln x=2.3 \log_{10} x$, we can rewrite the above equation:

$$\ln \mathrm{k}=\ln \mathrm{A}-\frac{\mathrm{E}}{\mathrm{RT}}$$

or

$$\log k=\log A-\frac{E}{2.3 \times 8.3 \times \mathrm{T}}$$

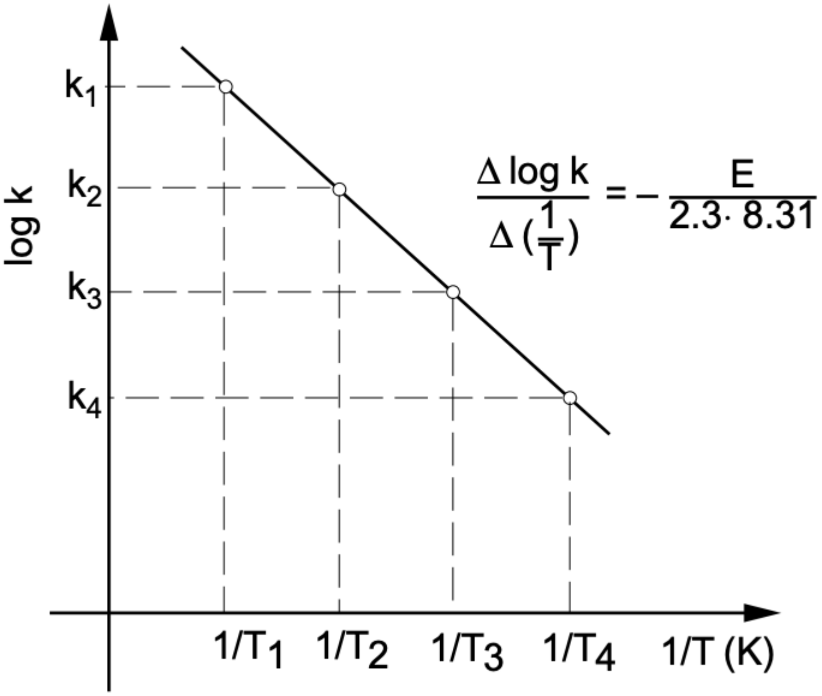


Figure 6 Arrhenius plot permitting the determination of activation energies

If the above equation is obeyed, a plot of log k versus 1/T (fig. 6) will be a straight line from which the characteristic activation energy can be determined since the slope is –E/19.15. The reaction constant (log A) may in turn be evaluated by extrapolating the rate line to the point at which 1/T equals zero.

It is important to realize that many reactions involve a succession of steps, in which case the rate is controlled by the slowest step. The corresponding values of E and A must be determined by experimental methods.

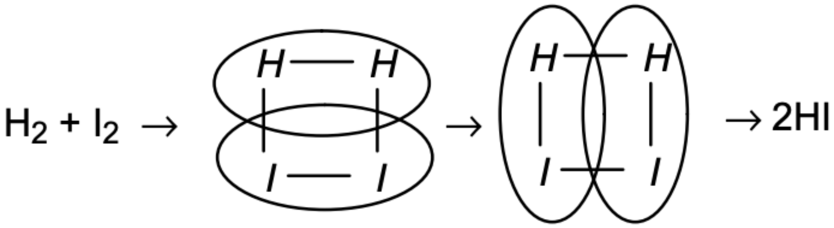
1.8.6: 6. THE ARRHENIUS THEORY

Arrhenius developed a primarily qualitative theory for molecular reactions which led to empirical expressions for the rate constant. Later theories (which are beyond the scope of 3.091) elaborate and make these original ideas more quantitative.

The very simple (reversible) vapor-phase reaction of hydrogen and iodine to give hydrogen iodide can be used to illustrate the ideas of Arrhenius. The reaction

$$\mathrm{H_2 + I_2 \rightarrow 2HI}$$

apparently proceeds by a one-step (one collision) four-center process such that the path of the reaction can be depicted as follows:



For more complicated systems, even when a mechanism has been postulated, it is not so easy to see how the electrons and atoms move around as the reaction proceeds. However, even Arrhenius recognized that any reaction process can proceed first by means of the formation of some “high-energy species” (which we now call the “activated-complex”) and secondly by the breakdown of this complex into products.

If the activated-complex is assumed to have an energy, $\mathrm{E_a}$, greater than the reactants, then, in analogy to earlier considerations, the number of activated-complex molecules compared with the number of reactant molecules can be written in terms of the *Boltzmann distribution* as:

$$\frac{[\text{activated }-\text{ complex molecules}]}{[\text{ reactant}]}=e^{-E_a/RT}$$

The rate of reaction thus becomes proportional to the concentration of activated-complex molecules:

$$\text{Rate} \propto (\text{activated-complex molecules})$$

or

$$\text{Rate } = A\times e^{-E_a/RT}\times \text{ reactants}$$

Making

$$k = Ae^{-E_a/RT}$$

we find

$$\text{Rate } = \mathrm{k}\,[\text{reactants}]$$

Moreover, the theory says that the empirical constant, $\mathrm{E_a}$, is to be interpreted as the energy of the activated-complex compared with that of the reactant molecules.

The idea of an activated-complex can be presented on a plot (fig. 7) of the energy of

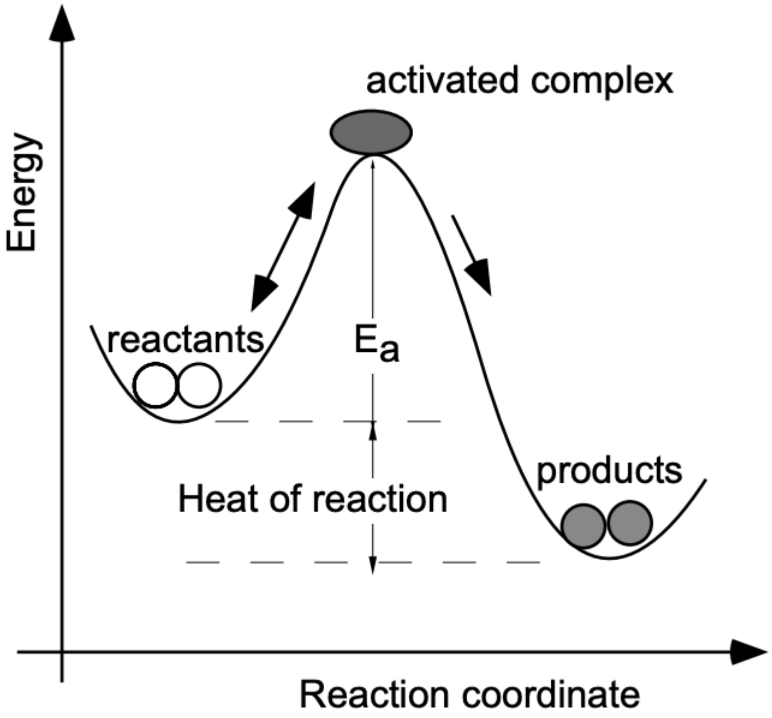


Figure 7 Schematic of a reaction via activated complex formation

the system as ordinate versus the *reaction coordinate* as abscissa. The reaction coordinate is not any single internuclear distance, but rather depends on all the internuclear distances that change as the reactant molecules are converted into product molecules. In general it is impossible, and for the present purpose unnecessary, to give a quantitative description of the reaction coordinate. It consists of the transformation from reactants to products.

The Arrhenius theory leads to a considerable improvement in our understanding of the reaction process. It is, however, still a very qualitative theory in that it does not show how the pre-exponential factor A depends on the molecular properties of the reaction system, nor does it attempt to predict the value of E_a.

1.8.7: 7. THE ACTIVATION ENERGY

The basic distribution of molecular (or atomic) energies at two different temperatures is given in fig. 8. It can be shown that $e^{-E_a/RT}$ is the fraction of molecules or atoms having

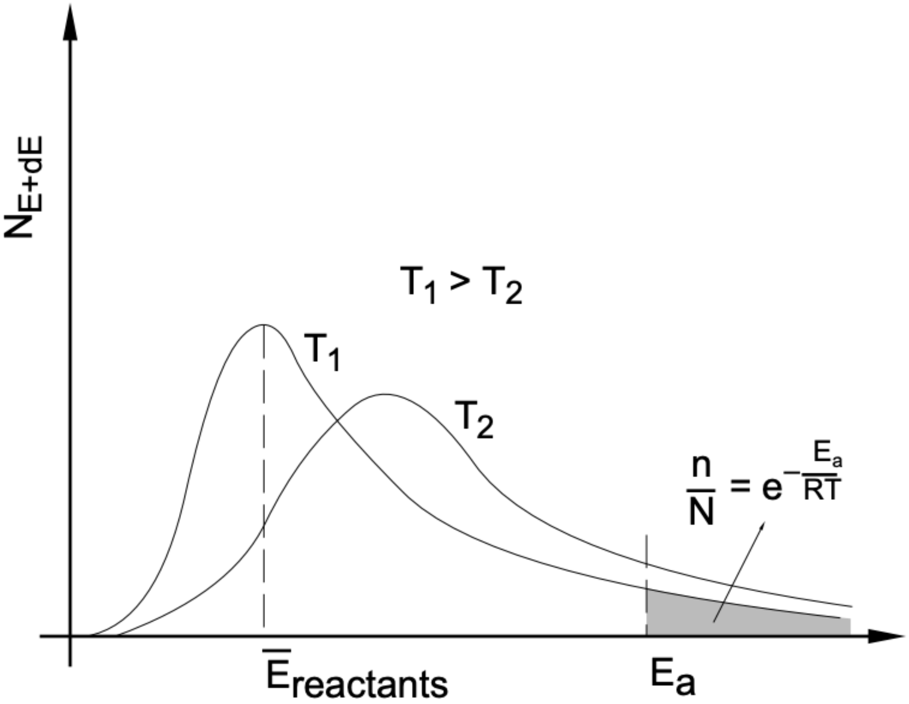


Figure 8 Maxwell Boltzmann energy distribution

an energy of $\mathrm{E_a}$ or greater. The Arrhenius equation holds only if the interacting species have between them at least the certain critical energy $\mathrm{E_a}$. Since the fraction having this energy or greater is $e^{-E_a/RT}$, the reaction rate is proportional to this quantity.

As the value of $\mathrm{E_a}$ increases, the energy requirement increases and it becomes more difficult for the molecules to acquire this energy. In contrast, $e^{-E_a/RT}$ increases rapidly with increasing temperature (T).

The change of a reaction rate with increasing temperature is usually much greater than expected from the corresponding increase in the average velocity of molecules and atoms. The average velocity of molecules and atoms is proportional to the square root of the absolute temperature. Thus, if the temperature is raised 10° from 298° to 308°, the average velocity increase, $(308/298)^{1/2}$, is but 2% whereas the rate of reaction increases by about 100%. From this we must conclude that the reaction rate is controlled not only by the number of collisions, but also by the activation energy.

We now realize that in order for a reaction to proceed we have to supply activation energy. We also know that for given conditions of concentration and T the rate of any reaction is inversely proportional to the energy of activation.

Since, particularly in industry, time is a major factor which can make a process economically feasible or unfeasible, considerable efforts have been put into accelerating reactions by means of *catalysts*. In catalytic reactions the “catalyst”, which effectively lowers the required activation energy (fig. 9), is characterized by the following criteria:

(1) unchanged chemically at the end of a reaction;

(2) required in small amounts only;

(3) catalytic action is frequently proportional to its surface area;

(4) catalysis can be selective: if different reactions are possible, catalysis can enhance the rate of either one without affecting the alternate reaction.

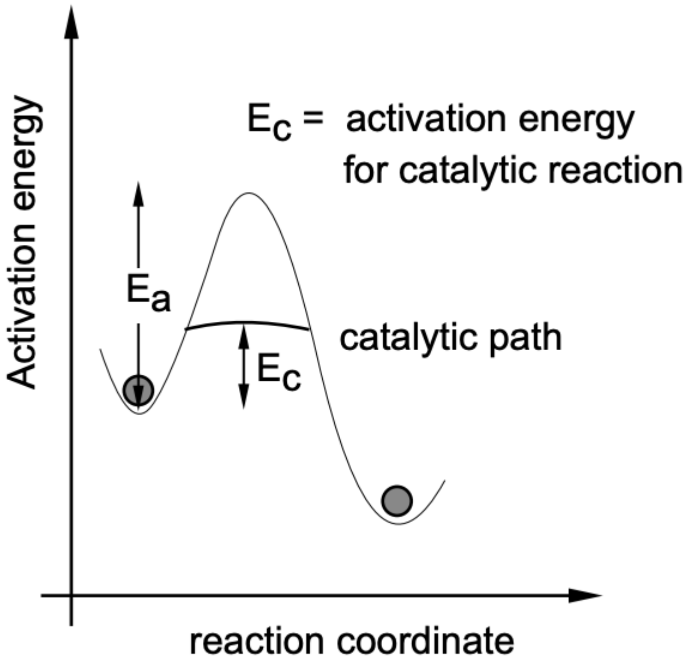


Figure 9 Effect of catalysis on activation energy in chemical reaction.

For example:

$$C_2H_5OH \rightarrow H_2C = CH_2 + H_2O \qquad \text{on } \gamma \text{ Alumina}$$
$$\text{(important in polymer chemistry)}$$
$$(\gamma \text{ Alumina: a cubic form of } Al_2O_3)$$
$$C_2H_5OH \rightarrow CH_3 - C^{\prime O}_{H} + H_2 \qquad \text{on Copper}$$

While the exact action of catalysis is still quite unclear, we do have some concrete information. The most frequently encountered case, heterogeneous catalysis (the presence of certain solids which increase gas reactions) is attributed to activation by adsorption. From infrared studies we know that upon adsorption of compounds the bonds within the compound are weakened and reactions can subsequently occur with decreased activation energy.

Catalysis has certainly had considerable impact on our daily life. Until 1940 gasoline was exclusively made from crude oil. Also, possibly more important, nitrates and ammonia came primarily from Chile (Chile saltpeter). In the Fischer-Tropsch process, coal and steam are converted into gasoline hydrocarbons with the aid of $Ni - Co$ catalysts. The Haber-Bosch process, $N_2 + 3H_2 \rightarrow 2NH_3$ (ammonia) $+99\text{ kJ}$, is likely the most important catalytic reaction practiced: From the "Le Chatelier" principle (if in a reaction the number of molecules present decreases, the reaction can be accelerated by applying increased pressures) we know that high pressures will favor this synthesis, but we also know that high temperature will favor the reverse reaction, i.e., decay of ammonia; at high temperatures complex molecular structures tend to decay to more elemental, basic species. Catalysis $(Fe, Al_2O_3 + K_2O$ in solid form) makes it possible at $400^\circ C$ and at about 600 atm to convert about 60% of the gas mixture $N_2 + 3H_2$ to NH_3. Nitrates (important as fertilizers and explosives) are predominantly produced by catalytic oxidation.

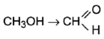
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad \text{over Pt at } 900^\circ C$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$3NO_2 + H_2O \rightarrow 2HNO_3 \text{ (nitric acid) } + NO$$

Other examples are:

* $SO_2 + 1/2O_2 \rightarrow SO_3$ over V_2O_5

* Synthetic rubber from butadiene and styrene

* Methanol from $CO + 2H_2 \rightarrow CH_3OH$ over $ZnO + Cr_2O_3$

* Formaldehyde from  $CH_3OH \rightarrow CH\overset{O}{\underset{H}{\lessgtr}}$ over Cu (important for plastics)

* In nature we have a large number of catalysts in the form of enzymes.

1.9: Diffusion

1.9.1: 1. DIFFUSION

At any temperature different from absolute zero all atoms, irrespective of their state of aggregation (gaseous, liquid or solid), are constantly in motion. Since the movement of particles is associated with collisions, the path of a single particle is a zigzag one. However, an aggregation of “diffusing” particles has an observable drift from places of higher to places of lower concentration (fig. 1). For this reason diffusion is known as a transport phenomenon.

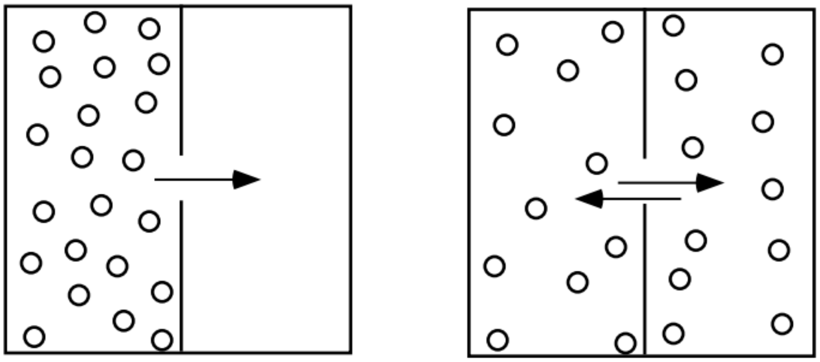


Figure 1 Mass transport, diffusion as a consequence of existing spacial differences in concentration.

In each diffusion reaction (heat flow, for example, is also a diffusion process), the flux (of matter, heat, electricity, etc.) follows the general relation:

Flux = (conductivity) x (driving force)

In the case of atomic or molecular diffusion, the “conductivity” is referred to as the *diffusivity* or the *diffusion constant*, and is represented by the symbol D. We realize from the above considerations that this diffusion constant (D) reflects the mobility of the diffusing species in the given environment and accordingly assumes larger values in gases, smaller ones in liquids, and extremely small ones in solids.

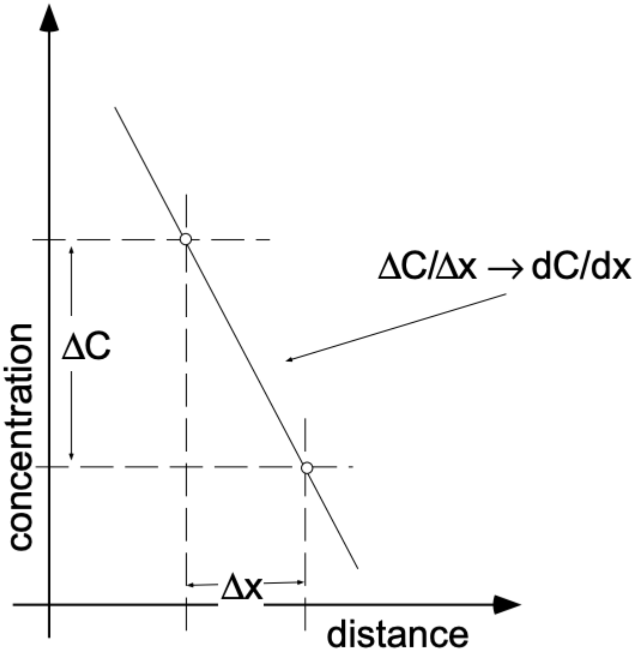


Figure 2 Concentration gradient (constant) in the x direction

The “driving force” for many types of diffusion is the existence of a *concentration gradient*. The term “gradient” describes the variation of a given property as a function of distance in the x-direction. If a material exhibits a linear variation of concentration with distance in the x-direction, we speak of a constant concentration gradient in the x-direction. The gradient itself is the rate of change of the concentration with distance (dc/dx), which is the same as the slope of a graph of concentration vs. position $(\Delta c/\Delta x)$ (see fig. 2).

Steady State and Nonsteady Diffusion

Diffusion processes may be divided into two types: (a) steady state and (b) nonsteady state. Steady state diffusion takes place at a constant rate - that is, once the process starts the number of atoms (or moles) crossing a given interface (the flux) is constant with time. This means that throughout the system dc/dx = constant and dc/dt = 0.

Nonsteady state diffusion is a time dependent process in which the rate of diffusion is a function of time. Thus dc/dx varies with time and dc/dt ≠ 0. Both types of diffusion are described quantitatively by Fick's laws of diffusion. The first law concerns both steady state and nonsteady state diffusion, while the second law deals only with nonsteady state diffusion.

1.9.2: 2. STEADY STATE DIFFUSION (FICK'S FIRST LAW)

On the basis of the above considerations, *Fick's First Law* may be formulated as:

$$\mathrm{J}=-\mathrm{D}\left(\frac{\mathrm{dc}}{\mathrm{dx}}\right)$$

In words: The diffusive flux is proportional to the existing concentration gradient.

The negative sign in this relationship indicates that particle flow occurs in a "down" gradient direction, i.e. from regions of higher to regions of lower concentration. The flux J can be given in units of atoms $/\mathrm{cm}^2$ s, moles/ cm^2 s, or equivalents. Correspondingly, the diffusivity (D) will assume the dimensions cm^2/s, as can be seen from a dimensional analysis:

$$\mathrm{J}\left(\frac{\text{moles}}{\mathrm{cm}^2\ \mathrm{s}}\right)=-\mathrm{D}\left(\frac{\mathrm{dc}}{\mathrm{dx}}\right)\left(\frac{\text{moles}\cdot\mathrm{cm}^{-3}}{\mathrm{cm}}\right)$$

Thus: $D=\mathrm{cm}^2/\mathrm{s}$

Like chemical reactions, diffusion is a thermally activated process and the temperature dependence of diffusion appears in the diffusivity as an "Arrhenius-type" equation:

$$D=D_0e^{-E_a/RT}$$

where D_o (the equivalent of A in the previously discussed temperature dependence of the rate constant) includes such factors as the jump distance, the vibrational frequency of the diffusing species and so on. Selected values of D, D_0 and E_a are given in Table 1 (a) and (b).

TABLE 1

(a) Selected Values of Diffusion Constants (D)

Diffusing Substance	Solvent	$T\,(^\circ\mathrm{C})$	$D\left(\mathrm{cm}^2\cdot\mathrm{s}^{-1}\right)$
Au	Cu	400	5×10^{-13}
Cu (Self-Diffusing)	(Cu)	650	3.2×10^{-12}
C	Fe (FCC)	950	10^{-7}
Methanol	H_2O	18	1.4×10^{-5}
O_2	Air	0	0.178
H_2	Air	0	0.611

(b) Selected Values of D_o and E_a for Diffusion Systems

Solute	*Solvent (host structure)*	D_o, $\mathrm{cm}^2\mathrm{s}$	E_a, *kJoules/mole*
1. Carbon	fcc iron	0.2100	142
2. Carbon	bcc iron	0.0079	76
3. Iron	fcc iron	0.5800	185
4. Iron	bcc iron	5.8000	251
5. Nickel	fcc iron	0.5000	276

Solute	*Solvent (host structure)*	D_o, cm^{2}s	E_a, *kJoules/mole*
6. Manganese	fcc iron	0.3500	283
7. Zinc	copper	0.0330	159
8. Copper	aluminum	2.0000	142
9. Copper	copper	11.0000	240
10. Silver	silver	0.7200	188

A typical application of Fick's first law: Determine the rate at which helium (He), held at 5 atm and $200^{\circ}\mathrm{C}$ in a Pyrex glass bulb of $50\ \mathrm{cm}$ diameter and a wall thickness (x) of $0.1\ \mathrm{cm}$, diffuses through the Pyrex to the outside. Assume that the pressure outside the tube at all times remains negligible (see fig. 3). (For the diffusion of gases it is customary, although not necessary, to replace the diffusion constant D with the Permeation constant K, normally given in units of $\mathrm{cm}^2/\mathrm{s}\cdot$ atm. Using the gas laws, K is readily converted to D if so desired.)

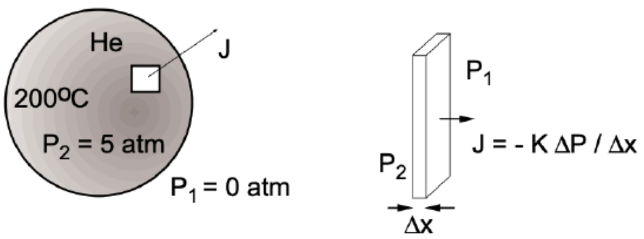


Figure 3 Conditions for outdiffusion of He from a glass bulb.

In the present system

$$\mathrm{K} = 1 \times 10^{-9}\ \mathrm{cm}^2/\mathrm{s}\cdot\mathrm{atm}$$

We can now set up the diffusion equation:

$$J = -\mathrm{K}\left(\frac{\mathrm{dP}}{\mathrm{dx}}\right) \quad \begin{array}{l}\text{(and operate with pressures instead}\\ \text{of concentrations)}\end{array}$$

We may now formally separate the variables and integrate:

$$\begin{gathered} J\mathrm{dx} = -\mathrm{KdP} \\ \int_{\mathrm{x}=0}^{\mathrm{x}=0.1} \mathrm{Jdx} = -\int_{\mathrm{p}_2=5}^{p_1=0} \mathrm{KdP} \\ \mathrm{J} = \mathrm{K}\frac{5.0}{0.1} \end{gathered}$$

We can forego the integration since $(\mathrm{dP}/\mathrm{dx}) = (\Delta\mathrm{P}/\Delta\mathrm{x})$ and we may immediately write:

$$\begin{aligned} \mathrm{J}(\text{ total }) &= -\mathrm{K}\frac{\Delta\mathrm{P}}{\Delta\mathrm{x}} \times \mathrm{A} = 5 \times 10^{-8} \times 7.9 \times 10^3 \\ \mathrm{J} &= 3.9 \times 10^{-4}?? \end{aligned}$$

The units of the flux may be obtained from a dimensional analysis:

$$\mathrm{J} = -\mathrm{K} \times \frac{\Delta\mathrm{P}}{\Delta\mathrm{x}} \times \mathrm{A} = \frac{\mathrm{cm}^2}{\mathrm{s}\cdot\mathrm{atm}}\ \frac{\mathrm{atm}}{\mathrm{cm}}\ \frac{\mathrm{cm}^2}{1} = \frac{\mathrm{cm}^3}{\mathrm{s}}$$

The total flux is $3.9 \times 10^{-4}\ \mathrm{cm}^3/\mathrm{s}$ (with the gas volume given for $0^{\circ}\mathrm{C}$ and $1\ \mathrm{atm}$). If the total gas flow by diffusion were to be determined for a specified time interval, the volume would be multiplied by the indicated time.

1.9.3: 3. NONSTEADY STATE DIFFUSION (FICK'S SECOND LAW)

The quantitative treatment of nonsteady state diffusion processes is formulated as a partial differential equation. It is beyond the scope of 3.091 to treat the equations in detail but we can consider the second law qualitatively and examine some relevant solutions quantitatively.

The difference between steady state and nonsteady state diffusion conditions can readily be visualized (fig. 4). In the first case we have, for example, the diffusion of gas

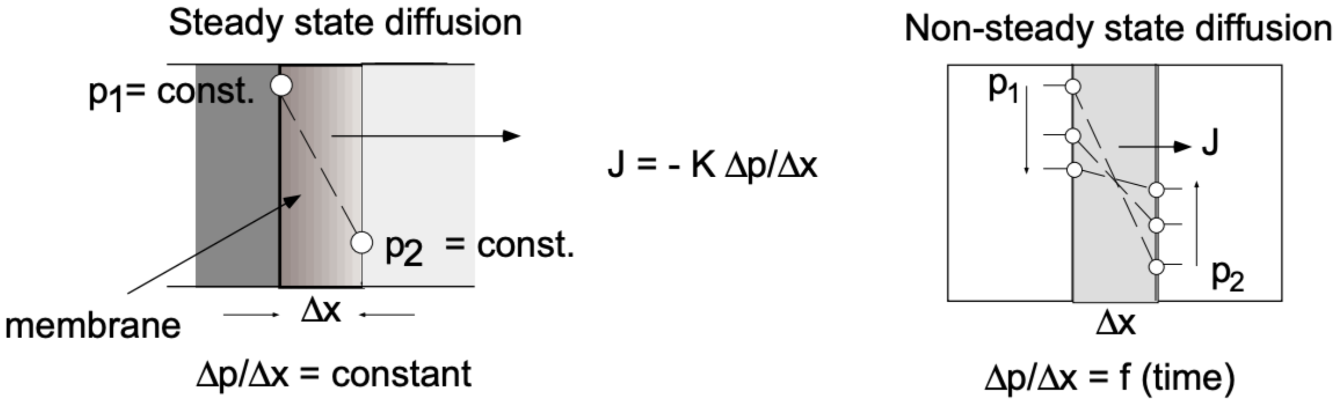


Figure 4 Steady state and Non-steady state diffusion

from an infinite volume (P_1 const) through a membrane into an infinite volume (P_2 const). The pressure gradient across the membrane remains constant as does the diffusive flux. In the second case we deal with diffusion from a finite volume through a membrane into a finite volume. The pressures in the reservoirs involved change with time as does, consequently, the pressure gradient across the membrane.

(You are not required to be familiar with the following derivation of the Second Fick’s Law, but you must know its final form.)

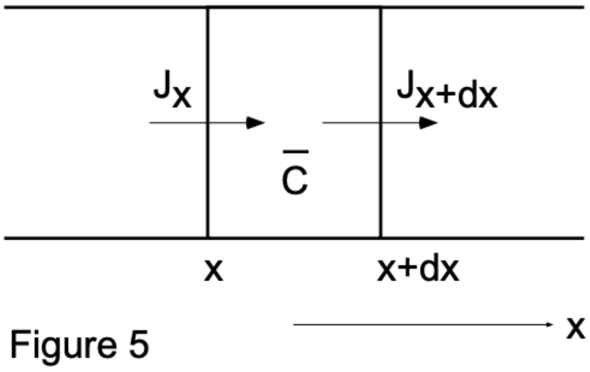


Figure 5

Consider a volume element (between x and x+dx of unit cross sectional area) of a membrane separating two finite volumes involved in a diffusion system (fig. 5). The flux of a given material into the volume element minus the flux out of the volume element equals the rate of accumulation of the material into this volume element:

$$J_x - J_{x+dx} = \frac{\partial \bar{c}}{\partial t} dx$$

[$\bar{c}$ is the average concentration in the volume element and $\bar{c}dx$ is the total amount of the diffusing material in the element at time (t).]

Using a Taylor series we can expand J_{x+dx} about x and obtain:

$$J_{x+dx} = J_x + \frac{\partial J_x}{\partial x} dx + \frac{\partial^2 J_x}{\partial x^2} \frac{dx^2}{2} + \dots$$

Accordingly, as dx $\rightarrow 0$:

$$\frac{\partial}{\partial x}\left(D \frac{\partial c}{dx}\right) = \frac{\partial c}{\partial t}$$

and if D does not vary with x (which is normally the case) we have the formulation of Fick's Second Law:

$$\frac{\partial \mathrm{C}}{\partial \mathrm{t}} = \mathrm{D}\frac{\partial^2 \mathrm{C}}{\partial \mathrm{x}^2} \quad \text{(Fick's Second Law)}$$

In physical terms this relationship states that the rate of compositional change is proportional to the “rate of change” of the concentration gradient rather than to the concentration gradient itself.

The solutions to Fick’s second law depend on the boundary conditions imposed by the particular problem of interest. As an example, let us consider the following problem (encountered in many solid state processes):

A frequently encountered situation is the diffusion of a component 2 into an infinite region of a material 1 (fig. 6) [planar diffusion of doping elements into semiconductors for the generation of junction devices (p-n junctions, junction transistors)]. The boundary conditions are: the concentration of component (2) at the surface of the solid phase $(x=0)$ remains constant at c_2 and the concentration of component (2) in the solid prior to diffusion is uniformly $c_{2'}$ (a). Under these boundary conditions the solution to Fick's second law assumes the form:

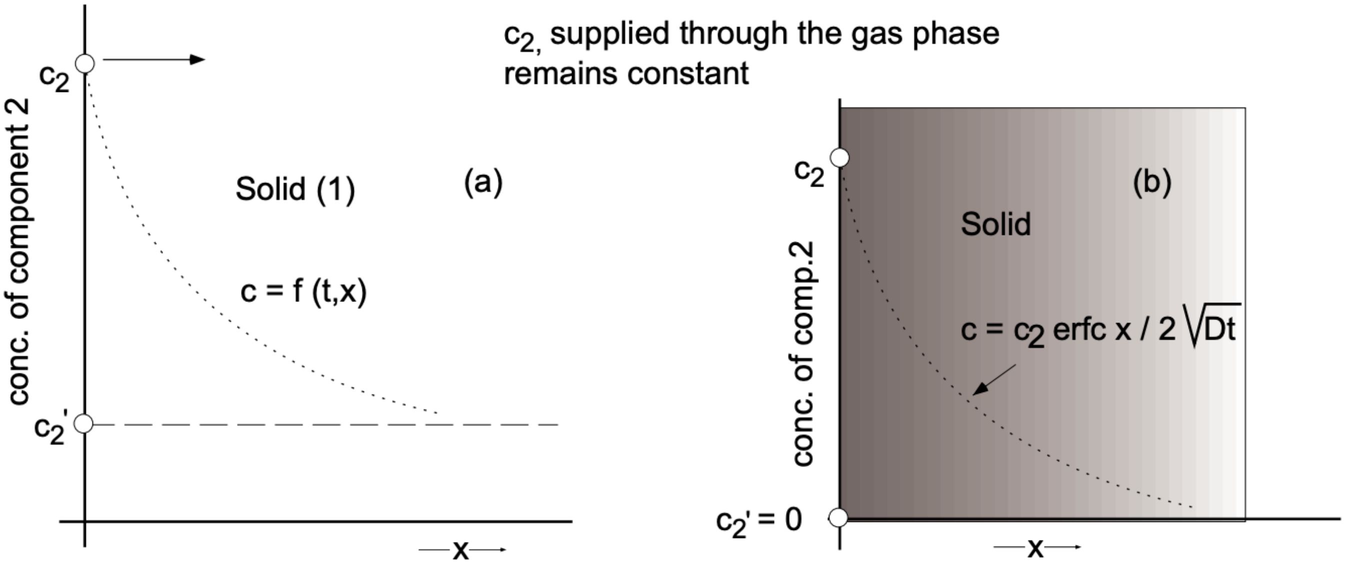


Figure 6 Diffusion at constant surface concentration; bulk concentration of component 2 at start of diffusion is c_2' (in a) and is zero (in b).

$$\frac{c_2 - c}{c_2 - c_{2'}} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

If no component (2) is originally in the solid matrix (1) (b), the above solution is simpler:

$$\begin{aligned}
\frac{c_2 - c}{c_2} &= \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \\
1 - \frac{c}{c_2} &= \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \\
\frac{c}{c_2} &= 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \\
\frac{c}{c_2} &= \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \\
c = c_2 &\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)
\end{aligned}$$

An analysis shows that the last form of the solution to Fick's law relates the concentration (c) at any position (x) (depth of penetration into the solid matrix) and time (t) to the surface concentration (c_2) and the diffusion constant (D). The terms erf and erfc stand for error function and complementary error function respectively - it is the Gaussian error function as tabulated (like trigonometric and exponential functions) in mathematical tables. Its limiting values are:

$$
\begin{array}{lll}
\operatorname{erf}(0) & =0 & \\
\operatorname{erf}(\infty) & =1 & \text{And for the complementary error function:} \\
\operatorname{erf}(-\infty) & =-1 & \text{erfc} = \text{(1-erf)}
\end{array}
$$

Another look at the above solution to the diffusion equation shows that the concentration (c) of component (2) in the solid is expressed in terms of the error function of the argument $x/2\sqrt{Dt}$. To determine at what depth a particular concentration (c^*) of (2) will appear, we substitute this concentration for (c) and obtain:

$$\frac{c^*}{c_2} = \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) = K$$

Since the error function is a constant, its argument must also be a constant:

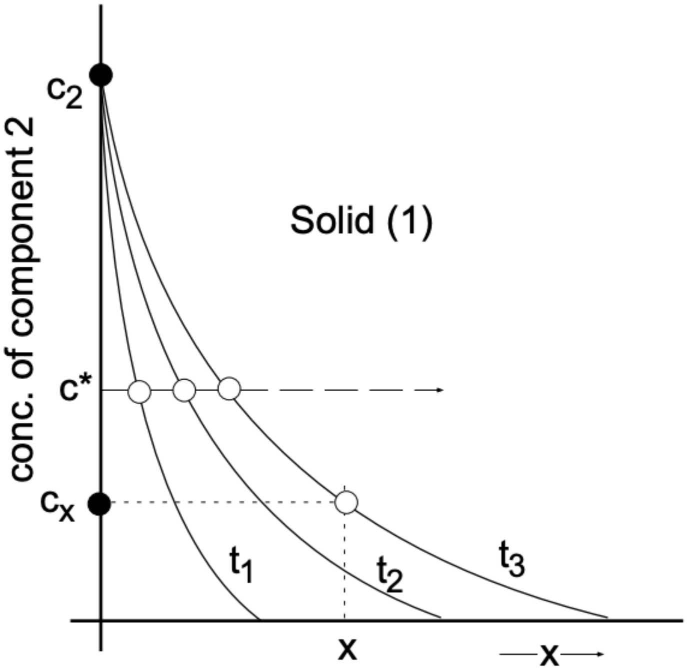


Figure 7 Advance of the concentration front (c*) as a function of trime

$$\frac{x}{2\sqrt{Dt}} = K'$$

Therefore, under the given boundary conditions:

$$
\begin{array}{l}
x = K' 2\sqrt{Dt} \\
x = K' \cdot \sqrt{Dt} \\
x \propto \sqrt{t}
\end{array}
$$

The depth of penetration of a specified concentration is found to be proportional to the square root of the time of diffusion.

1.9.4: 4. SELF-DIFFUSION

As previously indicated, the thermal motion of atoms in a lattice is a random process and as such will lead to local displacements of individual atoms. This random movement of atoms within a lattice (self-diffusion), which is not associated with any existing concentration gradients, can be readily demonstrated with the aid of “radioactive elements”. For example, nickel appears in nature in the form of several “stable isotopes”:

$$\mathrm{Ni}_{28}^{58}, \mathrm{Ni}_{28}^{60}, \mathrm{Ni}_{28}^{61}, \mathrm{Ni}_{28}^{62} \text{ and } \mathrm{Ni}_{28}^{64}$$

If Ni_{28}^{58} is irradiated with neutrons in a nuclear reactor, it will capture a neutron and become Ni_{28}^{59} which is radioactive (a radio-isotope).

$$\mathrm{Ni}_{28}^{58} + \mathrm{n} \rightarrow \mathrm{Ni}_{28}^{59} \rightarrow \mathrm{Co}_{27}^{59} + \gamma + \beta$$

Nickel 59 is characterized by its instability which leads to the emission of β and γ radiation, with a half-life of 8×10^4 years. Since this radiation can be measured by appropriate radiation detectors, it is possible to use Ni_{59} as a "tracer element" for studies of self-diffusion.

The radioactive nickel (which is identical to ordinary nickel with the exception of its radioactive properties) is electroplated onto normal nickel. This specimen is subsequently placed into a furnace and heated up to close to its melting point for an extended period of time. After removing the specimen, it is sectioned into slices parallel to the surface which contained the radioactive tracer element. With the aid of a radiation detector it can now be shown that the Ni_{59}, which originally was only at the surface, has diffused into the bulk material while simultaneously some bulk nickel has counter-diffused in the other direction. If this sample is heat-treated for a much longer time, sectioning and counting will reveal a completely uniform distribution of the radio-tracer element. It can thus be shown that self-diffusion does occur in solids, and quantitative measurements with tracer elements even permit the determination of self-diffusion coefficients.

1.9.5: 5. DIFFUSION MECHANISMS

The diffusion process in interstitial solid solutions, like that of carbon in iron, can readily be understood as a result of considerable differences in atomic diameters. However, the fact that Au diffuses faster in Pb than NaCl diffuses in water at $15^{\circ}\mathrm{C}$ cannot be readily explained. The magnitude of the observed activation energy indicates that a mechanism whereby atoms simply change places with each other has to be excluded. More reasonable mechanisms were suggested by Frenkel and Schottky. They proposed the existence of point defects (vacancies) in crystals which provide a mechanism by which atoms can move (diffuse) within a crystal. The concentration of such vacancies, as you recall, can be calculated from simple statistical calculations.

In most solids we are not dealing with single crystals but rather with polycrystalline materials which contain a large number of grain boundaries (internal surfaces). As expected, the rate of diffusion along grain boundaries is much higher than that for volume diffusion ($D_{\text{volume}} < D_{\text{g-boundary}}$). Finally, surface diffusion, which takes place on all external surfaces, is even higher $(D_{\text{volume}} < D_{\text{g-boundary}} < D_{\text{surface}})$. The respective activation energies for diffusion are:

$$E_a \text{ surface} < E_a \text{ grain boundary} < E_a \text{ volume}$$

1.9.5.0.1: Diffusion in Non-Metals

In non-metallic systems diffusion takes place by the same mechanisms as in metallic systems. Oxygen, for example, diffuses through many oxides by vacancy migration. In crystalline oxides and in silicate glasses as well, it is found that oxygen diffuses much more rapidly than the metallic ion. In glasses containing alkali atoms $\left(\mathrm{Na}^{+}, \mathrm{K}^{+}\right)$, the respective rates of diffusion are:

$$D_{\text{alkali}} > D_{\text{oxygen}} > D_{\text{silicon}} \tag{1.9.1}$$

corresponding to differences in bonding strengths. In polymer materials diffusion requires the motion of large molecules since intramolecular bonding is much stronger than intermolecular bonding. This fact explains that the diffusion rates in such materials are relatively small.

1.9.5.0.1: Gaseous Diffusion in Solids

Some gases, like hydrogen and helium, diffuse through some metals with ease even at room temperature. Helium, for example, will diffuse through quartz and steel and limits the ultimate vacuum obtainable in ultra-high vacuum systems. Hydrogen similarly diffuses readily through Ni at elevated temperatures. H_2 also diffuses at high rates through palladium - a phenomenon which is used extensively for hydrogen purification since that material is impervious to other gases.

TABLE 2: The Error Function

z	$erf(z)$	z	$erf(z)$
0	0	0.85	0.7707
0.025	0.0282	0.90	0.7970
0.05	0.0564	0.95	0.8209
0.10	0.1125	1.0	0.8427
0.15	0.1680	1.1	0.8802
0.20	0.2227	1.2	0.9103

z	$erf(z)$	z	$erf(z)$
0.25	0.2763	1.3	0.9340
0.30	0.3286	1.4	0.9523
0.35	0.3794	1.5	0.9661
0.40	0.4234	1.6	0.9763
0.45	0.4755	1.7	0.9838
0.50	0.5205	1.8	0.9891
0.55	0.5633	1.9	0.9928
0.60	0.6039	2.0	0.9953
0.65	0.6420	2.2	0.9981
0.70	0.6778	2.4	0.9993
0.75	0.7112	2.6	0.9998
0.80	0.7421	2.8	0.9999

SOURCE: The values of erf(z) to 15 places, in increments of z of 0.0001, can be found in the Mathematical Tables Project, “Table of Probability Functions . . .”, vol. 1, Federal Works Agency, Works Projects Administration, New York, 1941. A discussion of the evaluation of erf(z), its derivatives and integrals, with a brief table is given by H. Carslaw and J. Jaeger, in Appendix 2 of “Conduction of Heat in Solids”, Oxford University Press, Fair Lawn, NJ, 1959.

1.10: Phase Equilibria and Phase Diagrams

1.10.1: PHASE EQUILIBRIA AND PHASE DIAGRAMS

Phase diagrams are one of the most important sources of information concerning the behavior of elements, compounds and solutions. They provide us with the knowledge of phase composition and phase stability as a function of temperature (T), pressure (P) and composition (C). Furthermore, they permit us to study and control important processes such as phase separation, solidification, sintering, purification, growth and doping of single crystals for technological and other applications. Although phase diagrams provide information about systems *at equilibrium*, they can also assist in predicting phase relations, compositional changes and structures *in systems not at equilibrium*.

1.10.1.1: GASES, LIQUIDS AND SOLIDS

Any material (elemental or compound) can exist as a gas, a liquid or a solid, depending on the relative magnitude of the attractive interatomic or intermolecular forces vs the disruptive thermal forces. It is thus clear that the stability (existence) of the different states of aggregation, which are referred to as *phases*, is a function of temperature and pressure (since with increased pressure the atoms, for exampled of a gas phase, are closer spaced and thus subject to increased interatomic attraction).

In general terms, a “phase” is a homogeneous, physically distinct, mechanically separable portion of a material with a given chemical composition. To illustrate this definition, let us look at a few examples of common multi-phase systems. Ice cubes in water constitute a two-phase system (ice and liquid water), unless we include the vapor above the glass in our system, which would make it a three-phase system. A mixture of oil and water would also be a two-phase system. Just as oil and water represent two distinct liquid phases, two regions of a solid with distinctly different composition or structure separated by boundaries represent two solid phases.

If we look at a one-component system, such as liquid water, we recognize that because of the energy distribution of the water molecules, some water molecules will always possess sufficient energy to overcome the attractive forces on the surface of $\mathrm{H_2O}$ and enter into the gas phase. If thermal energy is continuously supplied to a liquid in an open container, the supply of high energy molecules (which leave the liquid phase) is replenished and the temperature remains constant - otherwise the loss of high energy molecules will lower the temperature of the system. The total quantity of heat necessary to completely "vaporize" one mole of a liquid at its boiling point is called its *molar heat of vaporization*, designated by $\Delta\mathrm{H_V}$. Similarly, the heat required to completely melt one mole of a solid (the heat required to break the bonds established in the solid phase) is called the *(latent) heat of fusion* ($\Delta\mathrm{H_V}$).

Visualize a liquid in a sealed container with some space above the liquid surface. Again, some of the most energetic liquid molecules will leave the liquid phase and form a "gas phase" above the liquid. Since gas molecules will thus accumulate in the gas phase (at a constant temperature), it is inevitable that as a result of collisions in the gas phase some molecules will re-enter the liquid phase and a situation will be established whereby the rate of evaporation will equal the rate of condensation – i.e., a dynamic equilibrium between the liquid and gas phase will exist. The established pressure in the gas phase is referred to as the *equilibrium vapor pressure*, which is normally significantly less for solids than for liquids.

For obvious reasons it is desirable to know for any given material the conditions (P, T) under which the solid state, the liquid state and the gaseous state are stable, as well as the conditions under which the solid and liquid phases may coexist. These conditions are graphically presented in *equilibrium phase diagrams*, which can be experimentally determined.

1.10.1.2: ONE-COMPONENT PHASE DIAGRAM

Figure 1 illustrates the temperatures and pressures at which water can exist as a solid, liquid or vapor. The curves represent the points at which two of the phases coexist in equilibrium. At the point T_t vapor, liquid and solid coexist in equilibrium. In the fields of the diagram (phase fields) only one phase exists. Although a diagram of this kind delineates the boundaries of the phase fields, it does not indicate the quantity of any phase present.

It is of interest to consider the slope of the liquid/solid phase line of the $\mathrm{H_2O}$ phase diagram. It can readily be seen that if ice $-$ say at $-2^{\circ}\mathrm{C}-$ is subjected to high pressures, it will transform to liquid $\mathrm{H_2O}$. (An ice skater will skate not on ice, but on water.) This particular pressure sensitivity (reflected in the slope of the solid/liquid phase line) is characteristic for materials which have a higher coordination number in the liquid than in the solid phase $(\mathrm{H_2O, Bi, Si, Ge})$. Metals, for example have an opposite slope of the solid/liquid phase line, and the liquid phase will condense under pressure to a solid phase.

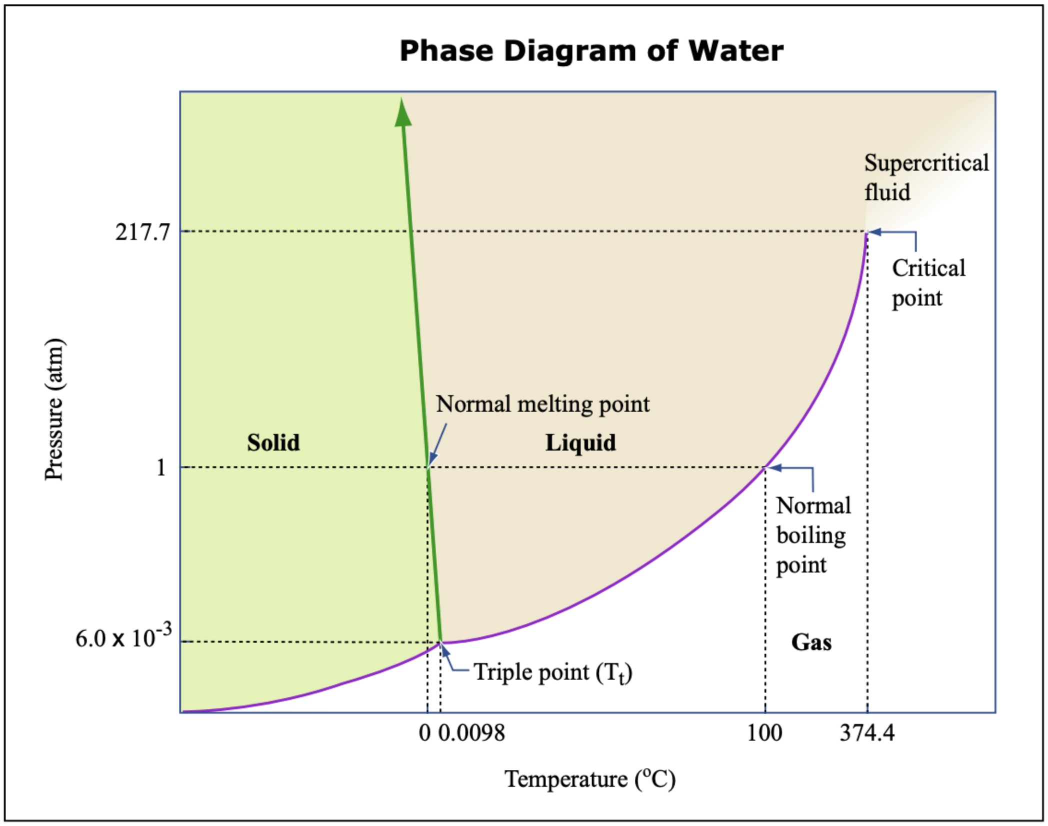


Image by MIT OpenCourseWare.

Fig. 1 Pressure/Temperature Diagram for Water. (Not drawn to scale.)

1.10.1.3: PHASE RULE AND EQUILIBRIUM

The phase rule, also known as the Gibbs phase rule, relates the number of components and the number of degrees of freedom in a system at equilibrium by the formula

$$F = C - P + 2 \tag{1}$$

where F equals the number of degrees of freedom or the number of independent variables, C equals the number of components in a system in equilibrium and P equals the number of phases. The digit 2 stands for the two variables, temperature and pressure.

$$\mathrm{CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)} \tag{2}$$

There are also three different chemical constituents, but the number of components is only two because any two constituents completely define the system in equilibrium. Any third constituent may be determined if the concentration of the other two is known. Substituting into the phase rule (eq. [1]) we can see that the system is univariant, since $F = C - P + 2 = 2 - 3 + 2 = 1$. Therefore only one variable, either temperature or pressure, can be changed independently. (The number of components is not always easy to determine at first glance, and it may require careful examination of the physical conditions of the system at equilibrium.)

The phase rule applies to dynamic and reversible processes where a system is heterogeneous and in equilibrium and where the only external variables are temperature, pressure and concentration. For one-component systems the maximum number of variables to be considered is two - pressure and temperature. Such systems can easily be represented graphically by ordinary rectangular coordinates. For two-component (or binary) systems the maximum number of variables is three pressure, temperature and concentration. Only one concentration is required to define the composition since the second component is found by subtracting from unity. A graphical representation of such a system requires a three-dimensional diagram. This, however, is not well suited to illustration and consequently separate two-coordinate diagrams, such as pressure vs temperature, pressure vs composition and temperature vs composition, are mostly used. Solid/liquid systems are usually investigated at constant pressure, and thus only two variables need to be considered – the vapor pressure for such systems can be neglected. This is called a condensed system and finds considerable application in studying phase equilibria in various engineering materials. A condensed system will be represented by the following modified phase rule equation:

$$F = C - P + 1 \tag{3}$$

where all symbols are the same as before, but (because of a constant pressure) the digit 2 is replaced by the digit 1, which stands for temperature as variable. The graphical representation of a solid/liquid binary system can be simplified by representing it on ordinary rectangular coordinates: temperature vs concentration or composition.

1.10.1.4: PHASE DIAGRAM

With the aid of a suitable calorimeter and energy reservoir, it is possible to measure the heat required to melt and evaporate a pure substance like ice. The experimental data obtainable for a mole of ice is shown schematically in fig. 2. As heat is added to the solid, the temperature rises along line "a" until the temperature of fusion (T_f) is reached. The amount of heat absorbed per mole during melting is represented by the length of line " b ", or $\Delta \mathrm{H}_{\mathrm{F}}$. The amount of heat absorbed per mole during evaporation at the boiling point is represented by line " d ". The reciprocal of the slope of line "a", (dH/dT), is the heat required to change the temperature of one mole of substance (at constant pressure) by $1^{\circ}\mathrm{CF}. (\mathrm{dH}/\mathrm{dT})$ is the molar heat capacity of a material, referred to as " C_{p} ". As the reciprocal of line "a" is C_p (solid), the reciprocals of lines "c" and "e" are C_p (liquid) and C_p (vapor) respectively.

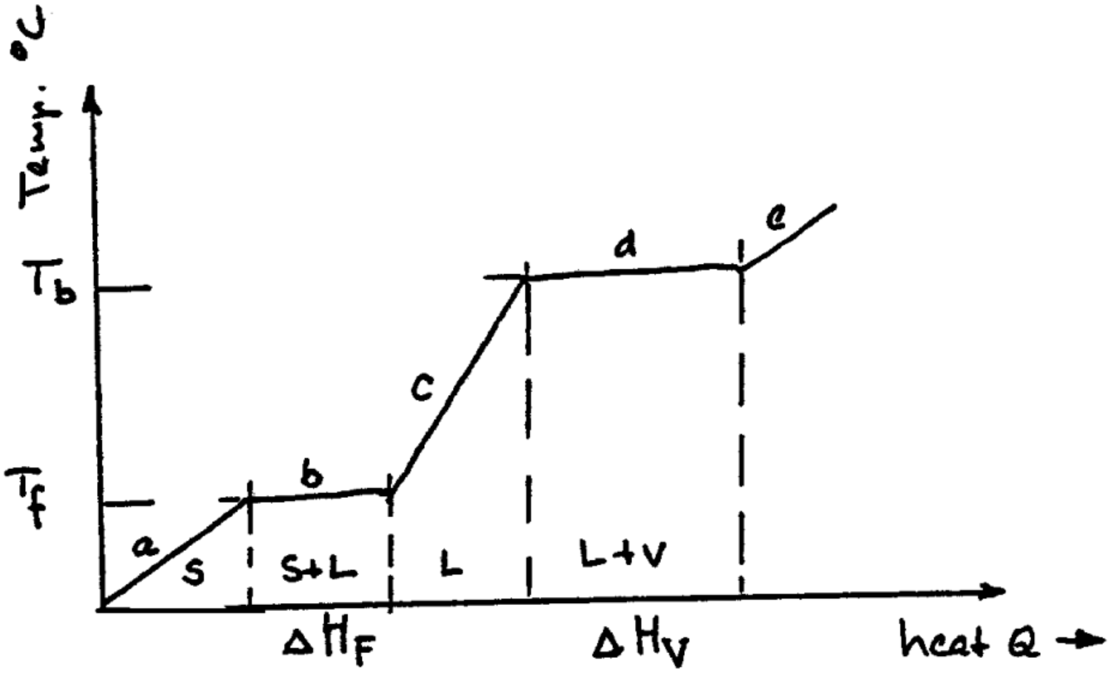


Fig. 2 H vs T Diagram for Pure $\mathrm{H_2O}$. (Not to scale.)

From a thermodynamic standpoint, it is important to realize that fig. 2 illustrates the energy changes that occur in the system during heating. Actual quantitative measurements show that 5.98 kJ of heat are absorbed at the melting point (latent heat of fusion) and 40.5 kJ per mole (latent heat of evaporation) at the boiling point. The latent heats of fusion and evaporation are unique characteristics of all pure substances. Substances like Fe, Co, Ti and others, which are allotropic (exhibit different structures at different temperatures), also exhibit latent heats of transformation as they change from one solid state crystal modification to another.

1.10.1.5: ENERGY CHANGES

When heat is added from the surroundings to a material system (as described above), the energy of the system changes. Likewise, if work is done on the surroundings by the material system, its energy changes. The difference in energy $(\Delta \mathrm{E})$ that the system experiences must be the difference between the heat absorbed (Q) by the system and the work (W) done on the surroundings. The energy change may therefore be written as:

$$\Delta \mathrm{E} = \mathrm{Q} - \mathrm{W} \tag{4}$$

If heat is liberated by the system, the sign of Q is negative and work done is positive. Q and W depend on the direction of change, but $\Delta \mathrm{E}$ does not. The above relation is one way of representing the **First Law of Thermodynamics** which states that the energy of a system and its surroundings is always conserved while a change in energy of the system takes place. The energy change, $\Delta \mathrm{E}$, for a process is independent of the path taken in going from the initial to the final state.

In the laboratory most reactions and phase changes are studied at constant pressure. The work is then done solely by the pressure (P), acting through the volume change, $\Delta \mathrm{V}$.

$$\mathrm{W}=\mathrm{P} \Delta \mathrm{V} \quad \$and\$ \quad \Delta \mathrm{P}=0 \tag{5}$$

Hence:

$$\mathrm{Q}=\Delta \mathrm{E}+\mathrm{P} \Delta \mathrm{V} \tag{6}$$

Since the heat content of a system, or the *enthalpy* H, is defined by.

$$\mathrm{H}=\mathrm{E}+\mathrm{PV} \tag{7}$$

$$\Delta \mathrm{H}=\Delta \mathrm{E}+\mathrm{P} \Delta \mathrm{V} \tag{8}$$

so that:

$$\Delta \mathrm{H}=\mathrm{Q}-\mathrm{W}+\mathrm{P} \Delta \mathrm{V} \tag{9}$$

or

$$\Delta \mathrm{H}=\mathrm{Q} \tag{10}$$

Reactions in which $\Delta \mathrm{H}$ is negative are called *exothermic* since they liberate heat, whereas *endothermic* reactions absorb heat. Fusion is an endothermic process, but the reverse reaction, crystallization, is an exothermic one.

1.10.1.6: ENTROPY AND FREE ENERGY

When a gas condenses to form a liquid and a liquid freezes to form a crystalline solid, the degree of internal order increases. Likewise, atomic vibrations decrease to zero when a perfect crystal is cooled to $0^{\circ} \mathrm{K}$. Since the term *entropy*, designated by S, is considered a measure of the degree of disorder of a system, a perfect crystal at $0^{\circ} \mathrm{K}$ has zero entropy.

The product of the absolute temperature, T, and the change in entropy, $\Delta \mathrm{S}$, is called the entropy factor, $\mathrm{T}\ \Delta \mathrm{S}$. This product has the same units (Joules/mole) as the change in enthalpy, $\Delta \mathrm{H}$, of a system. At constant pressure, P, the two energy changes are related to one another by the Gibbs free energy relation:

$$\Delta \mathrm{F}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S} \tag{11}$$

where

$$\mathrm{F}=\mathrm{H}-\mathrm{TS} \tag{12}$$

The natural tendency exhibited by all materials systems is to change from one of higher to one of lower free energy. Materials systems also tend to assume a state of greater disorder whereby the entropy factor $\mathrm{T} \Delta \mathrm{S}$ is increased. The free energy change, $\Delta \mathrm{F}$, expresses the balance between the two opposing tendencies, the change in heat content $(\Delta \mathrm{H})$ and the change in the entropy factor $(T \Delta S)$.

If a system at constant pressure is in an equilibrium state, such as ice and water at $0^{\circ} \mathrm{C}$, for example, at atmospheric pressure it cannot reach a lower energy state. At equilibrium in the ice-water system, the opposing tendencies, $\Delta \mathrm{H}$ and $\mathrm{T} \Delta \mathrm{S}$, equal one another so that $\Delta \mathrm{F}=0$. At the fusion temperature, T_{F}:

$$\Delta \mathrm{S}_{\mathrm{F}}=\frac{\Delta \mathrm{H}_{\mathrm{F}}}{\mathrm{T}_{\mathrm{F}}} \tag{13}$$

Similarly, at the boiling point:

$$\Delta S_{v}=\frac{\Delta H_{v}}{T_{v}} \tag{14}$$

Thus melting or evaporation only proceed if energy is supplied to the system from the surroundings.

The entropy of a pure substance at constant pressure increases with temperature according to the expression:

$$\Delta S=\frac{C_p\Delta T}{T} \quad (\text{since }:\Delta H=C_p\Delta T\ ) \tag{15}$$

where $\mathrm{C_p}$ is the heat capacity at constant pressure, $\Delta \mathrm{C_p}$, $\Delta \mathrm{H}$, T and $\Delta \mathrm{T}$ are all measurable quantities from which $\Delta \mathrm{S}$ and $\Delta \mathrm{F}$ can be calculated.

1.10.1.7: **F vs T**

Any system can change spontaneously if the accompanying free energy change is negative. This may be shown graphically by making use of F vs T curves such as those shown in fig. 3.

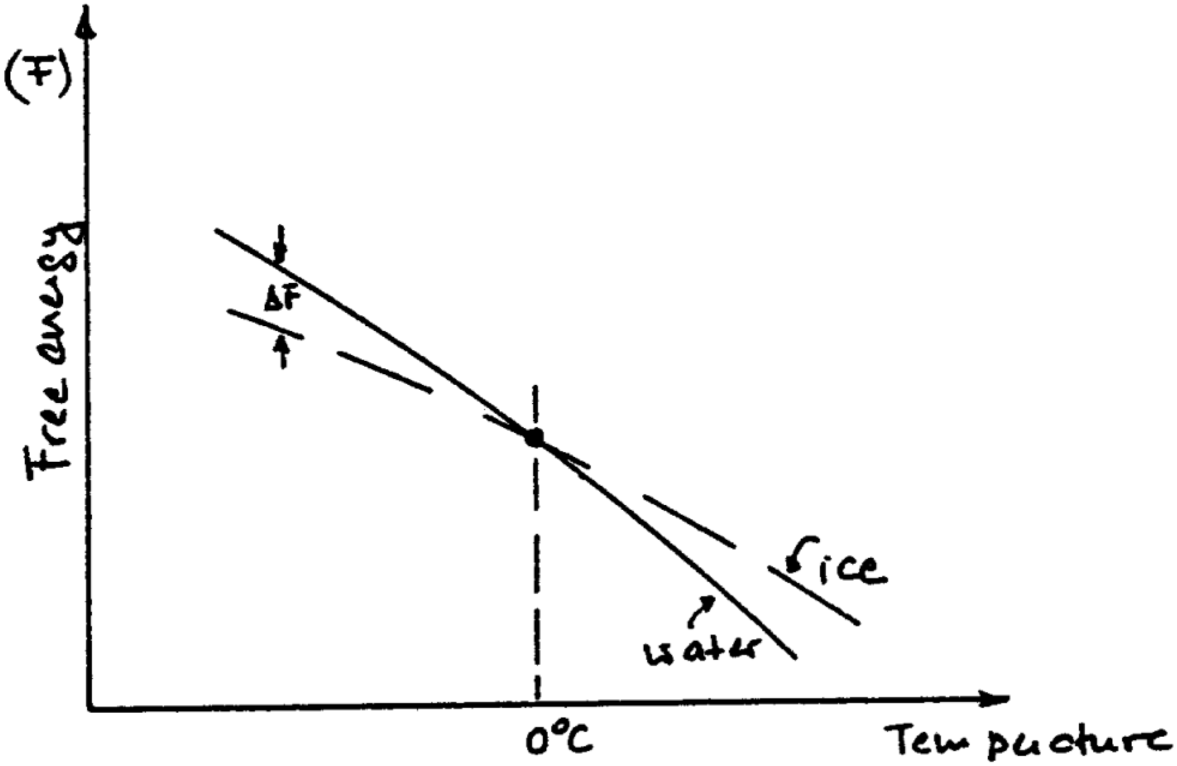


Fig. 3 Free energy is a function of temperature for ice and water.

The general decrease in free energy of all the phases with increasing temperature is the result of the increasing dominance of the temperature-entropy term. The increasingly negative slope for phases which are stable at increasingly higher temperatures is the result of the greater entropy of these phases.

1.10.2: PHASE DIAGRAMS (TWO-COMPONENT SYSTEMS)

1.10.2.1: SOLID SolutionS

A solution can be defined as a homogeneous mixture in which the atoms or molecules of one substance are dispersed at random into another substance. If this definition is applied to solids, we have a *solid solution*. The term “solid solution” is used just as “liquid solution” is used because the solute and solvent atoms (applying the term solvent to the element in excess) are arranged at random. The properties and composition of a solid solution are, however, uniform as long as it is not examined at the atomic or molecular level.

Solid solutions in alloy systems may be of two kinds: substitutional and interstitial. A substitutional solid solution results when the solute atoms take up the positions of the solvent metal in the crystal lattice. Solid solubility is governed by the comparative size of the atoms of the two elements, their structure and the difference in electronegativity. If the atomic radii of a solvent and solute differ by more than 15% of the radius of the solvent, the range of solubility is very small. When the atomic radii of two elements are equal or differ by less than 15% in size and when they have the same number of valency electrons, substitution of one kind of atom for another may occur with no distortion or negligible distortion of the crystal lattice, resulting in a series of homogeneous solid solutions. For an unlimited solubility in the solid state, the radii of the two elements must not differ by more than 8% and both the solute and the solvent elements must have the same crystal structure.

In addition to the atomic size factor, the solid solution is also greatly affected by the electronegativity of elements and by the relative valency factor. The greater the difference between electronegativities, the greater is the tendency to form compounds and the smaller is the solid solubility. Regarding valency effect, a metal of lower valency is more likely to dissolve a metal of higher valency. Solubility usually increases with increasing temperature and decreases with decreasing temperature. This causes precipitation within a homogeneous solid solution phase, resulting in hardening effect of an alloy. When ionic solids are considered, the valency of ions is a very important factor.

1.10.2.2: CONSTRUCTION OF EQUILIBRIUM PHASE DIAGRAMS OF TWO-COMPONENT SYSTEMS

To construct an equilibrium phase diagram of a binary system, it is a necessary and sufficient condition that the boundaries of one-phase regions be known. In other words, the equilibrium diagram is a plot of solubility relations between components of the system. It shows the number and composition of phases present in any system under equilibrium conditions at any given temperature. Construction of the diagram is often based on solubility limits determined by thermal analysis – i.e., using cooling curves. Changes in volume, electrical conductivity, crystal structure and dimensions can also be used in constructing phase diagrams.

The solubility of two-component (or binary) systems can range from essential insolubility to complete solubility in both liquid and solid states, as mentioned above. Water and oil, for example, are substantially insoluble in each other while water and alcohol are completely intersoluble. Let us visualize an experiment on the water-ether system in which a series of mixtures of water and ether in various proportions is placed in test tubes. After shaking the test tubes vigorously and allowing the mixtures to settle, we find present in them only one phase of a few percent of ether in water or water in ether, whereas for fairly large percentages of either one in the other there are two phases. These two phases separate into layers, the upper layer being ether saturated with water and the lower layers being water saturated with ether. After sufficiently increasing the temperature, we find, regardless of the proportions of ether and water, that the two phases become one. If we plot solubility limit with temperature as ordinate and composition as abscissa, we have an isobaric [constant pressure (atmospheric in this case)] phase diagram, as shown in fig. 4. This system exhibits a *solubility gap*.

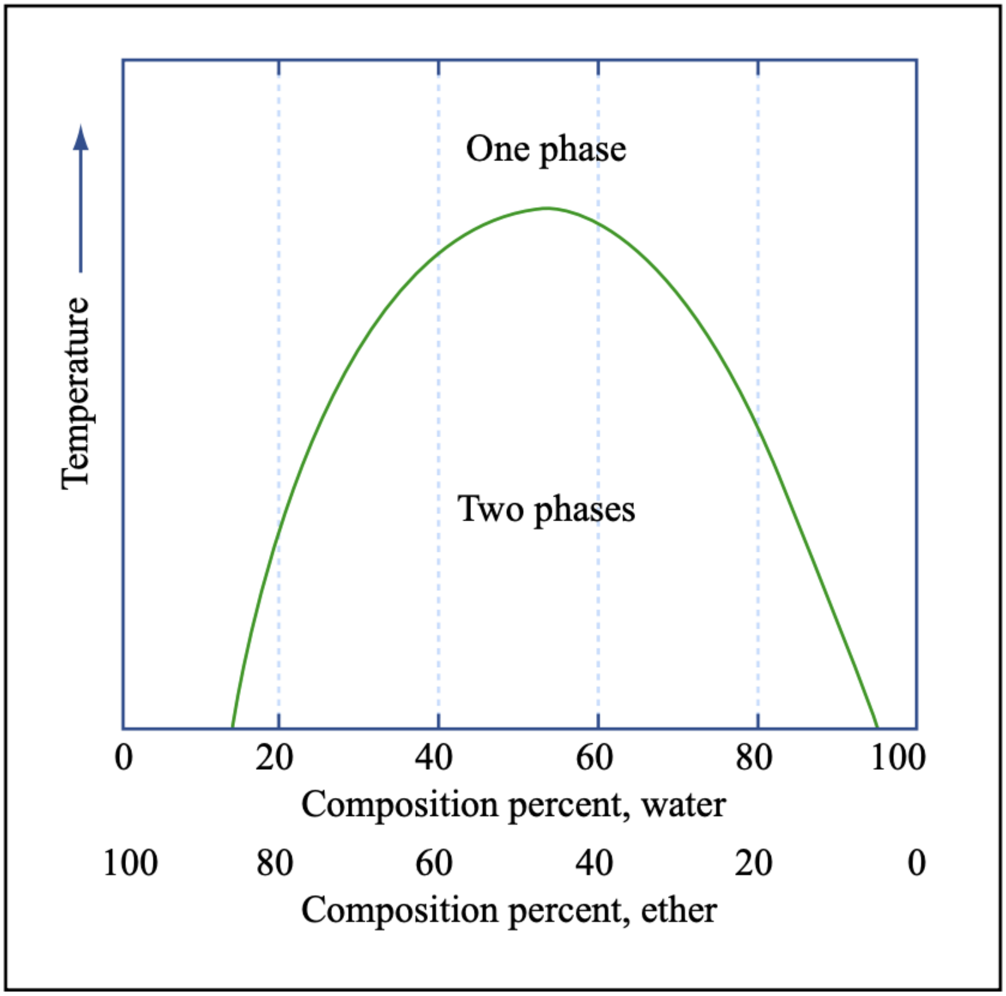


Image by MIT OpenCourseWare.

Fig. 4 Schematic representation of the solubilities of ether and water in each other.

1.10.2.3: COOLING CURVES

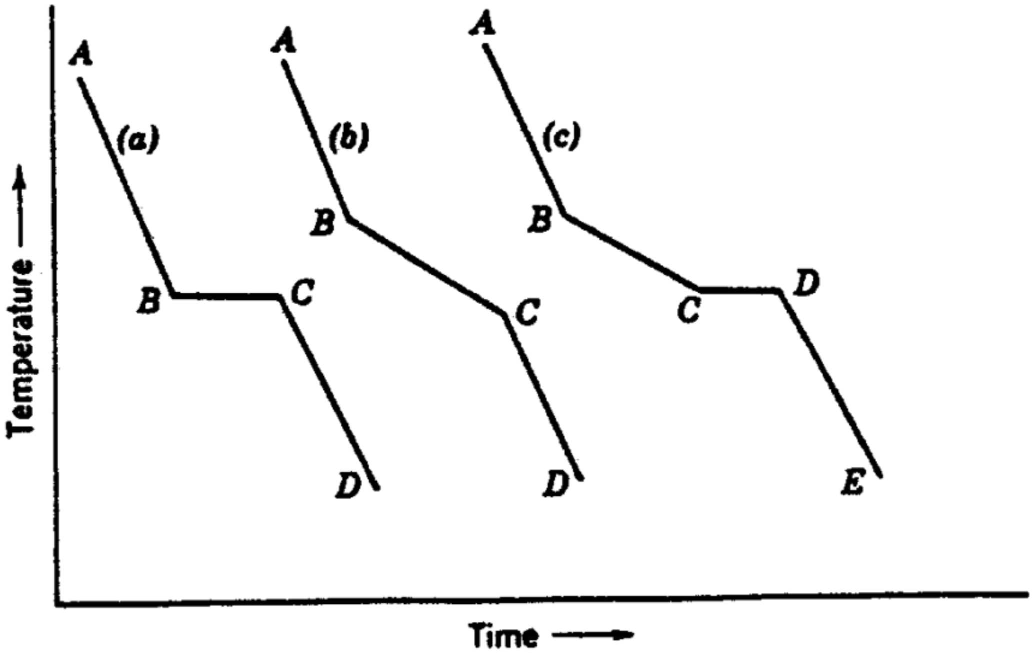


Fig. 5 Cooling curves: (a) pure compound; (b) binary solid solution; (c) binary eutectic system.

1.10.2.4: SOLID Solution EQUILIBRIUM DIAGRAMS

Read in Jastrzebski: First two paragraphs and Figure 3-4 in Chapter 3-8, "Solid Solutions Equilibrium Diagrams," pp. 91-92.

Read in Smith, C. O. The Science of Engineering Materials. 3rd ed. Englewood Cliffs, NJ: Prentice-Hall, 1986. ISBN: 9780137948840. Last two paragraphs and Figure 7-8 in Chapter 7-3-1, "Construction of a Simple Equilibrium Diagram," pp. 247-248.

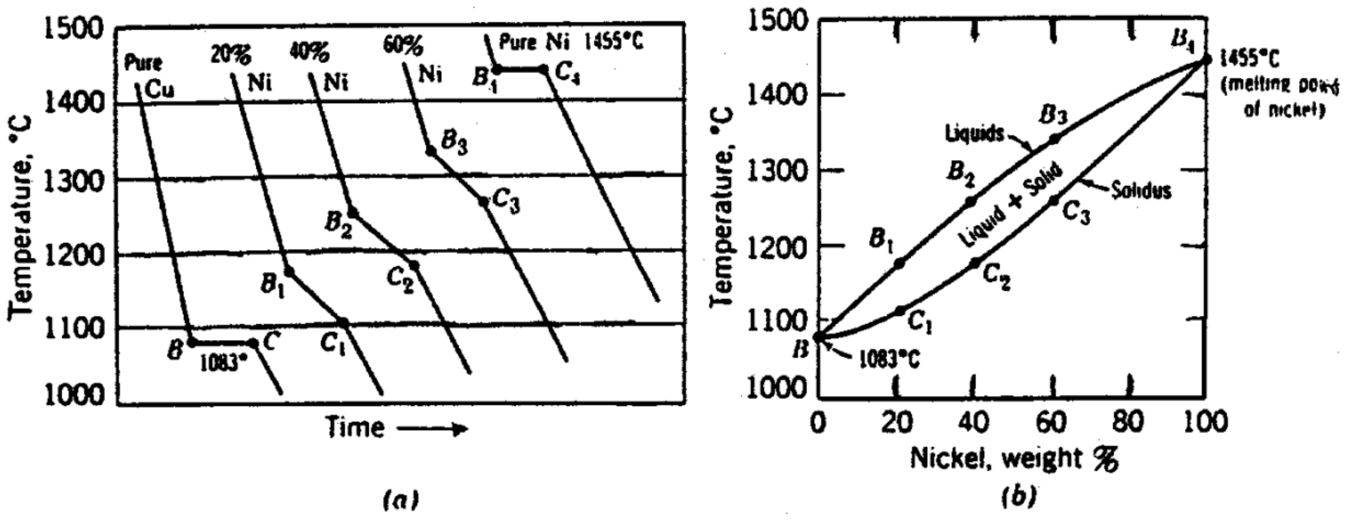


Fig. 6 Plotting equilibrium diagrams from cooling curves for Cu-Ni solid solution alloys. (a) Cooling curves; (b) equilibrium diagram.

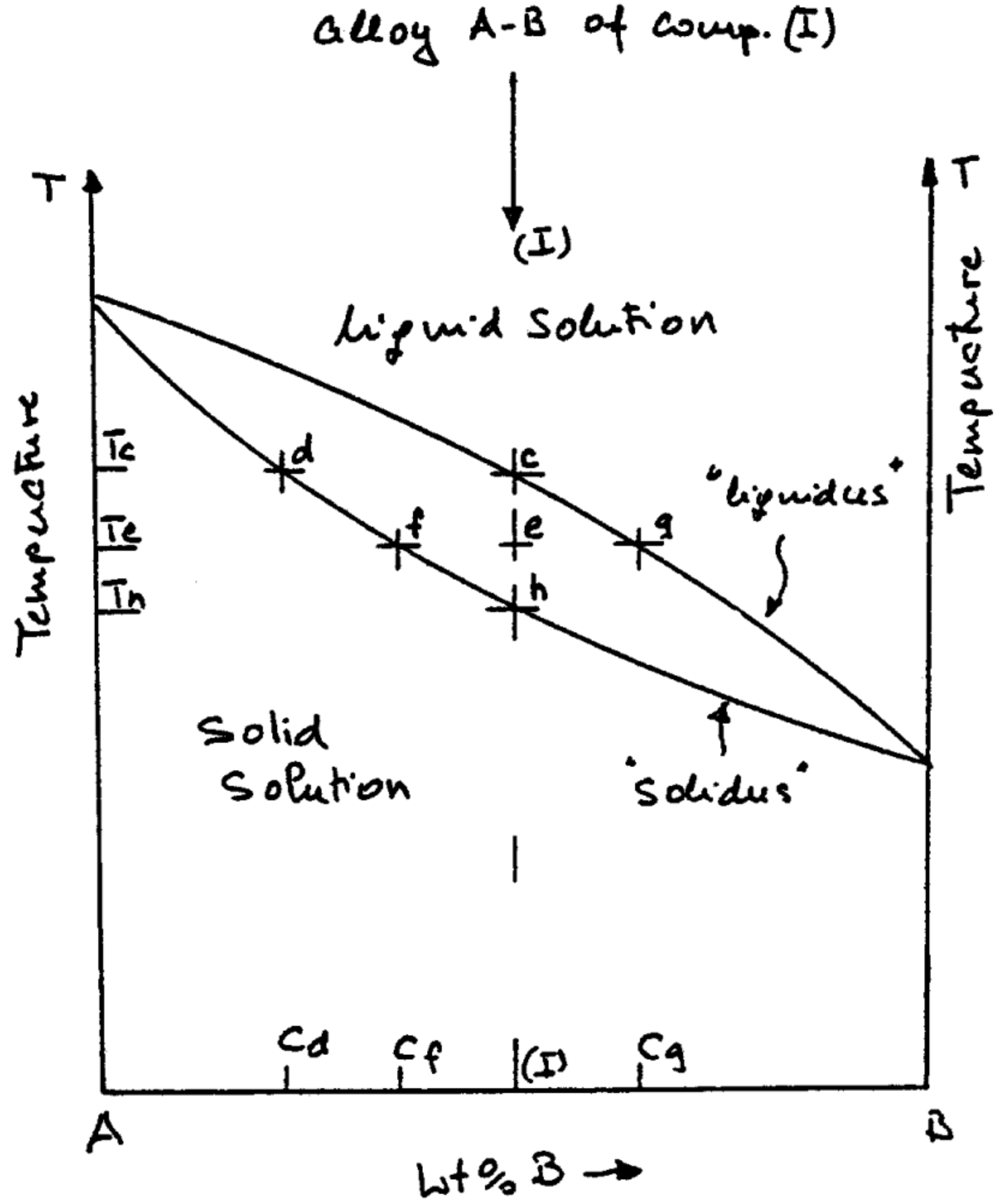


Fig. 7

1.10.2.5: INTERPRETATION OF PHASE DIAGRAMS

From the above discussion we can draw two useful conclusions which are the only rules necessary for interpreting equilibrium diagrams of binary systems.

Rule 1 - Phase composition: To determine the composition of phases which are stable at a given temperature we draw a horizontal line at the given temperature. The projections (upon the abscissa) of the intersections of the isothermal line with the liquidus and the solidus give the compositions of the liquid and solid, respectively, which coexist in equilibrium at that temperature. For example, draw a horizontal temperature line through temperature T_e in fig. 7. The T_e line intersects the solidus at f and the liquidus at g, indicating solid composition of $f\%$ of B and $(100-f)\%$ of A. The liquid composition at this temperature is g$\%$ of B and $(100-\mathrm{g})\%$ of A. This line in a two-phase region is known as a tie line because it connects or "ties" together lines of one-fold saturation - i.e., the solid is saturated with respect to B and the liquid is saturated with respect to A.

Rule 2 - The Lever Rule: To determine the relative amounts of the two phases, erect an ordinate at a point on the composition scale which gives the total or overall composition of the alloy. The intersection of this composition vertical and a given isothermal line is the fulcrum of a simple lever system. The relative lengths of the lever arms multiplied by the amounts of the phase present must balance. As an illustration, consider alloy I in fig. 7. The composition vertical is erected at alloy I with a composition of $e\%$ of B and $(100-e)\%$ of A. This composition vertical intersects the temperature horizontal (T_e) at point e. The length of the line " $f-e-g$ " indicates the total amount of the two phases present. The length of line "$e-g$" indicates the amount of solid. In other words:

$$\frac{\mathrm{eg}}{\mathrm{fg}} \times 100 = \% \text{ of solid present}$$

$$\frac{\mathrm{fg}}{\mathrm{fg}} \times 100 = \% \text{ of liquid present}$$

These two rules give both the *composition* and the *relative quantity* of each phase present in a two-phase region in any binary system in equilibrium regardless of physical form of the two phases. The two rules apply only to two-phase regions.

1.10.2.6: ISOMORPHOUS SYSTEMS

An isomorphous system is one in which there is complete intersolubility between the two components in the vapor, liquid and solid phases, as shown in fig. 9. The $\mathrm{Cu-Ni}$ system is both a classical and a practical example since the monels, which enjoy extensive commercial use, are $\mathrm{Cu-Ni}$ alloys. Many practical materials systems are isomorphous.

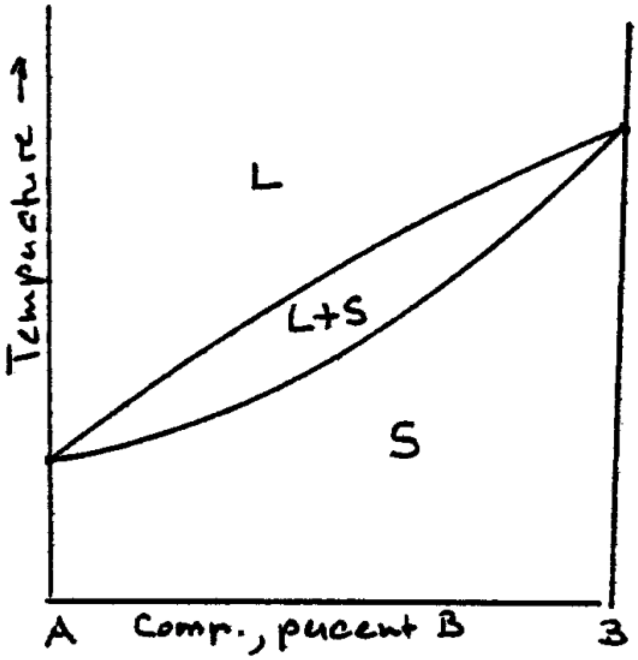


Fig. 9 Schematic phase diagram for a binary system, A-B, showing complete intersolubility (isomorphism) in all phases.

1.10.2.7: INCOMPLETE SOLUBILITY

Read in Smith, C. O. The Science of Engineering Materials. 3rd ed. Englewood

Cliffs, NJ: Prentice-Hall, 1986. ISBN: 9780137948840.

Chapter 7-3-5, "Incomplete Solubility," pp. 252-253.

1.10.2.8: EUTECTIC SYSTEMS

Read in Smith: Chapter 7-3-6, "Eutectic," pp. 253-256.

1.10.2.9: EQUILIBRIUM DIAGRAMS WITH INTERMEDIATE COMPOUNDS

Read in Jastrzebski, Z. D. *The Nature and Properties of Engineering Materials*. 2nd ed.

New York, NY: John Wiley & Sons, 1976. ISBN: 9780471440895.

Chapter 3-11,"Equilibrium Diagrams with Intermediate Compounds," pp. 102-103.

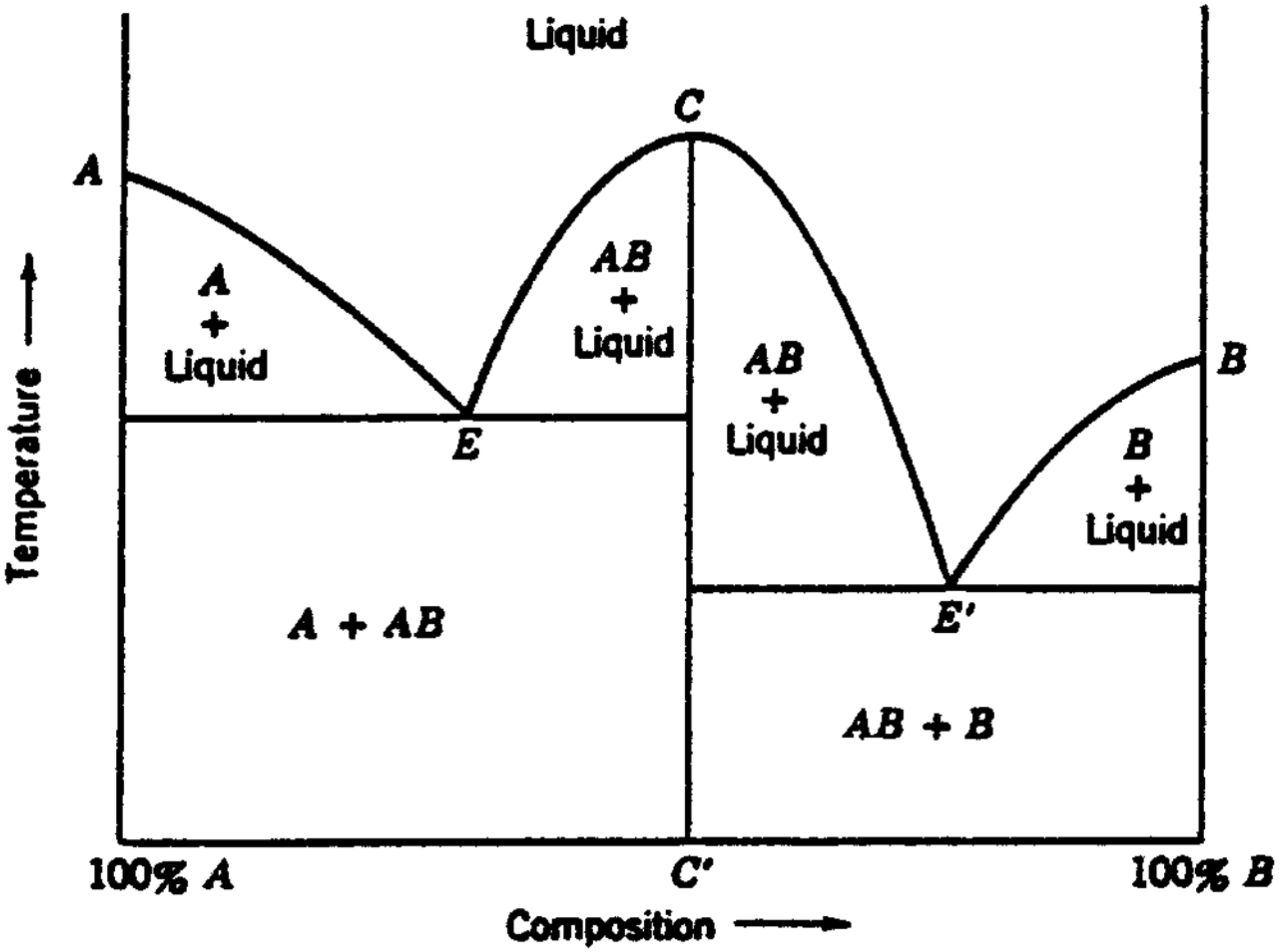


Fig. 15 Binary system showing an intermediate compound. C is the melting point (maximum) of the compound AB having the composition C’. E is the eutectic of solid A and solid AB. E’ is the eutectic of solid AB and solid B.

1.10.3: TWO-COMPONENT SYSTEMS

A pressure-temperature diagram is extremely useful when one wishes to discuss a one-component system. A component in this case is an element or compound (for example, Fe, MgO, or H_2O). As long as there is only one component present, the system may be adequately described by the two variables, pressure and temperature. In a two-component system, a third variable is needed; this is composition. The two-component system may be described by a three dimensional pressure - temperature composition diagram. It is however in the framework of this course not appropriate to deal with the complexities of the 3D phase diagram at this point and, since most materials are used under isobaric (constant pressure) conditions, we will first discuss an isobaric two-dimensional diagram of temperature versus composition. At a later point we will explain how the one component pressure-temperature and the isobaric two-component temperature-composition diagrams may be combined to construct the three-dimensional pressure-temperature-composition diagram of a two-component system.

1.10.4: Temperature-composition diagrams

A two-component temperature-composition diagram at constant pressure is called a binary phase diagram or equilibrium diagram. Temperature is plotted as the ordinate and composition as the abscissa. In the system AB, the composition is usually expressed in terms of the mole fraction of B, x_B, or the weight percent of B, w/o B. (The mole fraction of B is equal to the number of moles of B divided by the sum of the number of moles of A plus the number of moles of B. The weight percent of B is equal to the product of 100 and the weight of B divided by the sum of the weights of A and B.) The composition need not be specified in terms of A

since the sum of the mole fraction of B and the mole fraction of A is equal to one, and the sum of the weight percent of A and the weight percent of B is equal to 100. For pure A, both x_B and w/o B are zero; and for pure B they are one and 100, respectively.

A typical binary phase diagram (Figure 1) indicates those phases present in equilibrium at any particular temperature and composition at the constant pressure for which the phase diagram was determined. At low temperatures, the only phase present is the solid designated by S in the phase diagram. Pure A melts at the temperature T_{fA} and pure B melts at the temperature T_{fB} Alloys of composition between pure $A\left(x_B=0\right)$ and pure $B\left(x_B=1\right)$ exist only in the solid state of aggregation until the temperature of the solidus line is reached. The solidus is represented in the phase diagram by the lower curve extending from $\mathrm{T_{fA}}$ to $\mathrm{T_{fB}}$. Below the solidus temperature only solid exists; but above the solidus, there is a two-phase region $(L+S)$ in which both liquid and solid phases are in equilibrium. The liquid-plus-solid region extends from the solidus temperature over a finite temperature interval for all alloys of the system AB. The extent of the temperature interval reduces to zero for the pure components A and B. since according to the one-component pressure-temperature diagram, at any particular pressure there is only one temperature at which liquid and solid are in equilibrium.

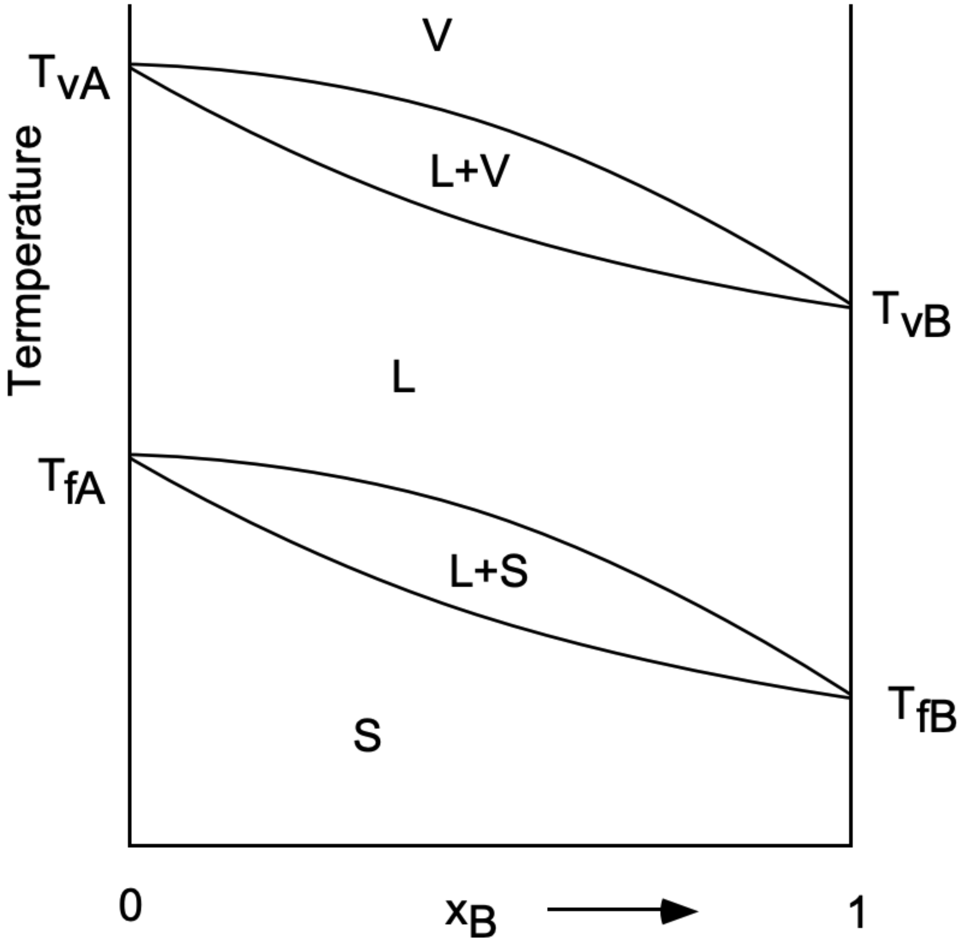


Figure 1 • Binary Phase Diagram. A binary phase diagram is an isobaric temperature composition diagram. In this case there is complete volubility in the solid, liquid, and vapor states of aggregation, and only one phase is found for each state of aggregation. At low temperatures, the material of any composition is solid; at higher temperatures there is a two-phase liquid-plus-solid region, a liquid region, a liquid-plus-vapor region and, at very high temperatures, an all-vapor region.

The upper boundary of the liquid-plus-solid region is the liquidus temperature. Above this temperature, any alloy of the system exists as a liquid phase until the temperature increases to that level at which vaporization begins. The pure compositions A and B vaporize completely at T_{vA} and T_{vB}, because the liquid and vapor phases for a pure component at constant pressure can be in equilibrium at only one temperature. Alloys of intermediate composition do not completely vaporize at any one temperature but over a finite temperature interval.This is shown in the phase diagram of Figure 1 by the liquid-plus-vapor $(L+V)$ region. At temperatures above this region, only the vapor phase exists.

Metallurgists or materials scientists are more often concerned with the liquid and solid phases and less often with the vapor phase. For this reason, and the fact that it is difficult to determine vapor phase diagrams, most binary diagrams extend no higher in temperature than the all-liquid region.

1.10.5: Cooling through a two-phase field

Solidification or melting of an intermediate alloy may be illustrated by the enlarged view of a two-phase field shown in Figure 2.

If an alloy of composition $\mathrm{x_o}$, originally liquid at temperature $\mathrm{T_1}$, is cooled, it remains liquid until the temperature reaches the liquidus temperature at point 2. At this temperature T_2, the first particle of solid appears. This solid does not have the same composition as the parent liquid. The composition of the first solid formed at $\mathrm{T_2}$ is found by constructing an isothermal line from 2 to $2'$. This isotherm is called a tie-line. The composition of the solid and liquid phases in equilibrium at a particular temperature is given by the intersection of the tie-line at that temperature with the solidus and liquidus curves, respectively. Thus at temperature T_2, the solid has the composition $\times 2'$ and the liquid the composition x_2 (where $x_2 = x_0$).

Upon further cooling to T_3, the composition of the liquid has shifted to the left along the liquidus to $\times 3$, and the composition of the solid has shifted to the left along the solidus to $x3'$ because at T_3, the only liquid and solid compositions that can be in equilibrium with one another are $x3$ and $x3'$ respectively.

Despite the fact that both liquid and solid have compositions different from the alloy composition, the overall alloy (liquid and solid together) retains its original composition x_0. As the temperature approaches the solidus temperature $\mathrm{T_5}$, the solid composition approaches x', (where $x_5{}' = x_0$) and the last quantity of liquid of composition x_5 freezes. At temperatures below the solidus, the solid composition remains unchanged, for example, at $\mathrm{T_6}$ the solid composition is $\mathrm{x_0}$.

The above analysis applies only to solidification at such a slow rate of cooling that equilibrium is achieved at every temperature. This is not always the case, however.

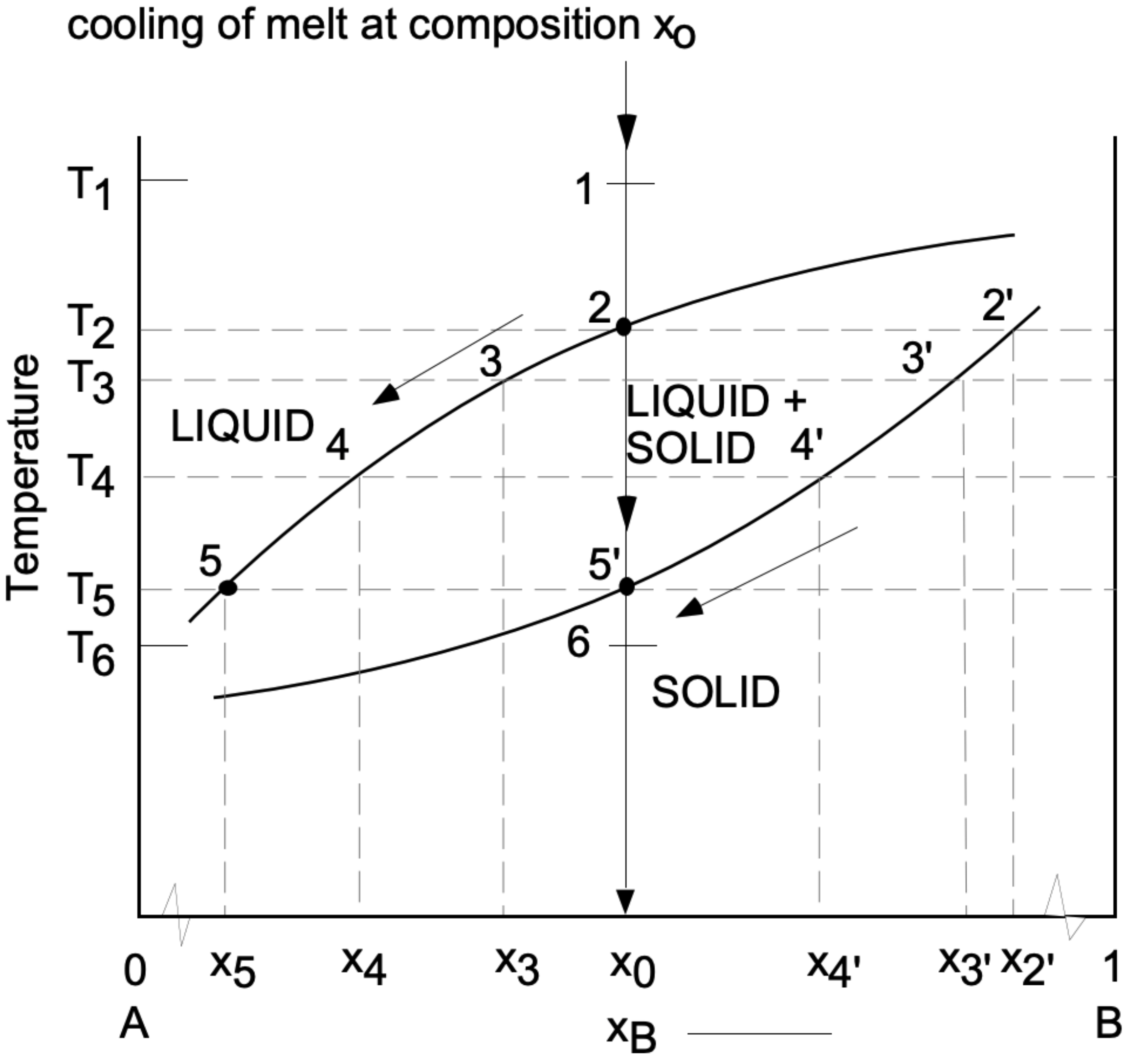


Figure 2 · Cooling Through a Two-Phase Field. As an alloy of composition x_0 is cooled from the liquid region through the two-phase liquid-plus-solid field, the first particle of solid forms at temperature T_2 and is of composition x_2,. The composition of the solid is given by the intersection of the isothermal tie line with the solidus, and the composition of the liquid by the intersection of the tie-line with the liquidus. As the temperature is decreased, the composition of the solid and of the liquid shifts to the left until at T_5 the solid is of composition x_0 and the last of the liquid freezes.

1.10.6: lever law

To determine exactly how much liquid and solid are present at any given temperature, let us derive a relation known as the "lever law." If one mole of alloy of composition x_0 is chosen as a basis, then, at any temperature T. the fraction of liquid f_L is found as follows: The sum of the fractions of liquid and solid must equal one, that is,

$$f_S + f_L = 1$$

The number of moles of B present in the alloy must be the same as the number of moles of B present in the solid phase plus the number of moles of B present in the liquid phase, that is,

$$x_O = x_S f_S = x L f_L$$

Since

$$f_S = 1 - f_L$$

we may substitute and obtain

$$x_O = x_S - x_S f L + x_L f_L$$

On rearranging and solving for f_{L} we find that

$$f_L=\left(x_S-x_0\right)/\left(x_S-x L\right).$$

This relation is called the "lever law" because the fraction of one of the two phases present is equal to the opposite side of the tie-line $\left(\mathrm{x}_{\mathrm{S}}-\mathrm{x}_{\mathrm{O}}\right)$ divided by the entire tie-line $\left(x_S-x_L\right)$ In this way the tie-line acts as though it were a lever whose fulcrum is at the point x_0. In a similar way it is found that

$$f_s=\left(x_O-x_L\right)/\left(x_S-x L\right).$$

CHAPTER OVERVIEW

2: Assessments

Topic hierarchy

2.1: Self-Assessment- Structure of the Atom + Answer
2.2: Self-Assessment- Bonding and Molecules + Answer
2.3: Self-Assessment- Electronic Materials + Answer
2.4: Self-Assessment- Crystalline Materials + Answer
2.5: Self-Assessment- Amorphous Materials + Answer
2.6: Self-Assessment- Aqueous + Answer
2.7: Self-Assessment- Solid Solutions
2.8: Self-Assessment- Reactions and Kinetics + Answer

2.1: Self-Assessment- Structure of the Atom + Answer

Problem #1

(a) Cerium has many isotopes (8 to be exact), but only $^{140}\mathrm{Ce}$ and $^{142}\mathrm{Ce}$ are present in substantial amounts. Which isotope of cerium is the most abundant?

Answer

from the periodic table, you see that the atomic mass of Ce is 140.115, which must be the weighted sum of the isotope masses here we assume that it is necessary to consider only $^{140}\mathrm{Ce}$ and $^{142}\mathrm{Ce}$ so, $(x$ mass of $^{140}\mathrm{Ce}\ )+(1-x)$ mass of $^{142}\mathrm{Ce}$ $=140.115$ for the purposes of this decision, we can approximate the atomic masses of the isotopes as ~ 140 for ^{140} and ~ 142 for $^{142}\mathrm{Ce}$ and solve for x $\mathrm{x}=0.94$ which means that $^{140}\mathrm{Ce}$ is the most abundant isotope of cerium

Production of chromium in an electric arc furnace would involve the reaction of carbon with chromium sesquioxide according to the following reaction:

$$\mathrm{Cr_2O_3}+a\mathrm{C}=b\mathrm{CO}+c\mathrm{Cr}$$

(i) Balance the equation, i.e., specify the values of a, b, and c. Insert the correct values below.

Answer

$\mathrm{Cr_2O_3}+3\mathrm{C}=3\mathrm{CO}+2\mathrm{Cr}$

(ii) Calculate the minimum amount of chromium (in kg) produced if the reaction consumed $333\ \mathrm{kgC}$ and produced the stoichiometric amount of Cr. Assume 100% efficiency.

Answer

$333\ \mathrm{kgC}=333000/12.011=27725$moles C the stoichiometric amount of Cr is $2/3$ amount of carbon on a molar basis. Therefore, amount of $\mathrm{Cr}=27725\times 2/3$ moles of $\mathrm{Cr}=(27725\times 2/3)\times 51.996=961\ \mathrm{kgCr}$

Problem #2

(a) Antimony has two isotopes, $^{121}\mathrm{Sb}$ and $^{123}\mathrm{Sb}$. Which isotope has the higher natural abundance?

Answer

from the periodic table, you see that the atomic mass of Sb is 121.757 which must be the weighted sum of the isotope masses
so, $(x$ mass of $^{121}\mathrm{Sb})+(1-\mathrm{x})$ mass of $^{123}\mathrm{Sb}=121.757$
for the purposes of this decision, we can approximate the atomic masses of the isotopes as ~ 121 for $^{121}\mathrm{Sb}$ and ~ 123 for $^{123}\mathrm{Sb}$ and solve for x
$\mathrm{x}=0.62$ which means that $^{121}\mathrm{Sb}$ is the more abundant isotope of antimony

(b) Production of hafnium by the Kroll Process would involve the reaction of magnesium with hafnium tetrachloride according to the following reaction:

$$\mathrm{HfCl_4}+a\mathrm{Mg}=b\mathrm{MgCl_2}+c\mathrm{Hf}$$

(i) Balance the equation, i.e., specify the values of a, b, and c. Insert the correct values below.

Answer

$\mathrm{HfCl_4}+2\mathrm{Mg}^2\quad 2\mathrm{MgCl_2}+\mathrm{Hf}$

(ii) Calculate the minimum amount of magnesium (in kg) needed to convert $111\ \mathrm{kgHfCl_4}$ into elemental hafnium.

Answer

$111\ \mathrm{kg HfCl_4} = 111000/[178.49 + (4 \times 35.45)] = 347\ \text{moles}\ \mathrm{HfCl_4}$
the stoichiometric amount of Mg is twice the amount of $\mathrm{HfCl_4}$ on a molar basis
$\therefore$ amount of $\mathrm{Mg} = 347 \times 2$ moles of $\mathrm{Mg} = (347 \times 2) \times 24.305 = 16.9\ \mathrm{kg Mg}$

Problem #3

(a) Show by means of a calculation that blue light of wavelength, $\lambda = 444\ \mathrm{nm}$, is not capable of exciting electrons in $\mathrm{Li^{2+}(g)}$ from the state $n = 2$ to $n = 4$.

Answer

let's equate the energy required to excite electrons in $\mathrm{Li^{2+}(g)}$ from the state $n = 2$ to $n = 4$ with the minimum energy needed from an incident photon to cause the excitation

$$\frac{hc}{\lambda} = KZ^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

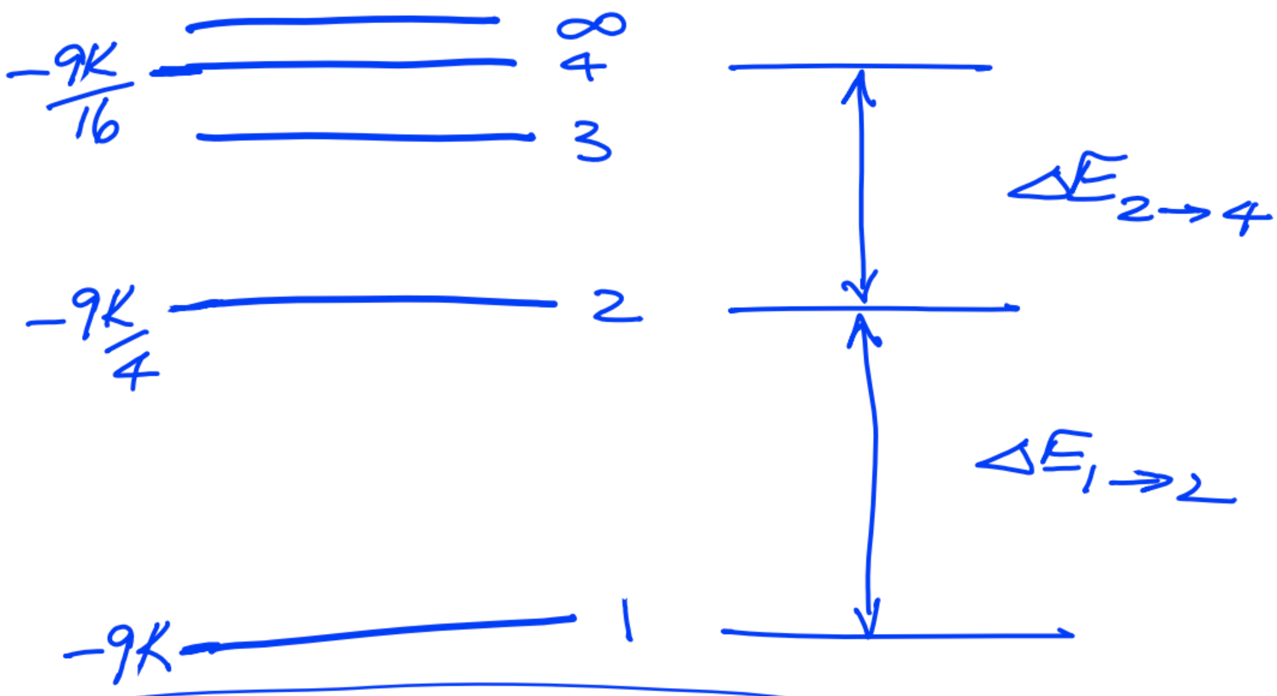
$$\therefore \lambda = \frac{hc}{KZ^2\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)} = \frac{6.6 \times 10^{-34} \times 3.00 \times 10^8}{2.18 \times 10^{-18} \times 3^2\left(\frac{1}{2^2} - \frac{1}{4^2}\right)}$$

$$= 5.38 \times 10^{-8}\ \mathrm{m} = 53.8\ \mathrm{nm} < 444\ \mathrm{nm}$$

$\therefore$ since E scales with $1/\lambda$, blue light of wavelength $\lambda = 444\ \mathrm{nm}$ does not have enough energy per photon to cause the excitation

(b) Is the value of the energy of transition from the state $n = 2$ to $n = 4$ in $\mathrm{Li^{2+}}$, $\Delta E_{2\to4}$, greater than or less than the value of the energy of transition from the state $n = 1$ to $n = 2$ in $\mathrm{Li^{2+}}$, $\Delta E_{1\to2}$? Explain with the use of an energy level diagram. There is no need to calculate the values of the two quantities.

Answer



clearly, $\Delta E_{1\to2} > \Delta E_{2\to4}$

Problem #4

(a) In a gas discharge tube what is the minimum frequency (v) of a photon capable of ionizing ground-state electrons in Li^{2+}?

Answer

here is the central concept: the energy of the incident photon must be at least as great as the ionization energy (I.E.)

Li^{2+} is a one-electron atom, so we can calculate the I.E. using the Bohr Model

$I.E. = E_\infty - E_1 = 0 - \left(-\frac{KZ^2}{n^2}\right)$, where $Z=3$ and $n=1$ for the ground-state of Li^{2+} and K is the ground-state energy of atomic hydrogen

energy of incident photon is given by $\mathrm{E} = \mathrm{h}v$

$$v = \frac{KZ^2}{h} \frac{\left(2.18 \times 10^{-18} J\right)(3)^2}{6.6 \times 10^{-34}} = 2.97 \times 10^{16}\ \mathrm{Hz}$$

(b) Explain with reference to the relevant physical forces why the value of the 1^{st} ionization energy of Li is less than the 3^{rd} ionization energy of Li.

Answer

the 1^{st} ionization represents the removal of one of the 3 electrons from neutral Li

the 3^{rd} ionization represents the removal of the single electron from the Li^{2+} ion

in the second case, the single electron ***alone*** feels the pull of the positive charge of the nucleus

in the first case the same positive charge is felt by three electrons; hence, each electron feels a weaker pull than is the case with a lone electron under the influence of the same positive charge

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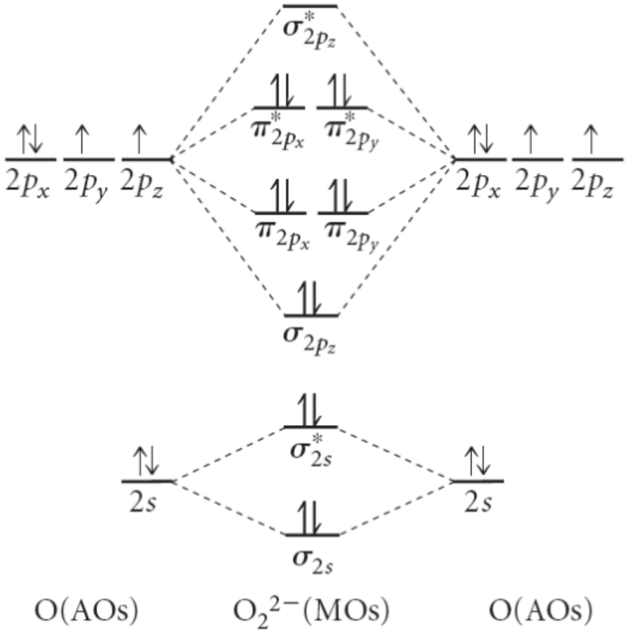
2.2: Self-Assessment- Bonding and Molecules + Answer

Problem #1

(a) Draw the energy level diagram that shows that the linear combination of atomic orbitals from two atoms of oxygen (O) results in the formation of the stable molecule, $\mathrm{O_2}^{2-}$. The molecular orbitals in $\mathrm{O_2}^{2-}$ increase in energy according to the sequence $\sigma_{2s}, \sigma_{2s}*, \sigma_{2p_z}, \pi_{2p_{x,y}}, \pi^*_{2p_{x,y}}, \sigma_{2p_z}*$.

Answer



(b) Indium phosphide (InP) is a semiconductor with a band gap, E_g, of $1.27\mathrm{eV}$. Calculate the value of the absorption edge of this material. Express your answer in meters.

Answer

for absorption of incoming radiation, the following must be true:

$E_{\text{radiation}} = E_g.$

using the Planck relationship gives the wavelength of the absorption edge

$$E_{\text{radiation}} = \frac{hc}{\lambda}$$
$$\therefore \lambda = \frac{hc}{E_g} = \frac{6.6 \times 10^{-34} \times 3 \times 10^8}{1.27 \times 1.6 \times 10^{-19}} = 9.74 \times 10^{-7}\ \mathrm{m}.$$

Problem #2

Chemical analysis of a silicon (Si) crystal reveals boron (B) at a level of 0.0003 atomic percent.

(a) Assuming that the concentration of thermally excited charge carriers from the Si matrix is negligible, calculate the density of free charge carriers (carriers $/\mathrm{cm}^3$) in this Si crystal.

Answer

each B atom will attract an electron and thus create a "mobile hole"; we only have to determine the number of B atoms $/\mathrm{cm}^3$ of Si. The atomic volume of the host crystal (Si) is given on your PT as $12.05\ \mathrm{cm}^3/\mathrm{mole}$

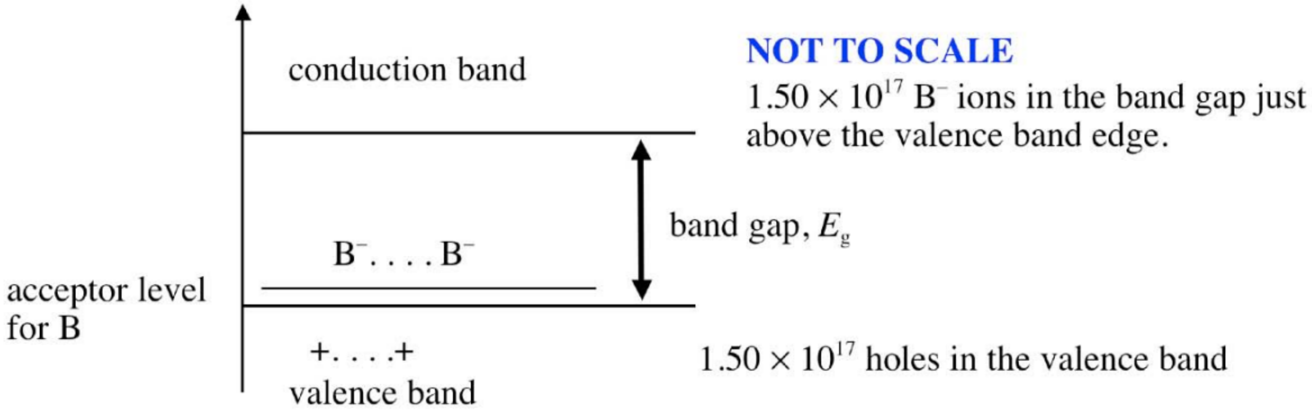
$$\#\text{Si atoms } /\text{cm}^3 = \frac{6.02\times 10^{23}\text{ atoms}}{1\text{ mole}} \times \frac{1\text{ mole}}{12.05\text{ cm}^3} = 5.00\times 10^{22}\quad \text{atoms } /\text{cm}^3$$

$$\therefore \#\text{ B atoms}/\text{cm}^3 = 5.00\times 10^{22}\times 0.0003\times 10^{-2} = 1.50\times 10^{17}\text{ B}/\text{cm}^3$$

thus, the number of free charge carriers ("holes") is $1.50\times 10^{17}/\text{cm}^3$; they are created through the acquisition of one electron by each B atom from the valence band of the host Si crystal.

(b) Draw a schematic energy band diagram for this material and label the valence band, conduction band, band gap, and the energy level associated with the B impurity.

Answer



2.3: Self-Assessment- Electronic Materials + Answer

Problem 1

Indium phosphide (InP) is a semiconductor with a band gap, E_g, of $1.27\mathrm{eV}$. Calculate the value of the absorption edge of this material. Express your answer in meters.

Answer

For absorption of incoming radiation, the following must be true:

$$\mathrm{E_{radiation}} = \mathrm{E_g}$$

Using the Planck relationship gives the wavelength of the absorption edge:

$$\mathrm{E_{radiation}} = \frac{\mathrm{hc}}{\lambda}$$

$$\lambda = \frac{\mathrm{hc}}{\mathrm{E_g}} = \frac{6.6\times10^{-34}\times3\times10^{8}}{1.27\times1.6\times10^{-19}} = 9.74\times10^{-7}\ \mathrm{m}$$

Problem 2

Chemical analysis of a germanium (Ge) crystal reveals antimony (Sb) at a level of 0.0002atomic percent.

a. Assuming that the concentration of thermally excited charge carriers from the Ge matrix is negligible, calculate the density of free charge carriers (carriers $/\mathrm{cm}^3$) in this Ge crystal.

Answer

Each Sb atom will donate an electron to the conduction band; we have only to determine the number of Sb atoms $/\mathrm{cm}^3$ of Ge. The atomic volume of the host crystal (Ge) is given on your PT as $13.57\ \mathrm{cm}^3/\mathrm{mole}$

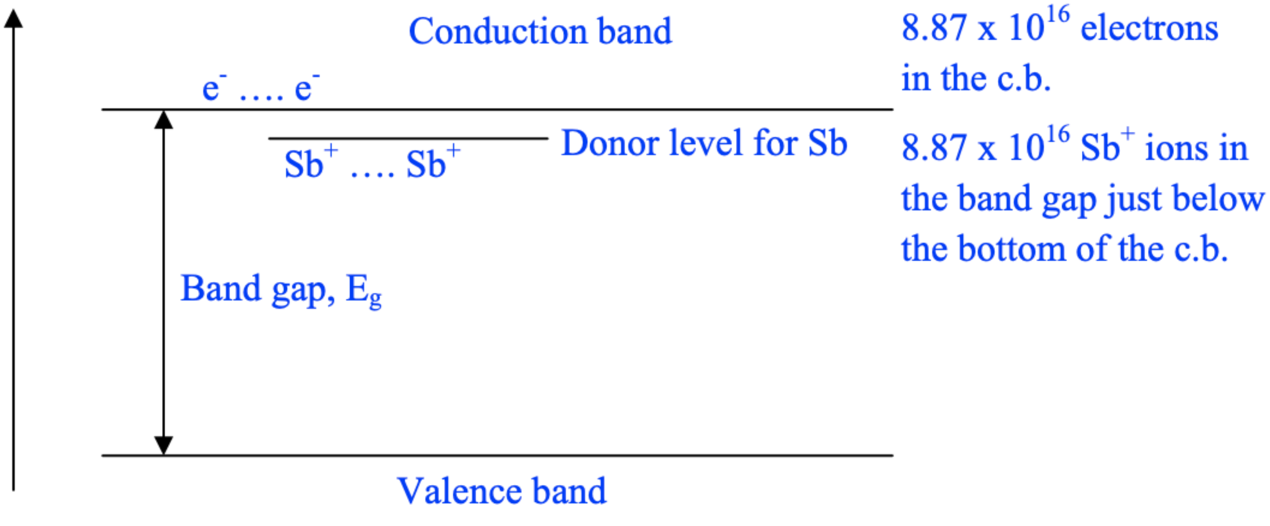
$$\#\mathrm{Ge\ atoms}\ /\mathrm{cm}^3 = \frac{6.02\times10^{23}\ \mathrm{atoms}}{1\ \mathrm{mole}} \times \frac{1\ \mathrm{mole}}{13.57\ \mathrm{cm}^3} = 4.44\times10^{22}\quad \mathrm{atoms}\ /\mathrm{cm}^3$$

$$\#\mathrm{Sb\ atoms}\ /\mathrm{cm}^3 = 4.44\times10^{22}\times0.0002\times10^{-2} = 8.87\times10^{16}\mathrm{Sb}/\mathrm{cm}^3$$

Thus, the number of free charge carriers is $8.87\times10^{16}/\mathrm{cm}^3$; they are created by the donation of one electron by each Sb atom to the conduction band of the host Ge crystal.

b. Draw a schematic energy band diagram for this material and label the valence band, conduction band, band gap, and the energy level associated with the Sb impurity.

Answer



2.4: Self-Assessment- Crystalline Materials + Answer

Problem 1

Calculate the acceleration potential that will result in electron diffraction from the (311) plane of platinum (Pt) at an angle, θ, of 33.3°. The lattice constant of platinum, a, has a value of 3.92Å.

Answer

$$\begin{aligned}
\lambda_e &= 2d_{(311)}\sin\theta = 2\frac{a}{\left(h^2+k^2+l^2\right)^{1/2}}\sin\theta \\
&= 2\times\frac{3.92}{\sqrt{11}}\times\sin 33.3^\circ = 1.30\text{Å} \\
q\bar{V} &= \frac{1}{2}mv^2 \therefore v = \sqrt{2e\bar{v}/m} \\
\lambda_e &= \frac{h}{mv} = \frac{h}{(2me\bar{v})^{-1/2}} \\
\therefore V &= \frac{h^2}{2\lambda^2 me} \\
&= \frac{\left(6.6\times10^{-34}\right)^2}{2\left(130\times10^{-10}\right)^2\times9.11\times10^{-31}\times1.6\times10^{-19}} \\
&= 88.4\bar{v}
\end{aligned}$$

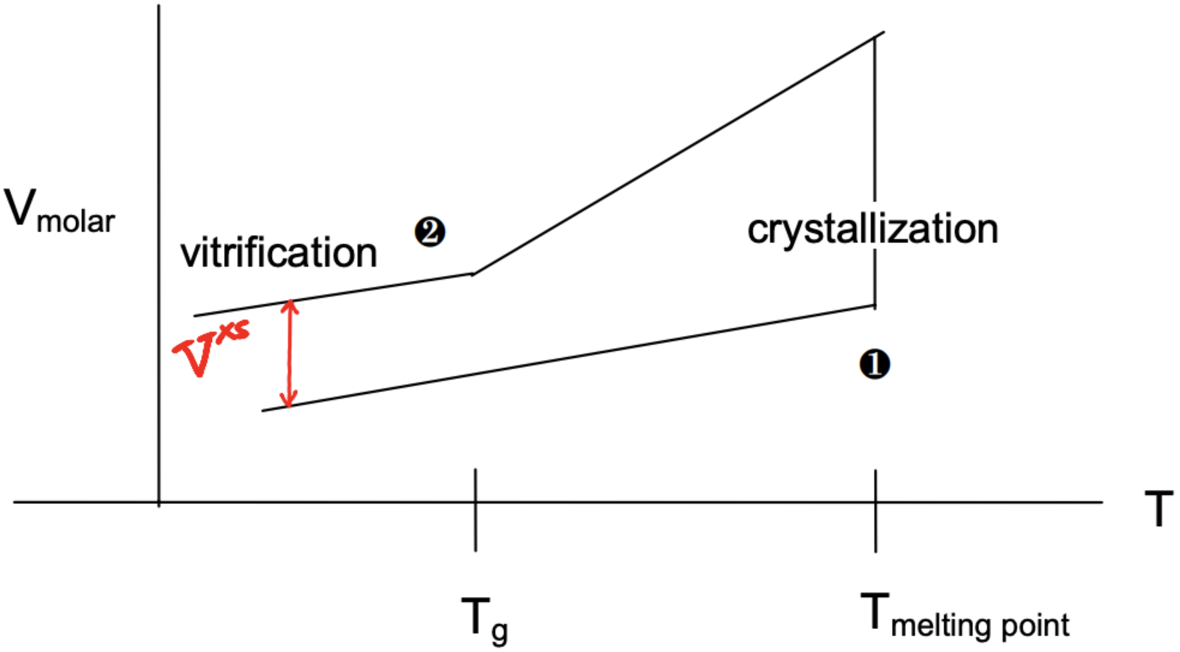
2.5: Self-Assessment- Amorphous Materials + Answer

(a) A melt of magnesium borate glass with the composition $20\%\mathrm{MgO}-80\%\ \mathrm{B_2O_3}$ is cooled at a rate of r_1. The glass transition temperature, T_g, is measured to be T_1. In order to raise the value of T_g to $T_2 > T_1$ while keeping the cooling rate equal to r_1, how should the MgO content of the glass be changed? Explain with reference to atomic structure.

Answer

Decrease the MgO concentration to less than 20%. The addition of MgO to $\mathrm{B_2O_3}$ modifies the melt by promoting chain scission of the borate network. The resulting decrease in viscosity of the melt confers greater mobility than would be the case at comparable undercooling at a lower MgO content and therefore reduces the excess volume of the solidified glass. We know from the relationship between volume and temperature that the value of T_g is given by the break in the V vs. T trace, and furthermore that T_g tracks with V^{xs}. To raise T_g is tantamount to raising $\mathrm{V^{xs}}$ which then argues for changing the composition of the melt in a way that raises its viscosity, i.e., decreasing the amount of modifier.

(b) On a plot of molar volume, $\mathrm{V_m}$, versus temperature, T, sketch cooling curves for a borate melt that solidifies to form (1) crystalline $\mathrm{B_2O_3}$; and (2) amorphous $\mathrm{B_2O_3}$. Indicate which material was cooled more quickly. No calculation necessary. Label the melting point of (1) and the glass transition temperature of (2). Indicate the excess molar volume, $\mathrm{V^{xs}}$, and describe why it is a measure of atomic disorder.



Answer

The glassy solid was cooled more quickly.

For a given compound, the crystal represents the tightest packing of atoms in order to establish the highest number of bonds and thereby achieve maximum decrease in energy. In the liquid state, the interatomic spacing is large in comparison to that of the solid state. Glass formation is the result of the inability of the atoms to reach the proper positions they would occupy in the crystal lattice owing to inadequate time to do assume said positions during cooling. In effect, the system is quenched en route from the loose packing of the melt to the tight packing of the crystal. The molar volume compares, on the basis of a constant mass of material (1 mole!) the degree to which the atomic packing of the solid reaches that of the crystal. The greater the deviation from this tight packing, the greater the deviation from crystallinity, and hence the greater the degree of disorder.

2.6: Self-Assessment- Aqueous + Answer

(a) The value of K_a for perchloric acid, $\mathrm{HClO_4}(aq)$, is 1×10^8 . Calculate the $p\mathrm{H}$ and the $p\mathrm{OH}$ of $1.11\ \mathrm{M}\ \mathrm{HClO_4}(aq)$ in water.

Answer

with a value of $K_a = 10^8$, $\mathrm{HClO_4}$ is a strong acid ⇒ complete dissociation

$$\begin{aligned} &\therefore 1.11 \mathrm{MHI(aq)} \Rightarrow 1.11 \mathrm{M} = \left[\mathrm{H}^+\right] = \left[\mathrm{ClO}_4^-\right] \\ &\therefore \mathrm{pH} = -\log_{10}\left[\mathrm{H}^+\right] = -\log_{10} 1.11 = -0.0453 \\ &\because \mathrm{pOH} + \mathrm{pH} = 14 \Rightarrow \mathrm{pOH} = 14.0453 \end{aligned}$$

(b) The compound, yttrium iodate, $\mathrm{Y(IO_3)_3}$, upon dissolution in water dissociates into $\mathrm{Y^{3+}}$ and solubility product, K_sp, of $\mathrm{Y(IO_3)_3}$.

Answer

$\mathrm{Y(IO_3)_3} = \mathrm{Y^{3+}} + 3\mathrm{IO_3^-}$, from which we get $K_\mathrm{sp} = \left[\mathrm{Y^{3+}}\right]\left[\mathrm{IO_3^-}\right]^3$

$\mathrm{c_s} = 2.22 \times 10^{-3} = \left[\mathrm{Y^{3+}}\right] = 1/3\left[\mathrm{IO_3^-}\right] = \left[\mathrm{IO_3^-}\right] = 3\left[\mathrm{Y^{3+}}\right]$

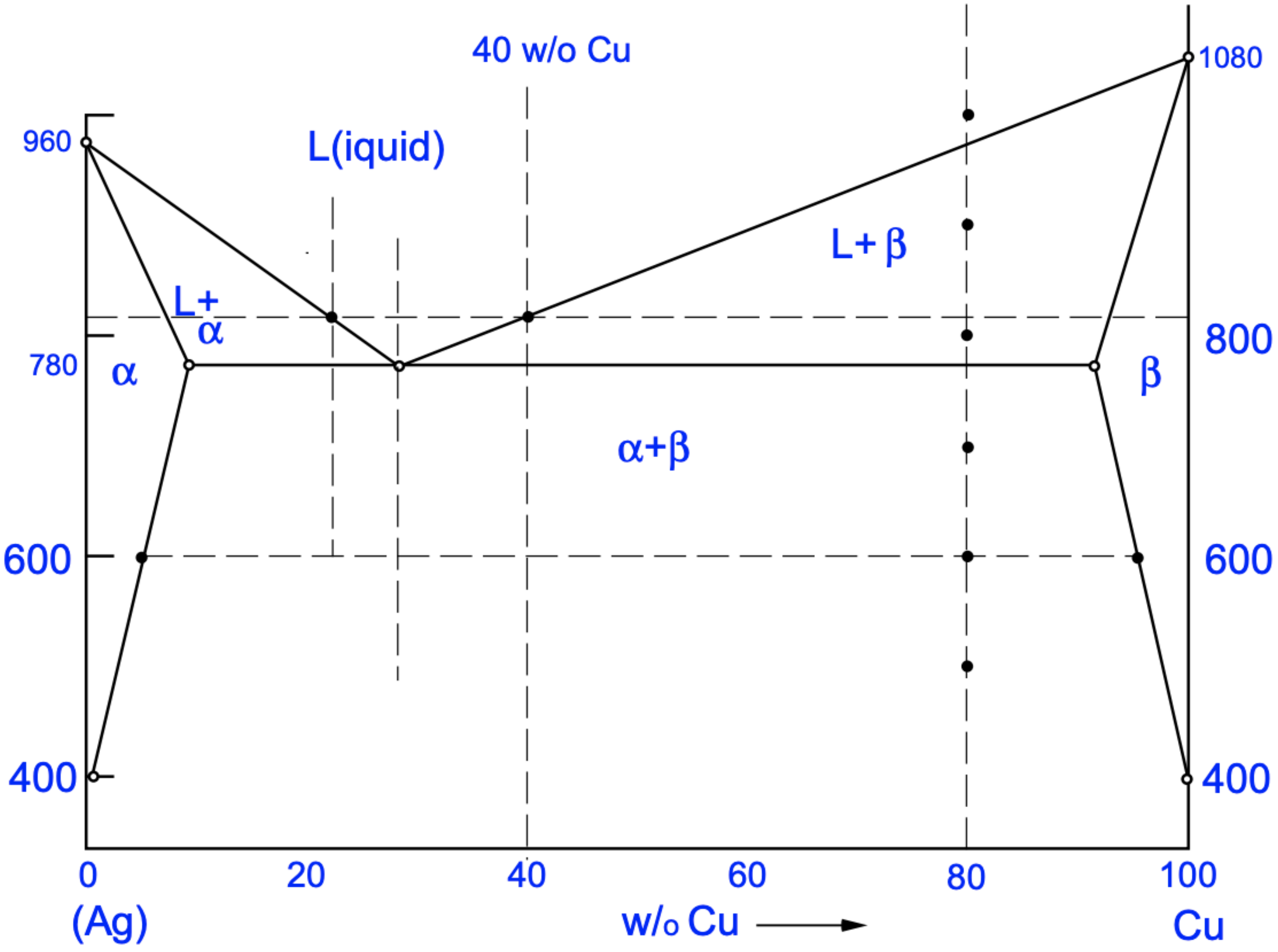
$\therefore K_\mathrm{sp} = \mathrm{c_s}(3\mathrm{c_s})^3 = 27\mathrm{c_s}^4 = 27\left(2.22 \times 10^{-3}\right)^4 = 6.56 \times 10^{-10}$

2.7: Self-Assessment- Solid Solutions

(a) Construct the phase diagram (T, c) for $\mathrm{Ag}-\mathrm{Cu}$ given the following data. (Assume all phase lines to be straight.)

$\mathrm{T_M Ag}:$	$960^{\circ}\mathrm{C}$
$\mathrm{T_M Cu}:$	$1080^{\circ}\mathrm{C}$
$\mathrm{T_E}$ (Eutectic)	$780^{\circ}\mathrm{C}: \alpha[9\mathrm{wt.}\,\%\mathrm{Cu}]; \beta[92\mathrm{wt.}\,\%\mathrm{Cu}];$ Eutectic comp. $28\mathrm{wt.}\,\%\mathrm{Cu}$
	$400^{\circ}\mathrm{C}: \alpha[1\mathrm{wt.}\,\%\mathrm{Cu}]; \beta[100\mathrm{wt.}\,\%\mathrm{Cu}]$

Answer



(b) Determine the liquidus temperature for a $60\mathrm{wt.}\,\%\mathrm{Ag}-40\mathrm{wt.}\,\%\,\mathrm{Cu}$ alloy.

Answer

From the phase diagram in (a) liquidus T for $40\mathrm{wt.}\,\%\mathrm{Cu}$ alloy is $\approx 840^{\circ}\mathrm{C}$

(c) Determine which other Ag-Cu alloy composition has the same liquidus temperature as the one determined in (b).

Answer

From phase diagram in Prob. 3, other composition with same liquidus T is $\approx 20\mathrm{wt.}\,\%\mathrm{Cu}$

(d) 26 g of sterling silver $(92.5\mathrm{wt.}\,\%\mathrm{Ag}-7.5\mathrm{wt.}\,\%\mathrm{Cu})$ are melted together with 376 g of pure copper (Cu). Given the phase diagram for $\mathrm{Ag}-\mathrm{Cu}$, determine:

(i) the liquidus temperature for the alloy formed;
(ii) the solidus temperature for this alloy;
(iii) the composition of the alloy formed.

Answer

(i) From phase diagram in part (a), liquidus $\mathrm{T} \approx 1060^{\circ} \mathrm{C}$

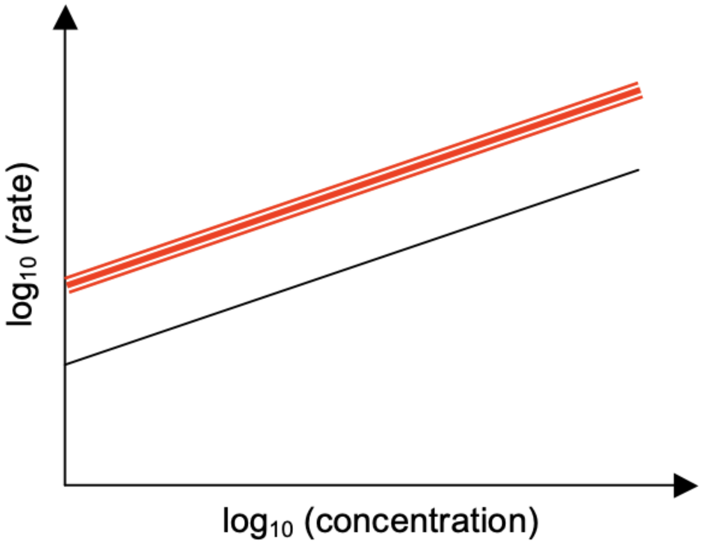
(ii) From phase diagram in part (a), solidus $\mathrm{T} \approx 870^{\circ} \mathrm{C}$

(iii) 26 g of Sterling Silver has $(26)(0.925)=24.05\ \mathrm{gAg}$ and $(26)(0.075)=1.95\ \mathrm{gCu}$ Total $\mathrm{Cu}=1.95+376=378$ g.

$$\text{wt. } \%\mathrm{Cu}=\frac{378\ \mathrm{gCu}}{24\ \mathrm{gAg}+378\ \mathrm{gCu}}=94$$

2.8: Self-Assessment- Reactions and Kinetics + Answer

1. Urbium (Ur) is an upscale element found in big cities. Its oxide $\left(\mathrm{UrO}_2\right)$ is not very stable and decomposes readily at temperatures exceeding $666^{\circ}\mathrm{C}$. The figure below shows how the rate of reaction varies with the concentration of UrO_2 at $777^{\circ}\mathrm{C}$. The rate, r, is in units of $\mathrm{M/s}$ and the concentration of UrO_2, c, is in units of $\mathrm{M}(\mathrm{mole/L})$. The slope has a value of 1.77 and the intercept has a value of 1.46.



(a) What is the order of reaction?

Answer

The order is the slope: 1.77

(b) Calculate the value of the rate constant. Pay strict attention to the units.

Answer

$$r=kc^n \rightarrow \log r=\log k+n \log c ; \text{when } c=1, r=k=10^{1.46}=28.8$$

$$\text{Units of } k=r/c^{\mathrm{n}}=(\mathrm{M/s})/\left(\mathrm{M}^{1.77}\right)=\mathrm{M}^{-0.77}/\mathrm{s} \rightarrow k=28.8 \mathrm{M}^{-0.77}/\mathrm{s}$$

(c) On the graph above, draw the line showing how the rate of reaction varies with the concentration of UrO_2 at $888^{\circ}\mathrm{C}$. No calculation necessary. Pay attention to relative values and slopes.

Answer

The upper line on the graph represents the isotherm at $888^{\circ}\mathrm{C}$. Note same slope as $777^{\circ}\mathrm{C}$ but greater value of r-intercept.

2. Show by a calculation that the diffusion length of boron (B) in germanium (Ge) is less than $1.0 \mu\mathrm{m}$ at a temperature of $1200\ \mathrm{K}$ for a diffusion time of 30 minutes. The diffusion coefficient of B in Ge at $1200\ \mathrm{K}, D_{\mathrm{B}}$, has the value of $2.0 \times 10^{-17}\ \mathrm{m}^2/\mathrm{s}$.

Answer

The diffusion length is approximated by the relationship $x=\sqrt{Dt}$ or $x=2\sqrt{Dt}$

$$\therefore \sqrt{Dt}=\sqrt{2.0 \times 10^{-17} \frac{\mathrm{m}^2}{\mathrm{s}} \cdot 30 \text{ min} \cdot 60 \frac{\mathrm{s}}{\mathrm{min}}}=1.90 \times 10^{-7}\ \mathrm{m}<1.0 \mu\mathrm{m}$$

CHAPTER OVERVIEW

3: Quizzes

Topic hierarchy

3.1: Quiz 1
3.2: Quiz 2
3.3: Quiz 3
3.4: Quiz 4
3.5: Quiz 5
3.6: Quiz 6
3.7: Quiz 7
3.8: Quiz 8.5
3.9: Quiz 9
3.10: Quiz 10

3.1: Quiz 1

1) Consider the combustion of a candle $(C_{25}H_{52})$ with oxygen (O_2) to form carbon dioxide (CO_2) and water (H_2O). A typical candle has 100 g of $C_{25}H_{52}$. Please answer the following questions:

a) (2 pts) Write the balanced reaction for the combustion of a candle (2 points).

b) (2 pts) You are in a closed room with a mole of O_2 molecules. If you light 5 candles, what will be the limiting reagent and how much excess (in grams) of either the O_2 or $C_{25}H_{52}$ will remain?

2) Your student ID is made of a plastic called polyvinyl chloride. The molecular unit in this material is C_2H_3Cl, and for this question you can assume the card is made of only this molecule, with a density of 1.4grams/cm^3. Please answer the following questions:

a) (1 pt) Use your 3.091 ruler to determine the mass of your student ID card in grams (assume a thickness of 2 mm and that the card is perfectly rectangular).

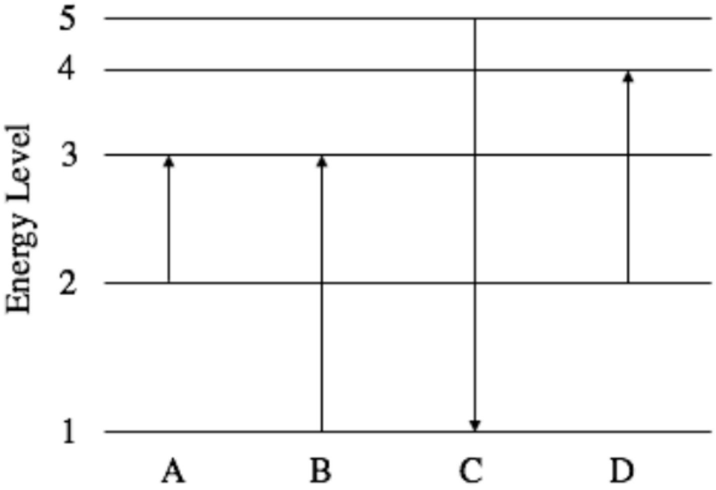
b) (2 pts) How many moles of C_2H_3Cl are in the ID card?

c) (2 pts) There are only 2 stable isotopes of chlorine, ^{35}Cl and ^{37}Cl. What is their relative abundance?

d) (1 pt) You take all the chlorine out of your card and us it to disinfect a 100,000-gallon swimming pool which requires 1 kg of Cl. How many ID cards do you need to disinfect the pool?

3.2: Quiz 2

1) Below is the energy level diagram showing the transitions made by an electron in a hydrogen atom according to the Bohr model.



a) Identify the highest energy absorption indicated among the four electron transitions indicated above and calculate the energy of the photon required to cause the transition in eV. (2 pts)

b) Will a transition starting from n=3 to n=2 emit a photon in the visible light range (390nm-700nm)? Can this photon ionize an electron in the n=3 level? (2pts)

c) Use your spectroscope to look at the lights above you. What is the minimum number of energy levels in a Bohr atom needed to produce these lines? (1 pt)

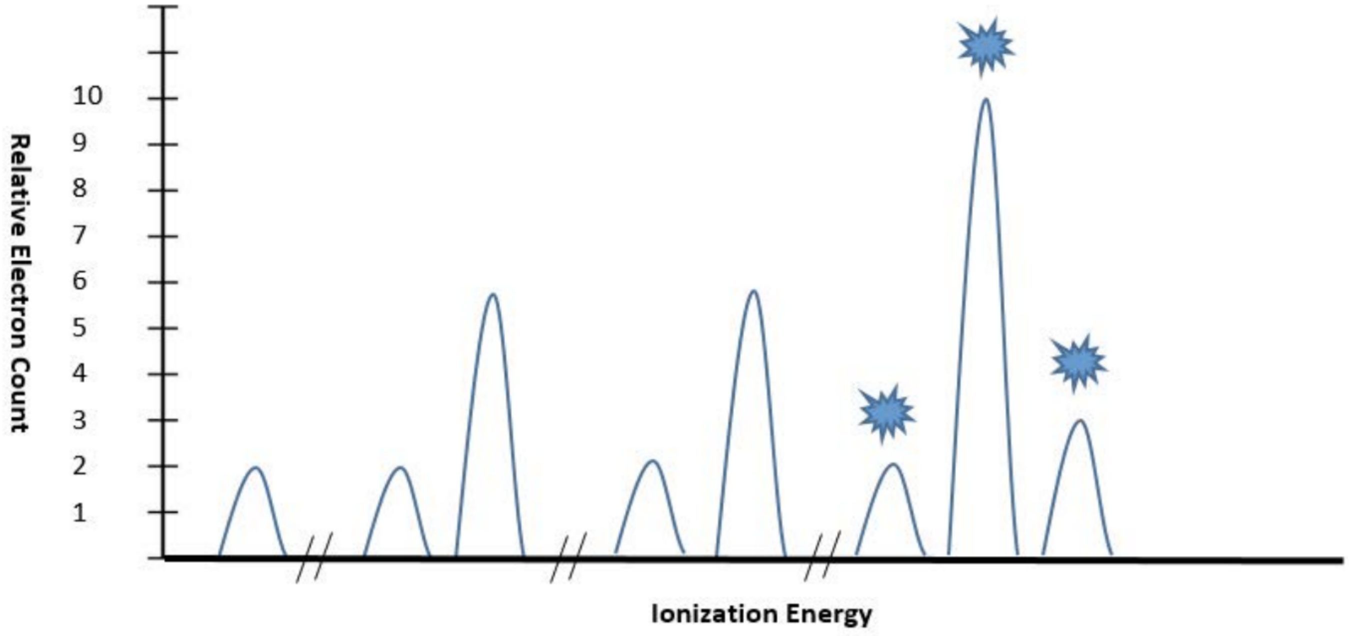
2) When humans are exposed to sunlight, Ultraviolet-B (UVB) light of wavelength $\sim \mathbf{295nm}$ reacts in our skin to make vitamin $D\,(C_{28}\mathrm{H}_{44}\mathrm{O})$. The recommended daily dose of vitamin D for adults is $\mathbf{0.1}$mg which amounts to $1.52 * 10^{17}$ molecules.

a) It takes **one photon to create one vitamin D molecule**. How many Joules of UVB energy does our body absorb per day to create the necessary amount of vitamin D? (3 pts)

b) About $2.5\ \mathrm{mW}\ \left(2.5 \times 10^{-3}\ \mathrm{J/s}\right)$ of vitamin D - producing UVB light strike our exposed skin when we're outside (with a t-shirt and shorts on).
If 5% of incident UVB light is utilized by our skin, how long should people spend outside to ensure they get the required dose of vitamin D? (2 pts)

3.3: Quiz 3

1) A scientist acquired the following photoelectron spectrum from a pure elemental sample.



a. What is the element? (1 pts)

b. Write the electronic configuration of the element in noble gas notation. (1 pts)

c. Write the electronic configuration of this element in box notation (you only need to show the electrons for the shells marked with stars). (2 pts)

d. This element is ionized to its +1 ion. What are the principal (n) and angular momentum (l) quantum numbers of the electron that's lost? (2 pts)

2) The solution provided contains potassium chloride (KCl) dissolved in water: use it to answer the following questions.

a. What is the conductivity of the solution? Assume the baseline conductivity of the water is negligible. (1pt)

b. Is the solid ionic or covalent? Why? (1pt)

c. Does magnesium oxide (MgO) have a higher or lower lattice energy than potassium chloride? Justify your answer. (2 pts)

d. One mole of potassium chloride (KCl) and one mole of nickel(II) chloride ($\mathrm{NiCl_2}$) are dissolved in equal volumes of water. Which would have a higher conductivity? (1 pt)

3.4: Quiz 4

1) Carbonic acid, H_2CO_3, is a product of CO_2 and H_2O and has contributed to ocean acidification. Please answer the following questions.

a) Draw the Lewis dot structure, with correct molecular geometry, that carbonic acid forms. (1 pt)

b) What geometry does the carbon in carbonic acid adopt according to VSEPR? (1 pt)

c) Will all the lone pairs lie in the same plane when the molecule is in the lowest energy state? (1 pt)

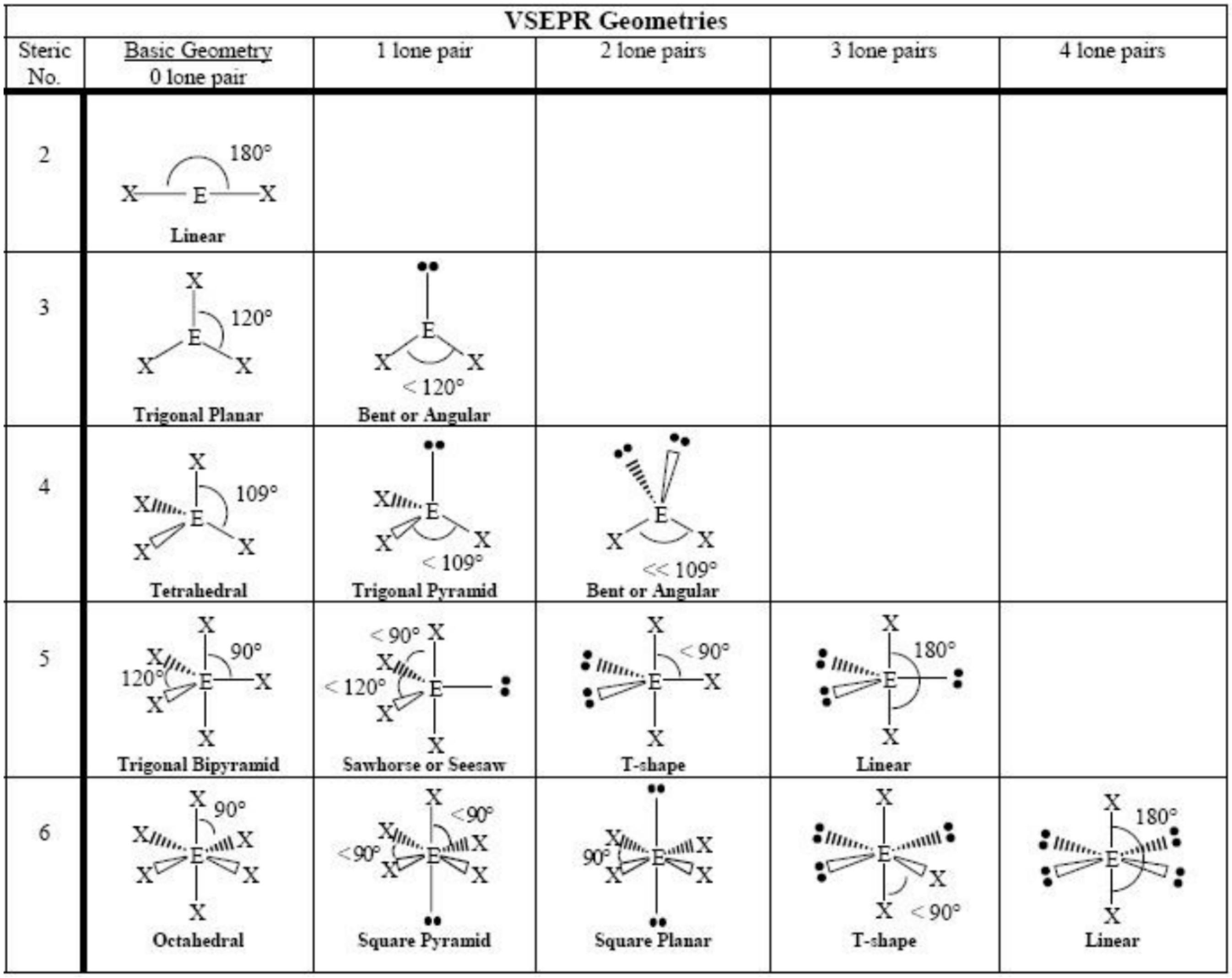
d) Where is the largest angle in the molecular structure? Please give your answer as $X-Y-Z$, where Y is the atom the angle is formed (i.e., the vertex). For example, $\mathrm{H-O-H}$ or $\mathrm{O-Fe-O}$. (1 pt)

e) Look at the 3D molecular model you built from last Wednesday's *Goodie Bag #4: VSEPR* for the molecule $\mathrm{H_3Si-SF_2-CN}$. What is the smallest angle in your structure? (1 pt)

2)

a) Draw **two** possible resonance structures for CH_3NCO. (4 pts)

b) Which of your two resonance structure contributes more to the resonance hybrid? Explain in one sentence. (1 pt)



VSEPR Geometries

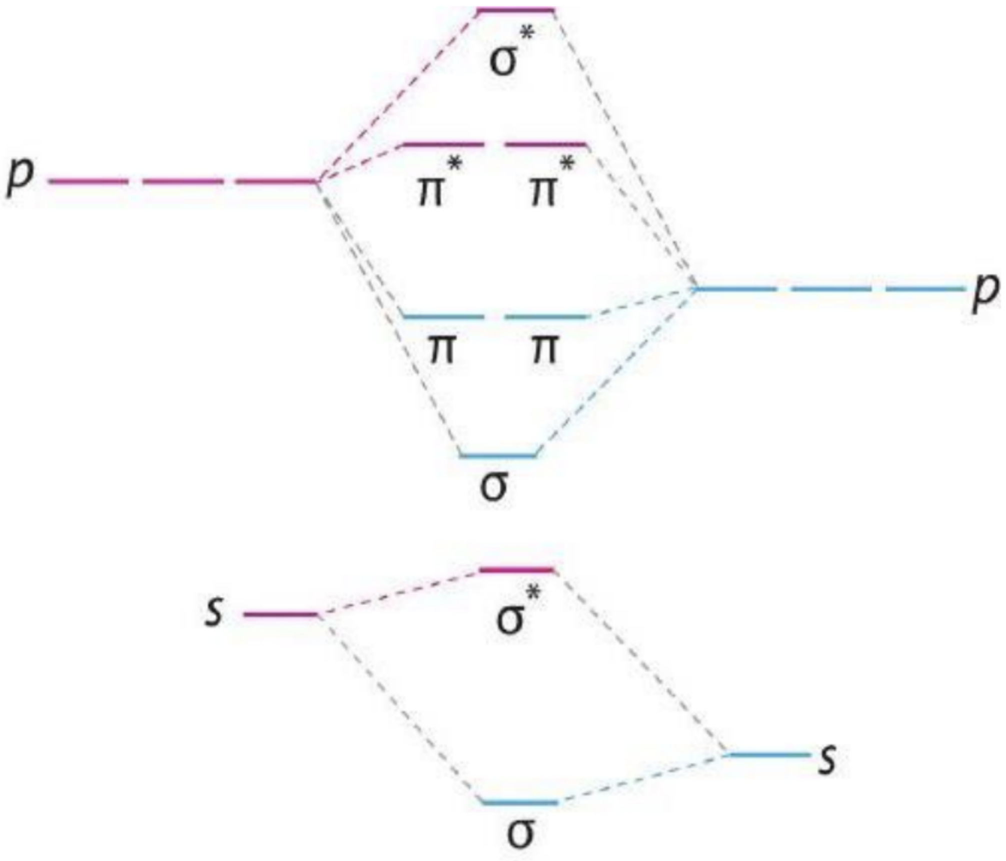
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal Planar	< 120° Bent or Angular			
4	109° Tetrahedral	< 109° Trigonal Pyramid	<< 109° Bent or Angular		
5	90° 120° Trigonal Bipyramid	< 90° < 120° Sawhorse or Seesaw	< 90° T-shape	180° Linear	
6	90° Octahedral	< 90° < 90° Square Pyramid	90° Square Planar	< 90° T-shape	180° Linear

VSEPR Geometries by Boundless Chemistry. License: CC BY-SA. This content is excluded from our Creative Commons license. For information, see https://ocw.mit.edu/fairuse.

3.5: Quiz 5

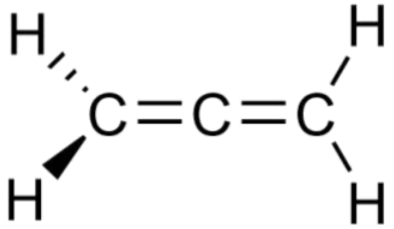
1. Consider the molecule $\mathrm{OBr^-}$.

a. Fill in the MO diagram for the molecule using arrow notation. Label each atomic orbital side with the correct atom. (2 pts)



b. What is the bond order? (1 pt)

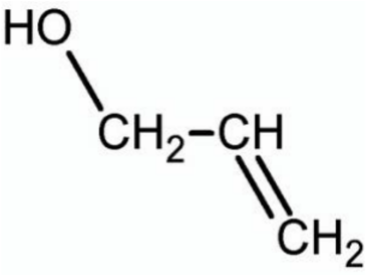
2. Allene is a compound with formula $\mathrm{C_3H_4}$ with the following Lewis dot structure:



a. Give the hybridization for all the carbons in the allene. (1 pt)

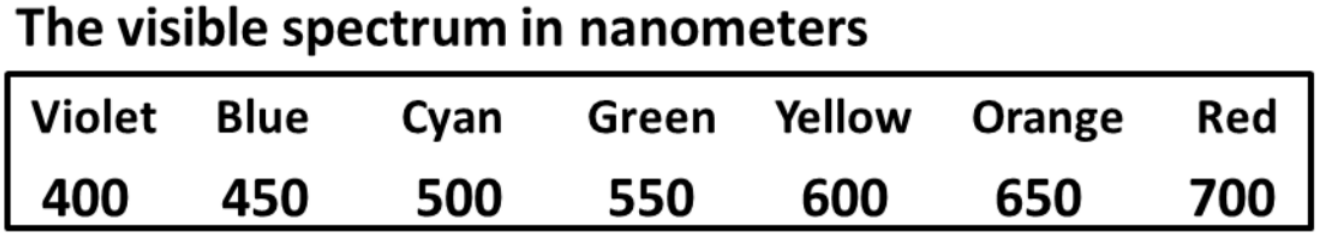
b. Label the individual bonds as sigma or pi bonds. (1 pt)

c. List the intermolecular interactions that could happen between only an allene and an allyl alcohol molecule. Allyl has the following structure: (1 pt)



d. Rank the following in order of ascending boiling point: pure allene, a mixture of allene and allyl alcohol, and pure allyl alcohol. (1 pt)

3. Given the visible spectrum below, answer the following questions.



The visible spectrum in nanometers

Violet	Blue	Cyan	Green	Yellow	Orange	Red
400	450	500	550	600	650	700

a. If you shine a violet light onto a red small LED, how much heat energy will a promoted electron in the red small LED dissipate? (2 pts)

b. Rank the amount of heat energy dissipated in the mystery LED, a red LED, and a blue LED if you were to shine a violet light onto them. (Hint: use your GB to help LEaD you to the answer) (1 pt)

3.6: Quiz 6

1. For p-type and n-type Si... (2 points)

a. What is a possible dopant atom?

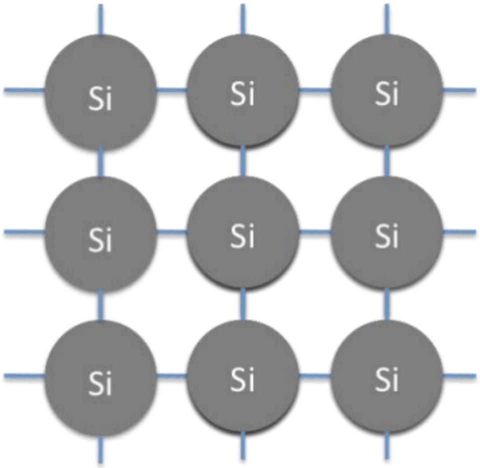
p-type: ________________ n-type: ________________

b. What are the charge carriers?

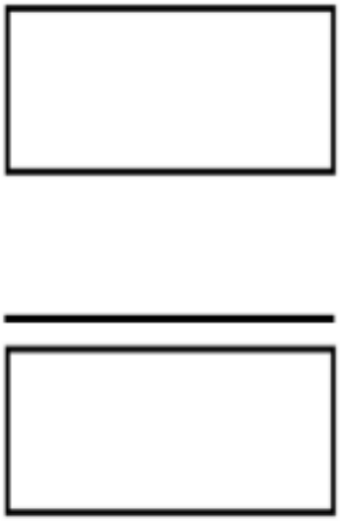
p-type: ________________ n-type: ________________

c. How many bonds does the dopant atom form once it has donated its charge carriers?

p-type: ________________ n-type: ________________



d. Label the structures below as p-type and n-type Si. Label conduction and valence bands, donor level, and acceptor level. (2 points)



e. For 100 g of Si, calculate the mass of As needed in order to have $3.091 * 10^{17}$ carriers $/\mathrm{cm}^3$. (2 points)

2. Lattice structures (You may want to use your pre-built FCC structure :))

a. The radius of a nickel atom is $r = 1.97\text{Å}$ What is the **volume packing fraction** of the FCC unit cell? (1 point)

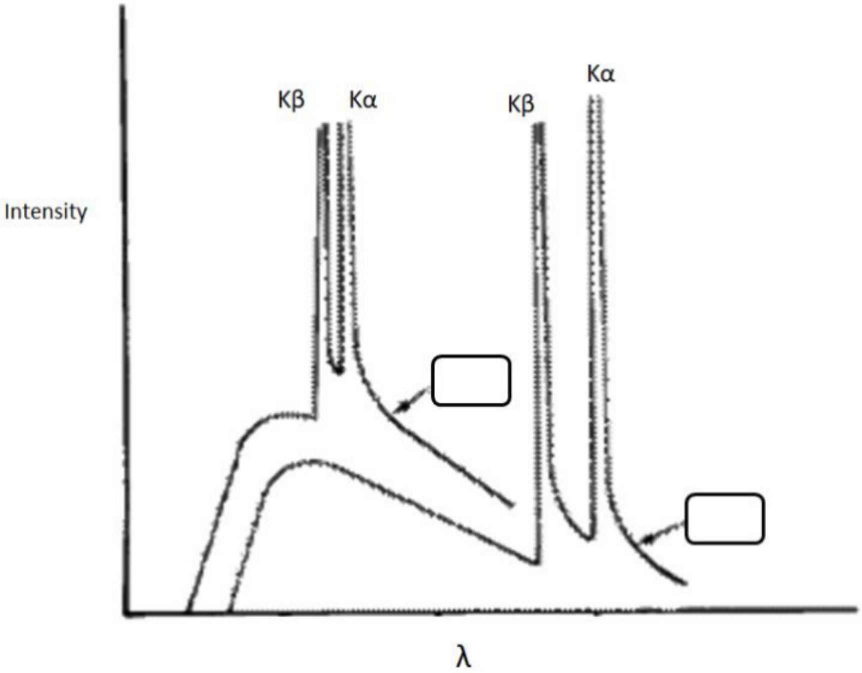
b. What is the direction of closest packing? (1 point)

c. Consider one face of your FCC lattice. How many nearest neighbors does the central atom have in the same plane? (1 point)

d. Under sufficient pressure, some elemental metals transitions from BCC to another cubic structure. What is the cubic structure that it transitions to? (1 point)

3.7: Quiz 7

1. You shoot energetic beams of electrons at molybdenum and copper samples and receive the emitted x-ray spectra shown below.



a. The samples were irradiated with beams with different amounts of energy. Draw an arrow to the curve that was irradiated with higher energy. (1 point)

b. Unfortunately, you forgot to label which spectrum came from which metal. Please fill in the boxes above with the correct metal. (1 point)

c. On the x-ray spectra above, draw in the characteristic peak corresponding to the copper Lα energy transition. (1 point)

2.

a. What planes would produce the first three peaks you would see for a BCC crystal structure? What about for FCC? Give the planes in the form of (hkl). (2 points)

b. Express $\frac{\sin^2\theta_n}{\sin^2\theta_1}$ in terms of Miller indices h_1, k_1, l_1 and h_n, k_n, and I_n where θ_n is the angle of the nth peak; h_1, k_1, and I_1 are the Miller plane indices of the first peak; and h_n, k_n, and I_n are the miller plane indices of the nth peak. Hint: take the ratio of two Bragg's law equations. (2 points)

You are given an XRD plot. Let’s try to find the lattice parameter of the mystery pure metal. (We do not have polonium in the lab.)

c. Fill out the table below in which the peaks are at $2\theta = 20^\circ, 28.4^\circ$, and 35.04°. (1 points)

Peak	**2θ**	$\frac{\sin^2\theta_n}{\sin^2\theta_1}$
1	20°	
2	28.4°	
3	35.04°	

d. Using the relationship derived in part b, what crystal structure is your mystery pure metal? (1 points)

e. Calculate the lattice parameter if the x-ray source has a wavelength of 1.7Å. $\left(10^{10}\text{Å} = 1 \text{ m}\right)$. (1 points)

3.8: Quiz 8.5

1) A pteropod shell (made of $\mathrm{CaCO_3}$) weighs $0.01\mathrm{mg}$. By the year 2100 the ocean will be 126% more acidic than pre-industrial levels if we continue on our current path. This will lead to the dissolution of the shell: $\mathrm{CaCO_3(\,s)} \rightarrow \mathrm{Ca^{2+}(aq)} + \mathrm{CO_3{}^{2-}}$ (aq)

You measure this reaction by weighing the shell vs. time every 1 hour and you record your results:

Experiment	$[\mathrm{CaCo_3}](\,\mathrm{mg})$
1 ($t = 0$ hr)	0.01
2 ($t = 1$ hr)	0.008
3 ($t = 2$ hrs)	0.006
4 ($t = 3$ hrs)	0.004

a) If the shell fully dissolves in 0.1 liters of water, what is the molar concentration of the resulting $\mathrm{CO_3{}^{2-}}$? (1.5 points)

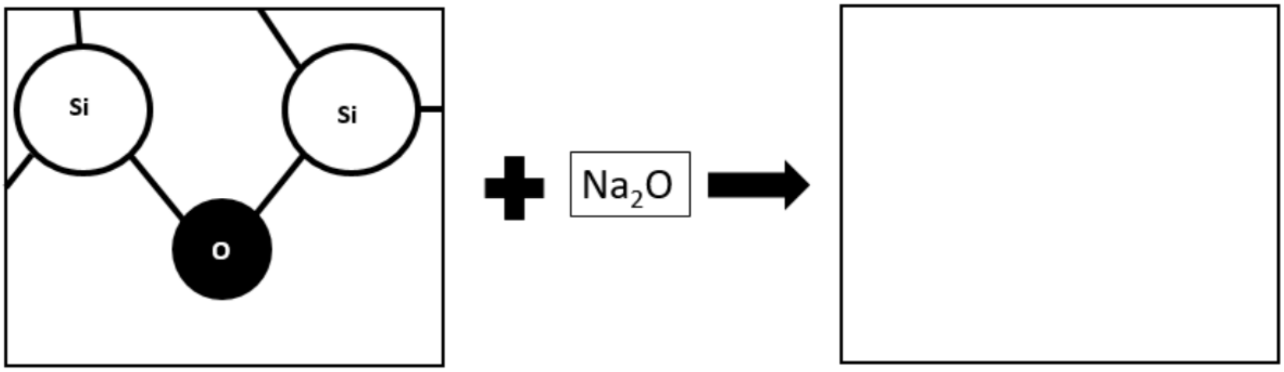
b) What is the order of the reaction? (1.5 points)

c) What is the rate of the reaction (expressed in M/s)? (1.5 points)

d) What is the rate constant for the reaction and what units does it have? (1.5 points)

2) You find a sheet of glass in the Glass Lab and want to increase its resistance to fracture, so you can throw baseballs at it. This glass is soda glass, meaning $\mathrm{Na_2O}$ was added in the melt.

a) A schematic of a 2D cross-section of amorphous $\mathrm{SiO_2}$ is shown below in one box. Draw how adding $\mathrm{Na_2O}$ changes this structure.



b) After adding $\mathrm{Na_2O}$, does the glass transition temperature increase, decrease, or stay the same?

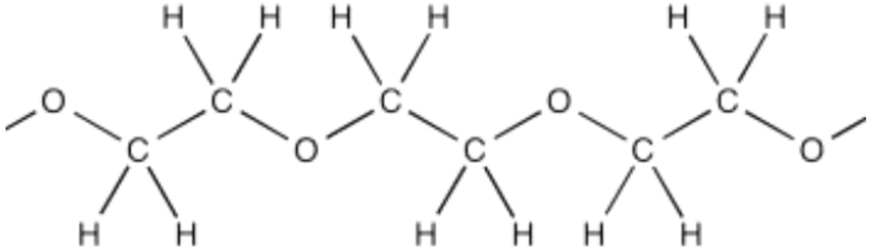
c) In order to strengthen the glass, you decide to use an ion exchange method. What is one ion that you could exchange in, and which ion leaves the glass during this process?

d) Describe how ion exchange increases the toughness of the glass, with reference to molar volume and the stress field.

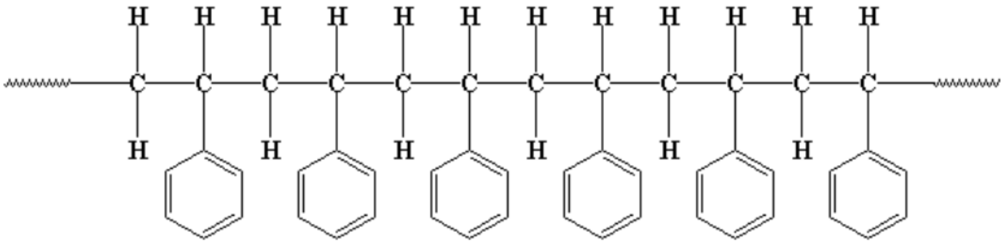
3.9: Quiz 9

1a) Circle the monomer (the smallest repeat unit) in the following two polymers (2 points):

Polyethylene glycol



Polystyrene



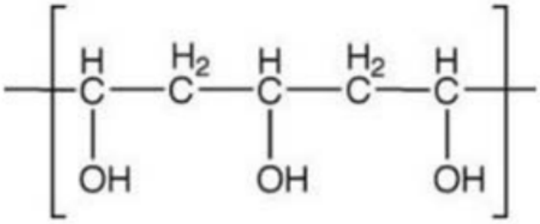
1b) What is the primary intermolecular force in polystyrene (1 point)?

1c) Which polymer would you expect to contain more crystalline regions? Explain in one sentence (1 point).

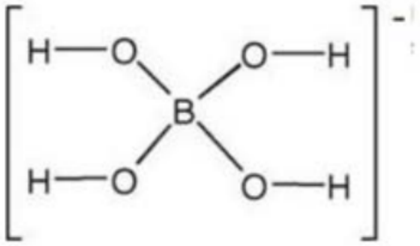
1d) Which polymer would you expect to be soluble in water? Explain in one sentence (1 point).

1e) One of these polymers is made via a radical process and the other is made via a condensation process. Which is made through a radical process (1 point)?

2. In your goodie bag, you mixed Elmer’s glue and Borax. The relevant chemical components are shown below:

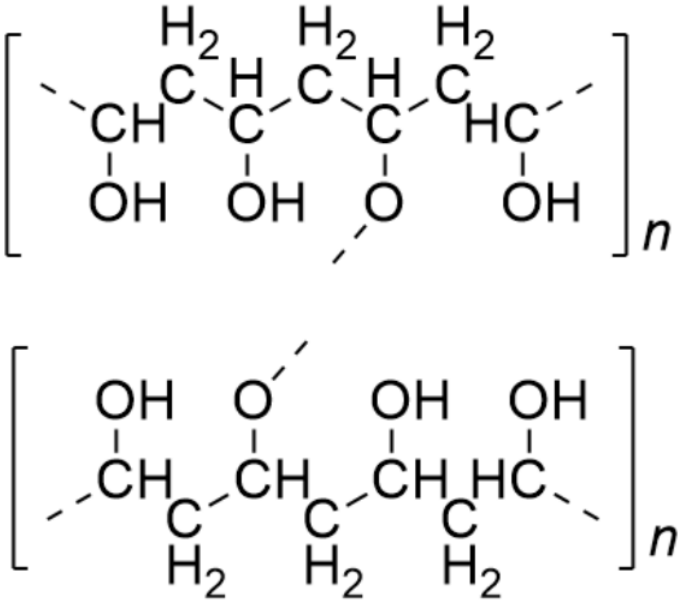


Elmer’s Glue

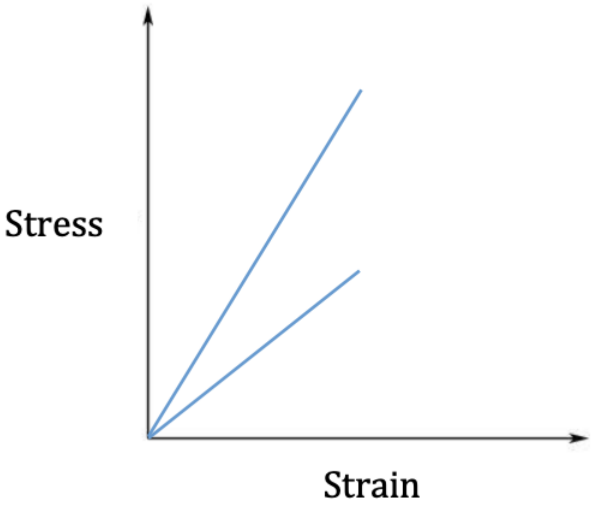


Borax

a) Draw the Borax component on the following strands of Elmer’s glue (2 point).



b) The below graph contains the elastic regions of two stress-strain curves, corresponding to regular Elmer's glue and Elmer's glue treated with Borax. Clearly label the two graphs as treated or untreated (2 points).



3.10: Quiz 10

You want to know how quickly your MIT acceptance balloon will run out of helium gas (He) inside of it. Since you tied the balloon so tightly, you neglect the pinhole at the neck and model the balloon as a closed sphere of latex.

Note: Assume that helium concentration inside the balloon remains constant.

1. The balloon is $0.1\ \mathrm{mm}$ thick. The concentration of He gas inside the balloon is $0.04462\mathrm{M}$ and outside the balloon is $2.32\times 10^{-7}\mathrm{M}$. If the diffusivity constant of helium through latex is $7\times 10^{-9}\ \mathrm{m}^2/\mathrm{s}$ at room temperature, what is the flux of helium gas through the latex balloon (Hint: $1L=0.001\ \mathrm{m}^3$)?

2. You're shocked to discover that the helium gas is diffusing through the balloon so quickly! In order to preserve the cherished memories of your MIT undergrad, you decide to slow the diffusion of helium through the balloon.

    a. What concentration of helium gas would you have to have outside the balloon to halve the flux?

    b. At what temperature would you have to store the balloon to halve the flux, compared to question 1 $\left(E_a=0.09\mathrm{eV}=1.44\cdot 10^{-20}\ \mathrm{J}\right)$?

    c. Your beloved balloon is exposed to the Boston winter! It lowers the temperature of the balloon below the glass transition temperature of the latex. How does this affect the diffusion of helium through the balloon?

    d. Your friend cross-linked the latex in her balloon before filling it with helium. How would this impact the diffusion of helium through the balloon?

    e. Name another way that you could decrease the flux of helium through the balloon.

CHAPTER OVERVIEW

4: Exams

4.1: Exam 1
4.2: Exam 2
4.3: Exam 3
4.4: Final Exam

4.1: Exam 1

Problem 1 (17 POINTS)

a) A Lithium ion $\left(\mathrm{Li}^{2+}\right)$ laser is emitting light of wavelength $450\ \mathrm{nm}$ due to electrons relaxing to energy level $n=4$ from some unknown energy level. What is the unknown energy level? [4 points]

b) Against all lab safety protocol (do. not. do), you grab a different laser and observe the light through your spectrometer. You observe 10 spectral lines. This means that there are at least how many possible energy levels? [2 points]

c) You purchase two new lasers that each emit one wavelength only: one emits $200\ \mathrm{nm}$ light, and the other emits $900\ \mathrm{nm}$ light. However, you mix up the lasers and don't know which is which. You shine each of these lasers onto a slab of metal. One laser ionizes electrons from the metal but the other doesn't. Which laser doesn't ionize the metal? Give one sentence explaining why. [2 points]

d) You begin to increase the frequency of the laser you named in part c). If you continue doing this, will you eventually observe electrons being emitted? Give **one** sentence explaining why or why not. [2 points]

e) You begin to increase the intensity of the laser you named in part c). If you continue doing this, will you eventually observe electrons being emitted? Give **one** sentence explaining why or why not. [2 points]

f) You find an article that says that electrons in your metal slab will start to be ionized at $500\ \mathrm{nm}$. If you switch to the laser from part c) that **DOES** ionize the metal (i.e. the one you didn't give in your answer to c)) and shine it on said metal, what will be the velocity of the emitted electrons? [5 points]

Problem 2 (24 POINTS)

NOTE: For each of the following questions, assume the atom or ion is in the ground state.

a) Write the ground state electron configuration for the following atoms and ions. [6 points]

- O^{2-}
- Si

b) For the following atoms and ions, draw a box-and-arrow diagram to represent the last completely or partially filled subshell, following Aufbau's rules for filling. You may use noble gas abbreviations for filled inner shells. [6 points]

- O^{2-}
- Si

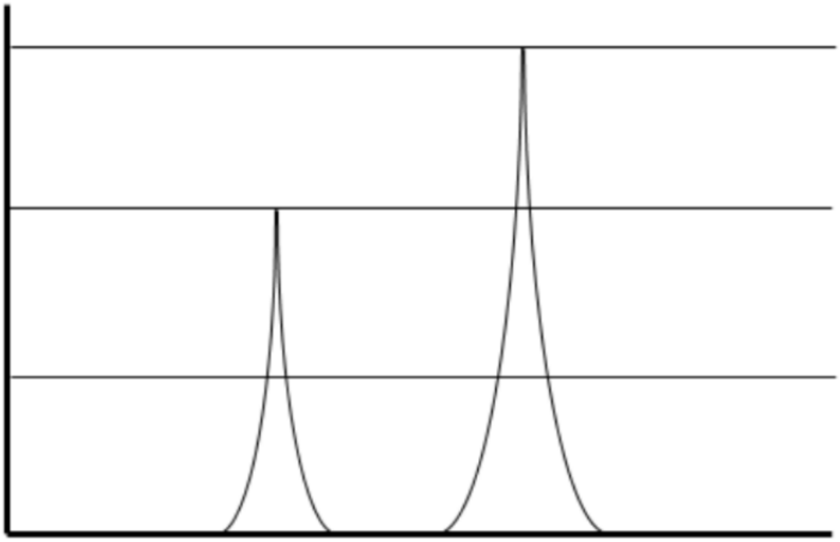
c) Paramagnetic materials are attracted by a magnetic field, but do not retain a magnetization when the external field is removed. Paramagnetism is caused by **unpaired electrons** in a material's atoms. Based on this information, which atom and/or ion in part A are paramagnetic, if any? [2 points]

d) Write the complete set of quantum numbers (the values for n, l, m_l, m_s) for each of the valence electrons in Si. [8 points]

e) How many of the electrons in Si have the same set of quantum numbers ($n, 1, \mathrm{m_l}, \mathrm{m_s}$)? [2 points]

Problem 3 (19 POINTS)

Below is the PES spectrum for the outer electrons of element X.



a) Label the axes and the direction of increasing ionization energy on this graph. The graph is plotted so that the highest peak corresponds to the electrons that are ionized first during the experiment. [3 points].

b) Element X has the same inner electron configuration as neon. Identify element X and label the peaks by subshell, including the number of electrons in each peak.

Note: only the peaks corresponding to valence electrons are shown in the graph. [6 points].

c) Consider an ion with the same electronic configuration as X but one more proton. On the graph above, draw the new PES spectrum for this ion. [4 points].

d) You were taking PES spectrum data for carbon in a vacuum. However, the seal on the vacuum machine broke and let in an unknown gas. The spectrum for carbon is still present, but you need to identify the unknown peaks. You observe the following on the contaminated spectrum:

i. There are 6 peaks total (including peaks from the carbon) on the spectrum

ii. Five peaks are of the same height

iii. One peak is three times higher than the others

What is the contaminating element? Explain your reasoning. [6 pts]

Problem 4 (17 POINTS)

a) You are trying to synthesize chocolate in the lab. The first step is to produce theobromine $\left(\mathrm{C_7H_8\,N_4O_2}\right)$, a component of cacao. The reaction in the cacao plant creates theobromine and $\mathrm{O_2}$ as byproducts. You have $\mathrm{N_2}, \mathrm{SO_2}, \mathrm{H_2O}, \mathrm{CO_2}$ available in the lab as **potential** reactants. Select your reactants and write the balanced reaction. [4 points]

b) Now you need sugar to make chocolate. Your reaction produced 2 moles of theobromine, and you have 5 moles of glucose $\left(\mathrm{C_6H_{12}O_6}\right)$ available in your lab. The recipe for chocolate calls for a $\mathbf{3:1}$ ratio of theobromine to glucose **by volume**. Is theobromine or glucose limiting, and how many cm^3 of the chocolate mixture can you produce? [10 points]

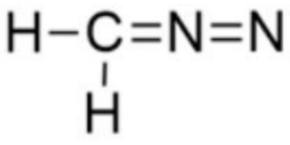
Density of theobromine: $1.52\ \mathrm{g/cm}^3$ at room temperature

Density of glucose: $1.54\ \mathrm{g/cm}^3$ at room temperature

c) Chocolate by itself it fine, but you conclude that the ultimate form of chocolate is chocolate-covered strawberries. It takes $0.5\ \mathrm{cm}^3$ of melted chocolate to cover an average strawberry. Now using the chocolate you made in part b, how many **moles of strawberries** could you cover in chocolate? Assume that the density change with temperature change is negligible. [3 points]

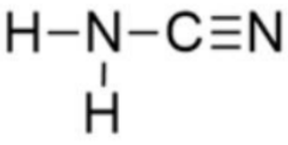
Problem 5 (23 POINTS)

a) Two structures with the formula $CH_2 N_2$ are drawn below. Draw the missing lone pairs (where applicable) and write the formal charge on each element. [8 points]



$\mathrm{H{-}\underset{\substack{|\\ H}}{C}{=}N{=}N}$

diazomethane



$\mathrm{H{-}\underset{\substack{|\\ H}}{N}{-}C{\equiv}N}$

cyanamide

b) Cyanamide is made industrially from calcium carbide (CaC_2), which in turn is made from calcium oxide (CaO). Write the charges on each element for calcium chloride $(CaCl_2)$, sodium chloride $(NaCl)$, calcium carbide (CaO), and magnesium carbide (MgO). [6 points]

$NaCl$	CaO	MgO
Charge on Na:	Charge on Ca:	Charge on Mg:
Charge on Cl:	Charge on O:	Charge on O:

c) Rank the compounds in terms of decreasing lattice energy. Explain in **one** sentence. [5 points]

HIGHEST ENERGY -----------------------> LOWEST ENERGY

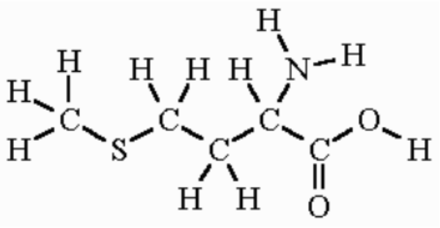
d) Write the Lewis structure for dichloromethane (CH_2Cl_2). [4 pts]

4.2: Exam 2

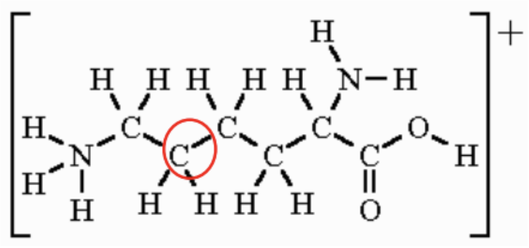
Problem 1 (17 POINTS)

a. Use the fact that $\mathrm{SeOF_2}$ is trigonal pyramidal to write the Lewis Dot Structure, including lone pairs, for $\mathrm{SeOF_2}$. (3 points)

b. Below is a drawing of two different amino acids, Methionine and Lysine, without any lone pairs drawn.



Methionine



Lysine

Name the VSEPR geometry around the following central atoms:

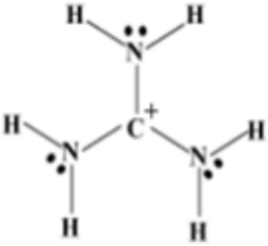
i.The sulfur in methionine (2 points)

ii.The circled carbon in lysine. (2 points)

iii.Which of these angles is smaller? Explain why or why not in ONE sentence. (2 points)

$$\mathrm{CH_2 - S - CH_2} \quad \text{OR} \quad \mathrm{CH_2 - CH_2 - CH_2}$$

c. Below is one structure for the molecule $[\mathrm{CH_6\,N_3}]^+$

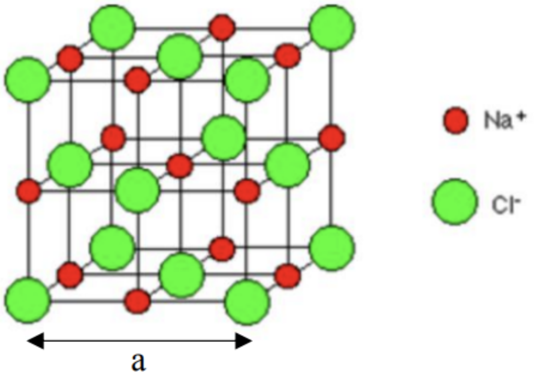


i. There are three other resonant structures for this molecule; what are they? (6 points)

ii. The structure that we gave you for $[\mathrm{CH_6\,N_3}]^+$ contributes the least to the overall bonding of the molecule (it is the least stable). Why? (2 points)

Problem 2 (23 POINTS)

NaCl is a compound that forms a rock salt structure (unit cell below). The radius of the $\mathrm{Na^+}$ atoms is 1.16Å; the radius of the $\mathrm{Cl^-}$ atoms is 1.67Å $(1\text{Å} = 10^{-10}\ \mathrm{m})$.

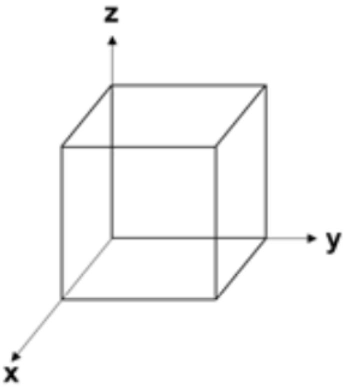


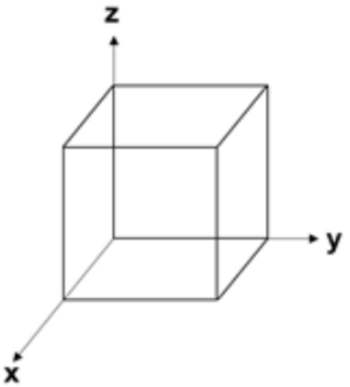
a. Name the Bravais lattice (lattice type) of NaCl. What is the basis? (2 points)

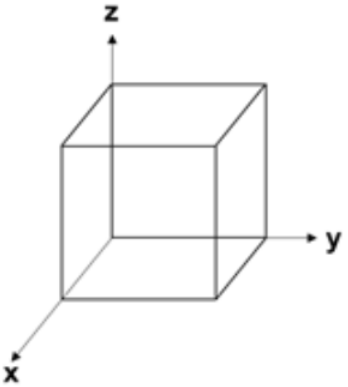
b. How many Na^+ ions are in the unit cell? How many Cl^- ions? (4 points)

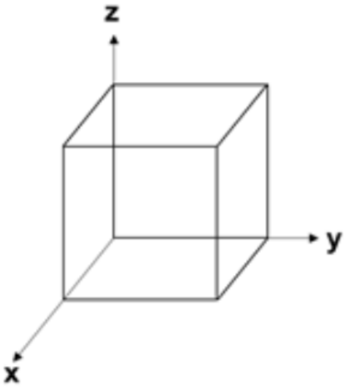
c. Determine the close-packed direction of this structure and use it to calculate the lattice parameter, a. (3 points)

d. Draw (211), [0$\bar{2}$1], [301], and (1$\bar{1}$0) in the boxes below. Make sure to label which is which. (8 points)









e. Which of the planes in part d is closer in distance to its equivalent plane in a neighboring cell? Show how you arrived at this answer. (4 points)

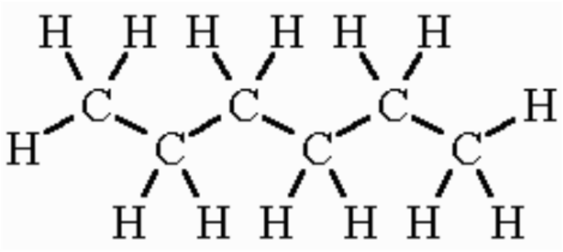
f. Using atomic packing factor, explain why calcium is denser than potassium. (2 points)

Problem 3 (18 POINTS)

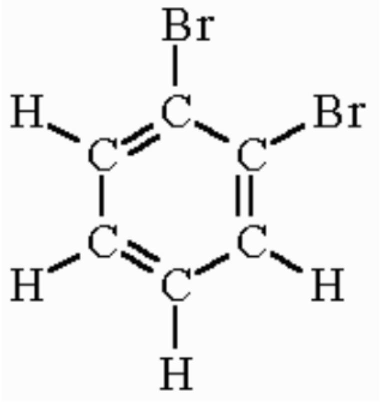
a. Rank the following intermolecular forces in terms of their average relative strength: London dispersion, hydrogen bonding, dipole-dipole, and dipole-induced-dipole. (4 points)

1. ____________________ (strongest)
2. ____________________
3. ____________________
4. ____________________ (weakest)

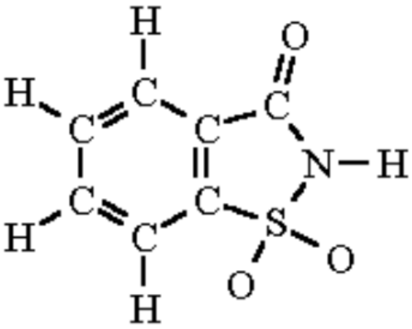
You have the four following molecules in liquid form in your lab cabinet.



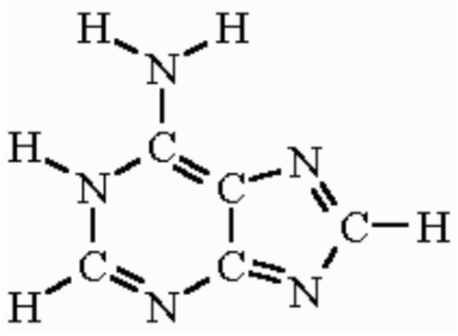
Molecule 1



Molecule 2



Molecule 3



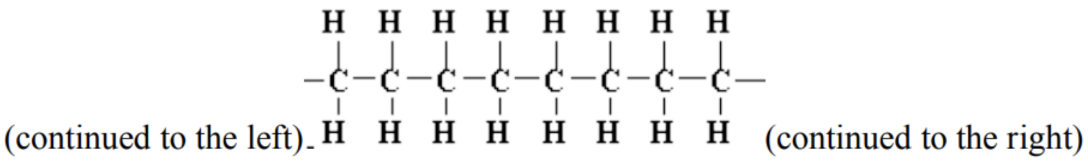
Molecule 4

b. Which has the highest boiling point? (2 points)

c. You make a mixture of two of the liquids.

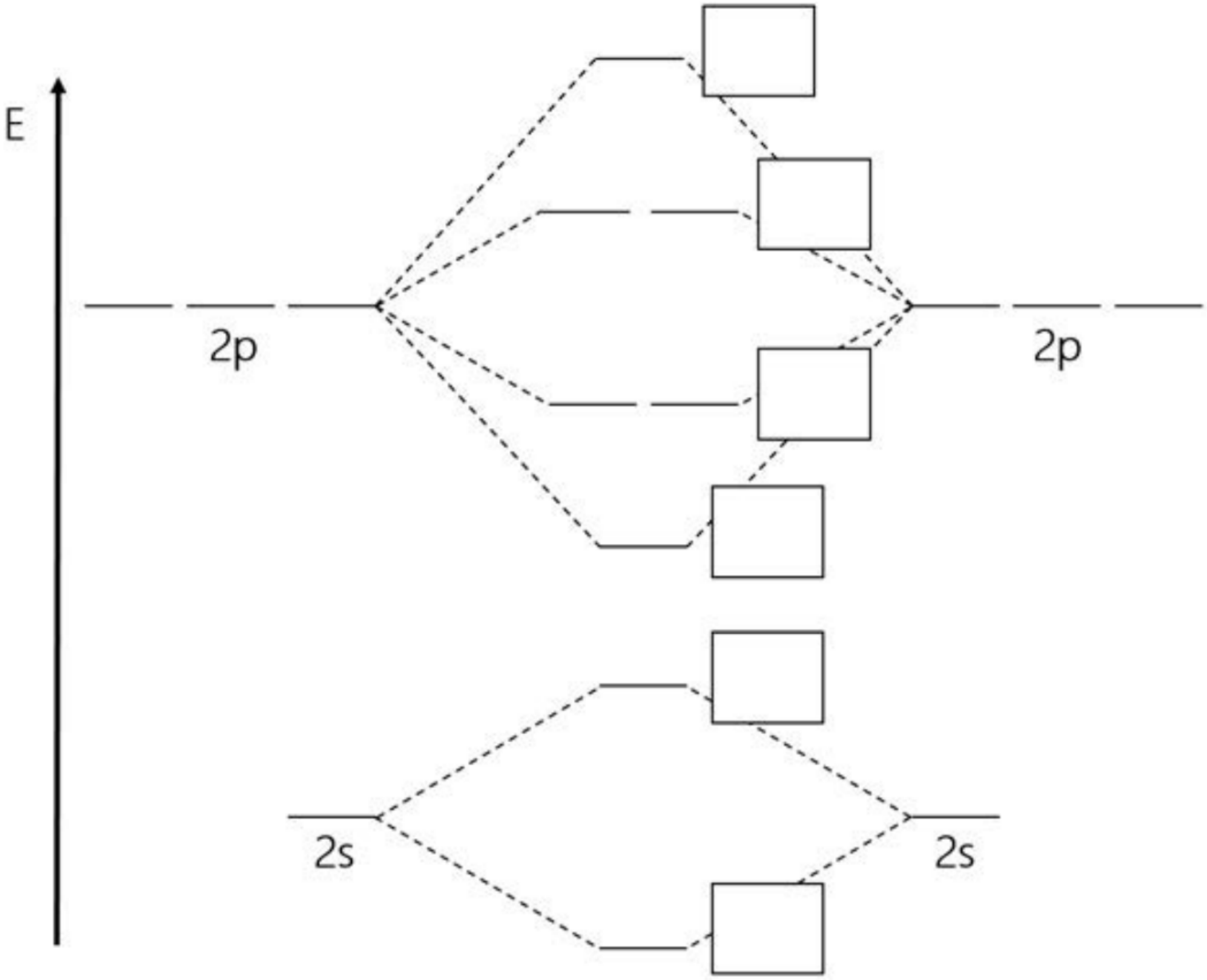
- i. If you wanted your mixture to have the LOWEST possible boiling point, which **two** of the four molecules would you choose? (4 points)
- ii. If you want your mixture to have the HIGHEST possible boiling point, which two of the four molecules would you choose? (4 points)

d. You have two samples of polyethylene, a polymer made of chains of carbon and hydrogen, as shown below. For one sample, each molecule chain is 50 units long and in the next sample, each chain is 500 units long. Which sample of plastic will be stronger? Why? (4 points)



Problem 4 (21 POINTS)

a. The molecular orbitals of a second-row diatomic molecule are shown in this figure. Label them each as σ, σ^*, π, or π^* by filling in the boxes provided. (The 2p and 2 s atomic orbitals are labelled for reference). (6 points)

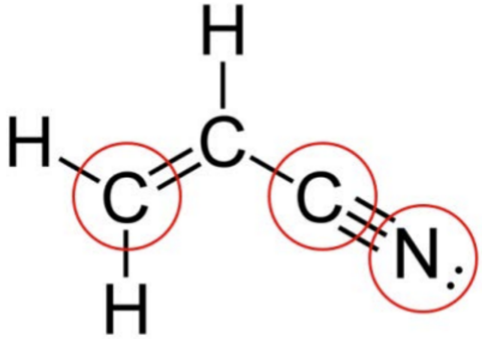


b. Circle which of the following this skeleton MO diagram could correspond to. (2 points)

C – C N – O H – F

c. Rank the following molecules in terms of stability: Li_2, Be_2 B_2, C_2 Be sure to show your work (no need to show MO diagrams). (8 points)

d. Acrylonitrile is a feedstock chemical used for the manufacture of “nitrile” polymers. Pictured below is its chemical structure. What is the hybridization of the circled atoms? (3 points)



Carbon on the right

Nitrogen

Carbon on the left

d. Give the total number of σ bonds and total number of π bonds in acrylonitrile. (2 points)

Problem 5 (21 POINTS)

a. UV light corresponds to wavelengths from $10-400\ \mathrm{nm}$. What is the range of band gaps corresponding to UV light? (3 points)

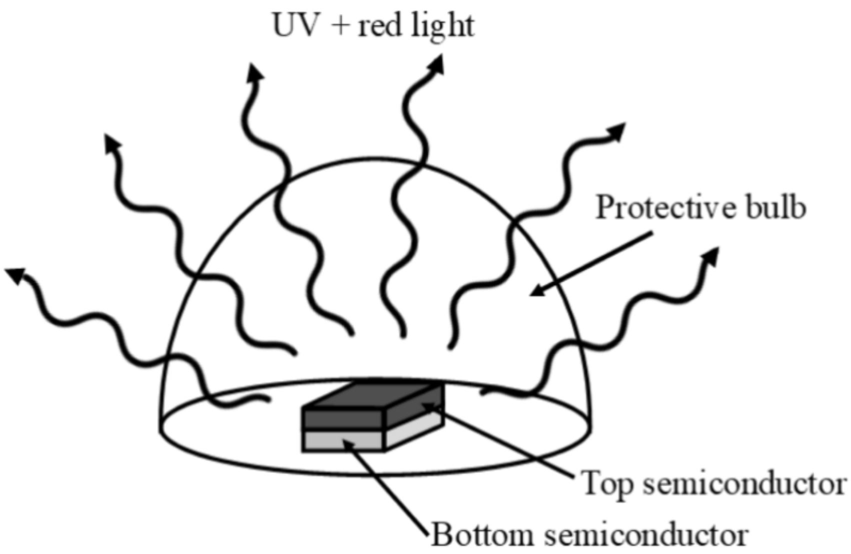
b. You only have two materials in the lab to build an LED: GaAs (band gap $1.42\mathrm{eV}$ at $300\ \mathrm{K}$) and GaN (band gap $3.2\mathrm{eV}$ at $300\ \mathrm{K}$). Which would you choose as a UV emitter? (3 points)

c. UV light can damage eyes, so you decide that for safety, your LED should emit in the visible range too. You recall that you can tune the band gap by alloying your material. Determine the fraction x of GaAs in your alloy such that $\mathrm{GaAs_xN_{1-x}}$ will emit red light (wavelength $700\ \mathrm{nm}$). Remember that the band gap of an alloy is the weighted average of the band gaps of its components. (3 points)

d. If you place the $\mathrm{GaAs_xN_{1-x}}$ adjacent to *your answer from (B)* your LED will emit both UV light and red light. However, you observe that it is really dim: you decide to dope it with Mg.

i. Is Mg an n - or p-type dopant in $\mathrm{GaAs_xN_{1-x}}$? (2 points)

ii. If you dope $1\ \mathrm{gGaN}$ with Mg such that $1\mathrm{Mg}$ atom replaces 1 in every $10^6\,\mathrm{Ga}$ atoms, how many extra carriers are produced? What kind of carriers are these? (4 points)



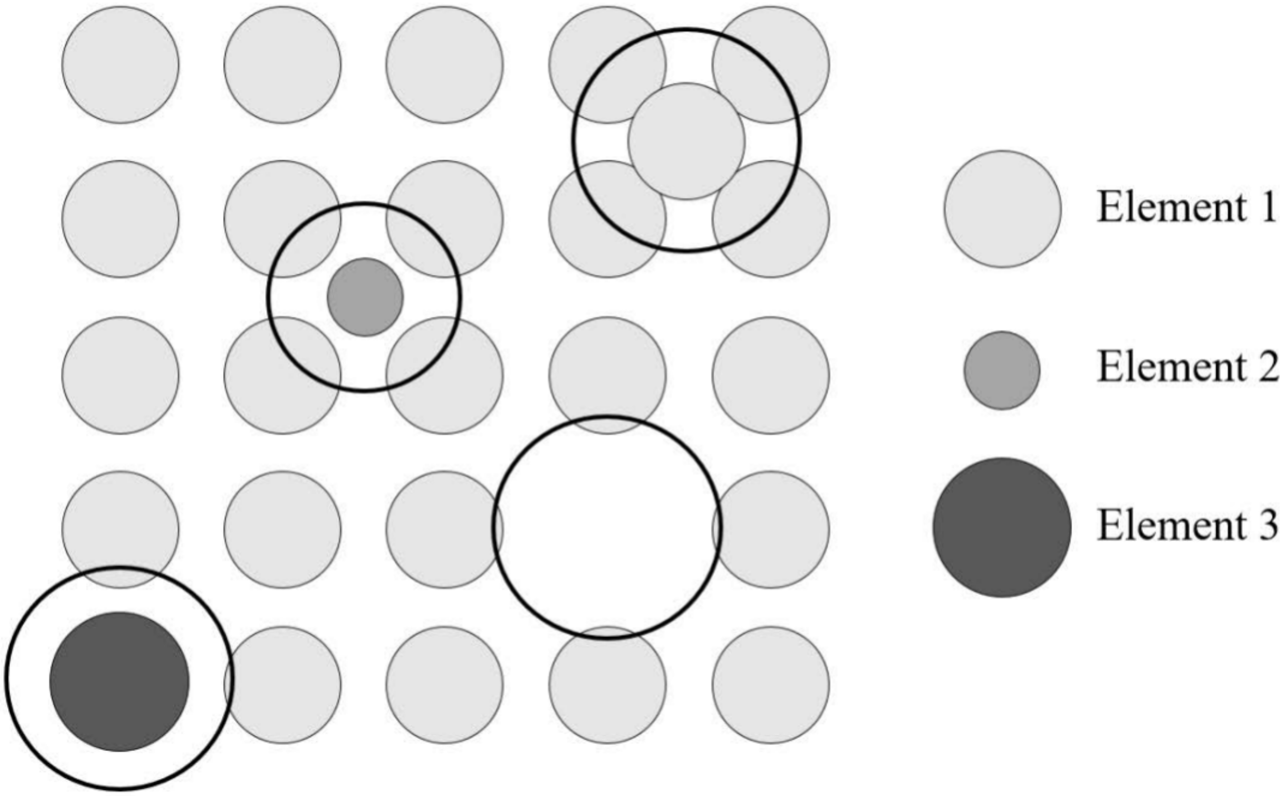
e. In order to get enough current to $\mathrm{GaAs_xN_{1-x}}$ and *your answer from (B)* processing requires that the two are stacked. Which should be on top to ensure no light is blocked? (3 points)

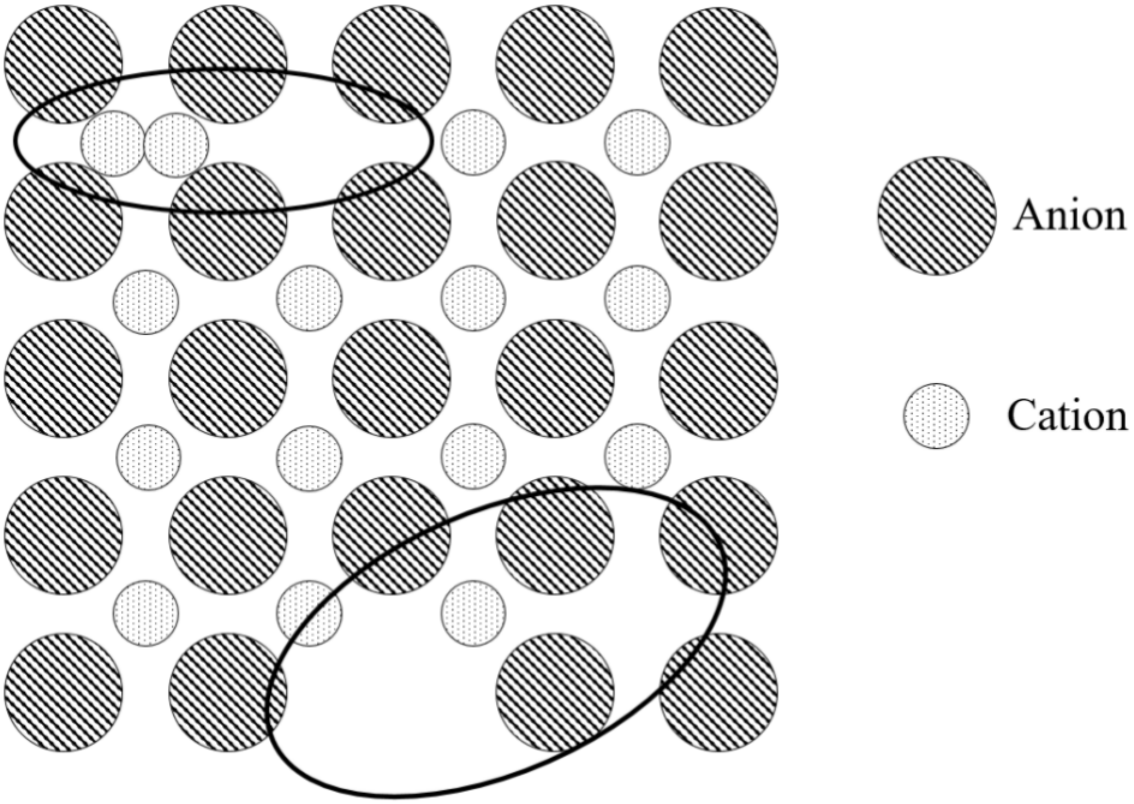
f. Do you expect a larger temperature-dependence of conductivity in the doped or the undoped GaAsN, at moderate temperatures? (3 points)

4.3: Exam 3

Problem 1 (23 POINTS)

a) In the 2 crystalline solids shown below, there are circled SIX different point defects TOTAL. **Label** each defect with its name. (6 points)





You decide to buy a ring from a jewelry store down on Mass Ave. Drawing on your deep knowledge of materials science from 3.091, you decide that a platinum ring is definitely the way to go. Unfortunately, the jeweler graduated from That School Down the

Street; you are upset by their claim that the ring is “defect-free crystalline platinum.” Let’s prove them wrong!

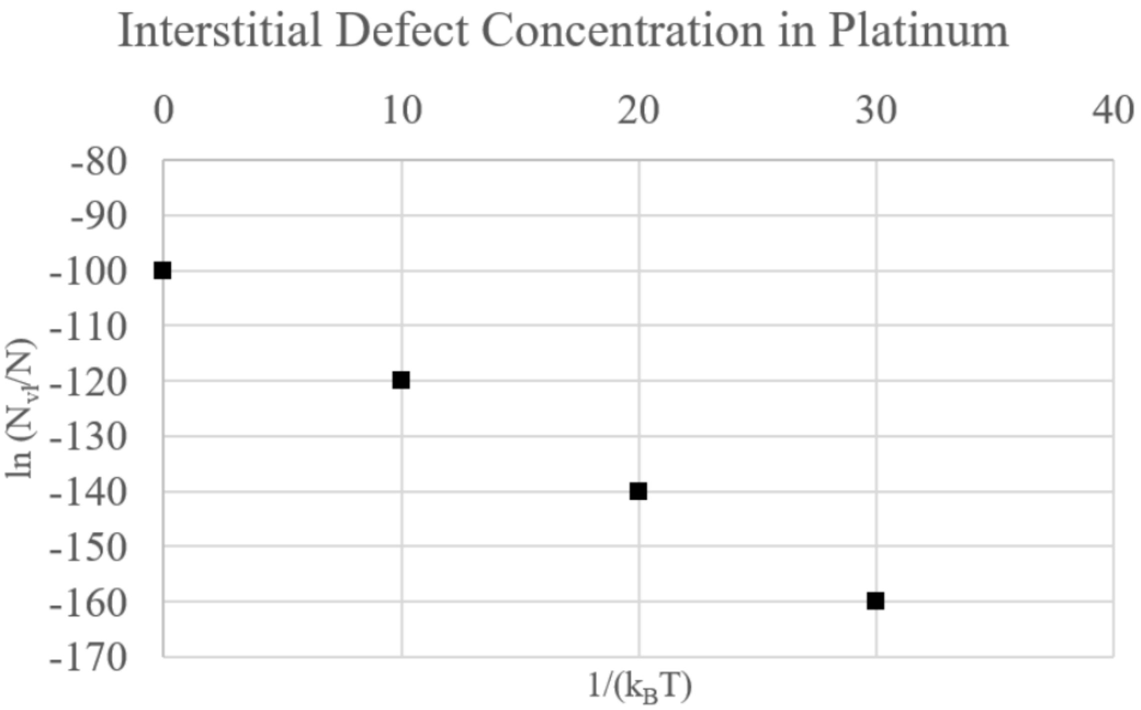
b) First, you weigh the ring: it’s exactly 2 grams. How many platinum atoms are in the ring? (2 points)

c) How many atomic sites are in the ring, N_{Pt}? (2 points)

d) It's a little chilly in the shop: $11^{\circ}C(284\ K)$. Assuming the ring is in thermal equilibrium, calculate the total number of vacancies, N_v, that you would expect at the current temperature. The constant, A, has a value of 1.11. Assume the vacancy formation energy for Pt is $0.96 eV$. (4 points)

e) The jeweler is stressed out by your frantic calculations and eager to prove they’re not cheating you; they hastily point out that the atoms that came from those vacancies are probably sitting in interstitial sites in the lattice. You quickly pull up a paper that has measured interstitial concentration in Pt.

Note: the units of interstitial defect concentration are mol/L.



i) Estimate the formation energy (in J) of an interstitial defect from the plot. How does this compare to the vacancy formation energy in Pt, which was given above as $0.96 eV$? *Hint*: assume that interstitial defect concentration follows an Arrhenius relationship. (5 points)

ii) Could the jeweler be right, based on the activation energies for interstitial formation and vacancy formation? In other words, could the atoms from the vacant sites have become interstitial defects? Explain your reasoning in one sentence. (4 points)

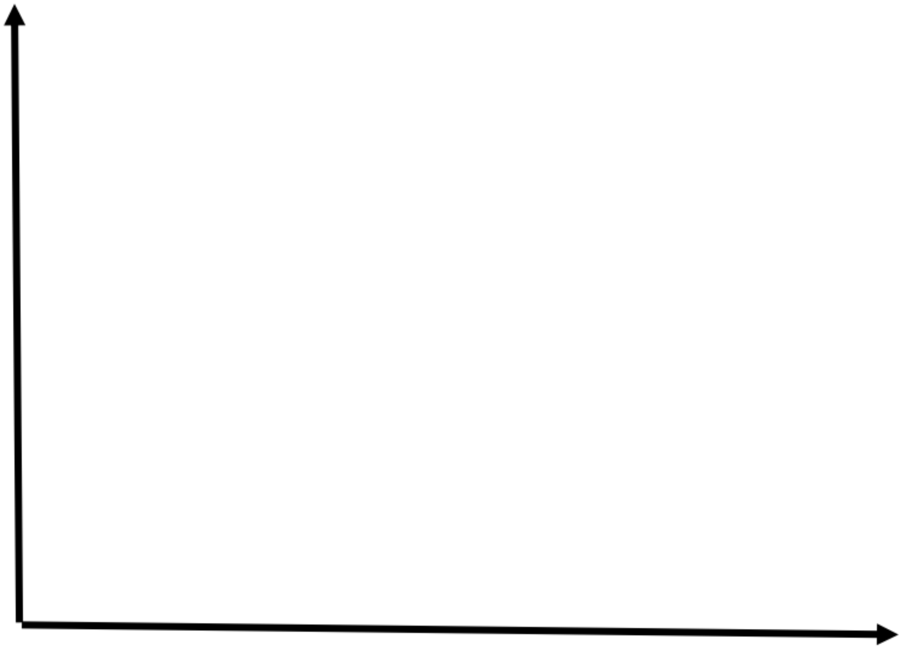
Problem 2 (20 POINTS)

a) Sketch the following on the axes provided:

i) A cooling curve (molar volume vs. temperature) for amorphous SiO_2 (3 points)

ii) A cooling curve (molar volume vs. temperature) for crystalline SiO_2 (3 points)

Please label curves i and ii.



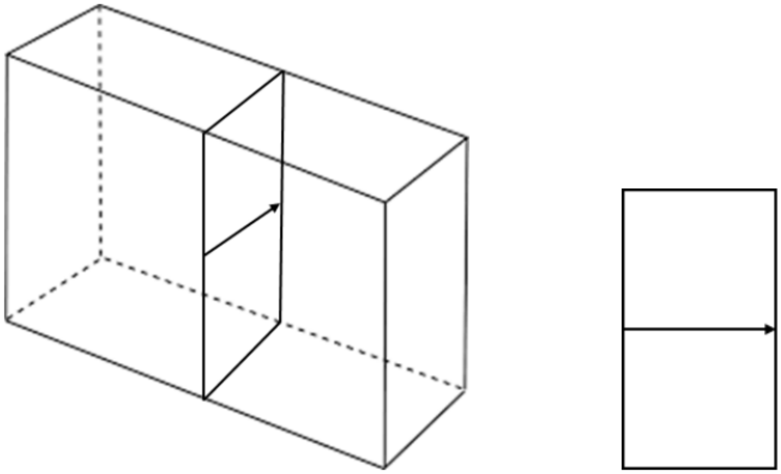
b) On your plot above, label:

i) the melting point(s) (2 points)

ii) the glass transition temperature(s) (2 points)

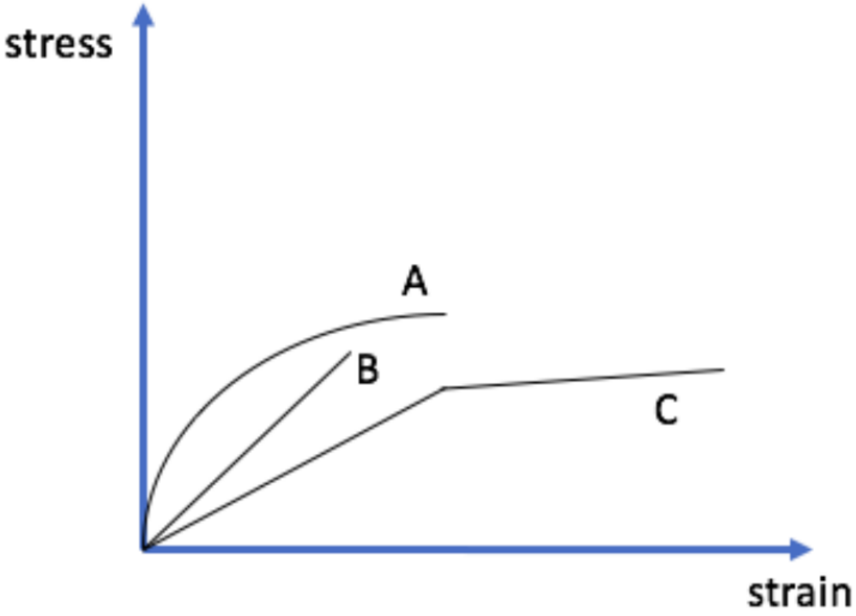
c) List **TWO** ways you could change the glass transition temperature. (4 points)

d) Tempered glass exhibits increased strength compared to regular glass. Consider a slice taken across a sheet of tempered glass:



With reference to your plot in a), explain how the molar volume changes across the slice. (4 points)

e) Which of the following stress-strain curves could correspond to the tempered glass above? Circle the letter corresponding to your chosen curve. (2 points)



Problem 3 (20 POINTS)

In GB8, we explored the impact of ocean acidification on pteropods by considering the dissolution of $\mathrm{CaCO_3}$ in a citric acid solution. Now, we'll consider a similar process, but using hydrofluoric acid instead. Hydrofluoric acid, HF, has a higher acid dissociation constant than citric acid.

a) Write out the acid dissociation reaction for hydrofluoric acid. Label the conjugate acid/base pairs. (5 points)

b) What is the concentration (M) of a solution containing $0.05\ \mathrm{g}$ of HF in $0.1\ \mathrm{L H_2O}$? (3 points)

c) If the acid dissociation constant for hydrofluoric acid is $\mathrm{K_a} = 7.2 \times 10^{-4}$, what is the pH of the solution from part b)? (4 points)

e) If we had given you hydrofluoric acid $\left(\mathrm{K_a} = 7.2 \times 10^{-4}\right)$ rather than citric acid $\left(\mathrm{K_a} = 1.8 \times 10^{-5}\right)$ in the goodie bag, would you expect the shells to have dissolved faster or slower? Briefly explain why. (4 points)

f) Explain **what** would happen to the pH of the hydrofluoric acid solution if it were to sit in a $\mathrm{CO_2}$ environment for a few hours, and **why**. (4 points)

Problem 4 (21 POINTS)

To compensate for some of the oxygen consumed by burning the candle on one of your many Friday night dates, you decide to run a reaction that produces $\mathrm{O_2}$ gas **as fast as possible**. You recall two options:

$$(p) 2\mathrm{NO_2} \rightarrow 2\mathrm{NO(g)} + \mathrm{O_2(\,g)} \quad \text{OR} \quad (q) \mathrm{O_3} + \mathrm{Cl} \rightarrow \mathrm{ClO(g)} + \mathrm{O_2(\,g)}$$

You are able to find some information about the reaction (p) : its **rate law** is

$$\text{rate } = \mathrm{k}\left[\mathrm{NO_2}\right]$$

(Note: reactions p and q have the same numerical value for their reaction constants)

Trial #	$[\mathrm{O_3}]$ M	$[\mathrm{Cl}]$ M	rate M/s
1	0.07	0.25	10
2	0.14	0.25	20
3	0.07	0.5	20

a) Use the experimental data in the table above about reaction (q) to determine its:

i. Rate law (5 points)

ii. Overall order (2 points)

iii. Value of k, the reaction constant (5 points)

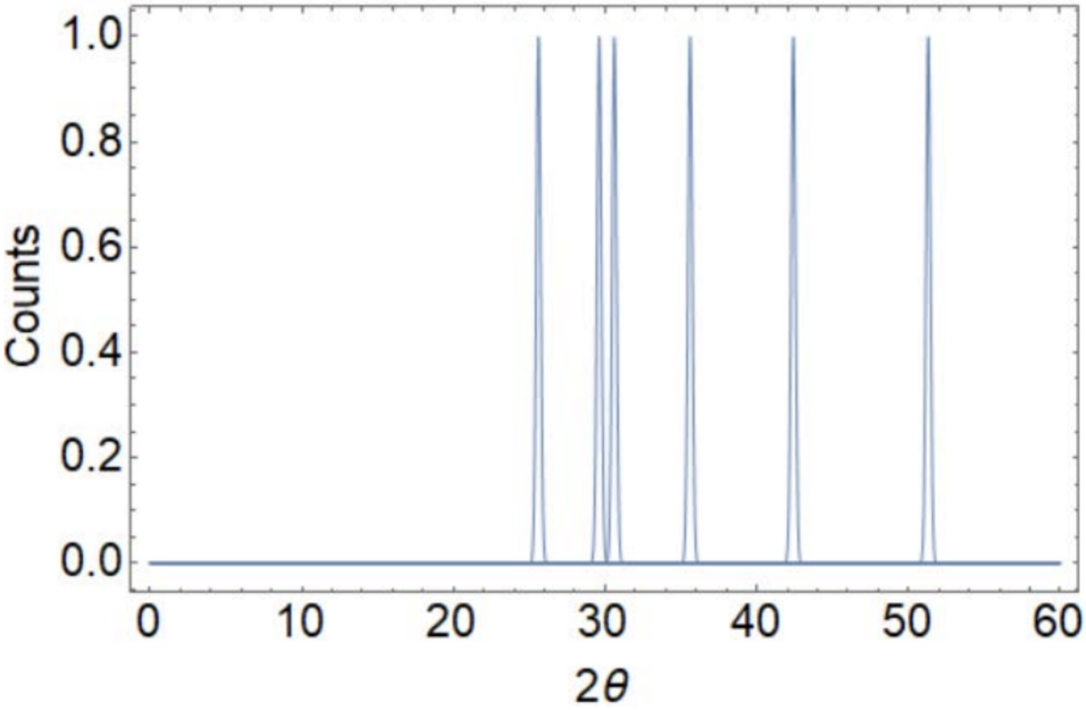
b) Plot the linear version of the integrated rate law that describes $2\mathrm{NO}_2 \rightarrow 2\mathrm{NO(g)} + \mathrm{O}_2(\mathrm{~g})$. Label the axes, y-intercept, and slope. (5 points)

c) If you have 2 mols of $\mathrm{NO}_2, 1\ \mathrm{molofCl}$, and $1\ \mathrm{mol}$ of O_3 available (but you can only run one reaction), which reaction would you choose to produce oxygen the fastest? Justify your answer with ONE sentence. (4 points)

Problem 5 (16 POINTS)

Your research supervisor wants you to characterize two pure elemental powders she found in the back of the lab. Unfortunately, time on the XRD machine is very limited; to save time, you mix **BOTH POWDERS** together and perform XRD on the mixture.

You get the following plot of intensity (counts) vs. 2θ (degrees):



From the plot, you have the following data to help identify the samples. You may find it helpful to add columns to assist your thinking (ungraded).

2θ (degrees)	$(\sin\theta)^2$
25.6	0.049
29.6	0.065
30.7	0.070
35.6	0.093
42.4	0.131
51.3	0.187

a) Use selection rules to determine the crystal structures of the samples (8 points) Note: Assume sample 1 corresponds to the element with the lowest 2-theta peak.

Sample 1: ______________________________ Sample 2: ______________________________

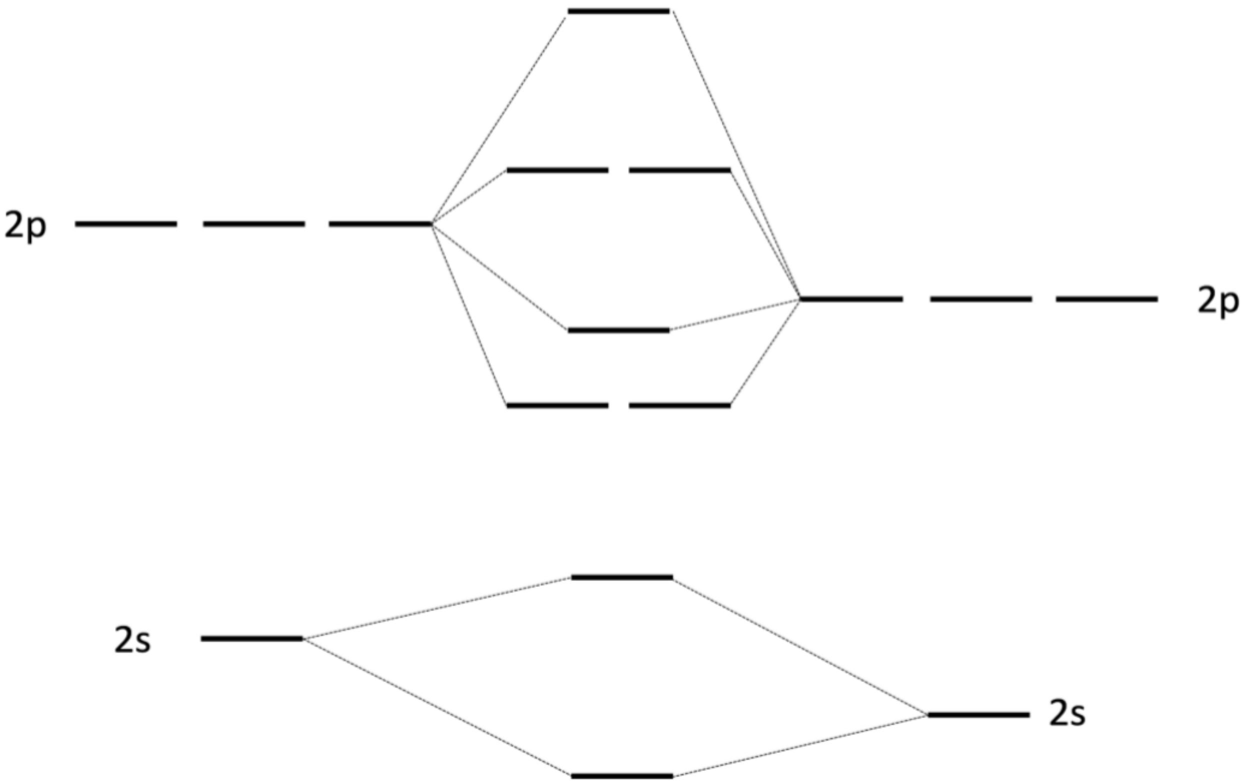
b) What are the lattice constants of the samples? Copper k-alpha radiation (wavelength=1.54 Angstroms) was used. Show your thinking! (8 points)

Sample 1: ______________________________ Sample 2: ______________________________

4.4: Final Exam

Problem 1 (21 POINTS)

a) i. Fill in atomic and Molecular orbitals for the MO diagram of Carbon Monoxide (CO) below (3 pts):



ii. Label the molecular orbitals as sigma or pi (2 pts)

iii. Label the molecular orbitals as bonding or antibonding (2 pts)

iv. What is the bond order of CO? (2 pts)

b) Methylamine $(\mathrm{H_3C-NH_2})$ is an organic compound that's used to synthesize lots of chemicals, ranging from photographic developers to cold medicine.

i. Draw a methylamine molecule, showing its 3D VSEPR geometry. Include any lone pairs. (3 pts)

ii. What is the shape predicted by VSEPR of the atoms around (2 pts) ...

C:_____________________
N:____________________

iii. Consider the two bond angles in methylamine below. Which is larger? (1 pt)

1) $\mathrm{H-C-N}$
2) $\mathrm{C-N-H}$

_________ Smaller _________ Larger

c) If we add an H^+ ion to methylamine, we get methylammonium $\left(\mathrm{CH_3NH_3^+}\right)$, an organic ion often used in perovskite solar cells.

i. Draw a methylammonium ion using its VSEPR geometry. Include any lone pairs. (2 pt)

ii. Label the formal charges on each atom on your drawing above (2 pts)

iii. Does methylammonium have any stable resonance structures? If so, draw one. If not, why not? (2 pts)

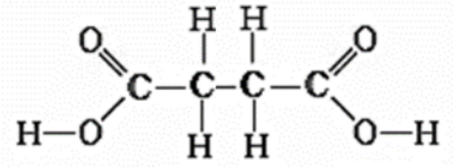
Problem 2 (17 POINTS)

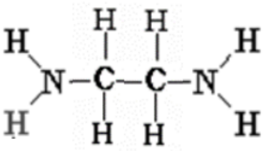
You are a new scientist at a fancy spacesuit company. To test your polymer knowledge, your boss has asked you to design a material for their newest spacesuit. Unfortunately, in spite of the critical nature of the spacesuit, the chemistry lab seems to be horribly underfunded, and you have only two polymers to choose from.

a) Polymer 1 is made from the monomer tetrafluoroethylene (C_2F_4). Draw the Lewis Structure for a single tetrafluoroethylene molecule. What is the hybridization of one of the carbon atoms? (4 pts)

b) Draw the repeat unit for a polymer made from polymerization of this monomer. What polymerization technique should you use? (3 pts)

c) Polymer 2 is a polymer made from the following monomers. Draw the corresponding polymer. What polymerization technique should you use? (5 pts)





d) The space suits must deflect water, i.e. the polymer shouldn't interact with H_2O. Which polymer should you choose? (Polymer 1 or 2) Give a one-sentence explanation making sure to include intermolecular forces. (3pts)

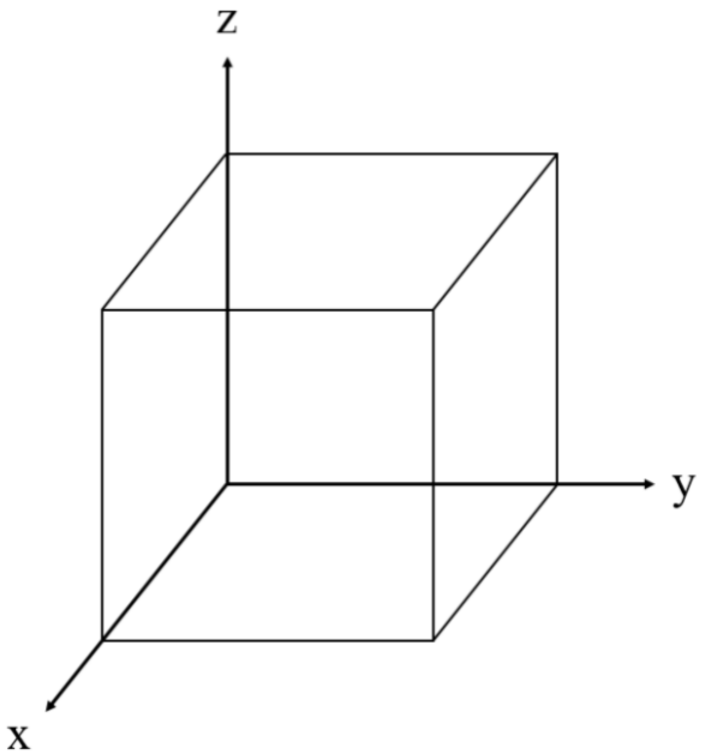
e) Your boss is worried that your space suit will tear too easily. How could you modify your polymer to improve its durability? (2 pts)

Problem 3 (21 POINTS)

3. Iron (Fe), which is an important component of many parts on the Apollo 3.091, forms a BCC structure at room temperature.

a) Draw the (110) plane of Fe on the graph provided below. (3 pts)

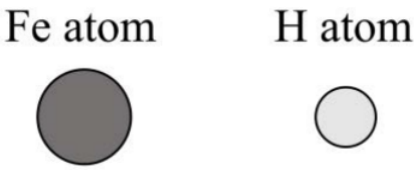
Modified image of astronaut working. Original image is in the public domain (source: NASA).



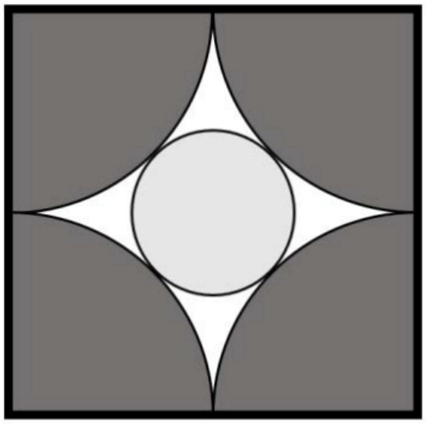
b) What is the **close-packed direction** of Fe? Indicate where this is in relation to the (110) plane drawn above by **DRAWING** it on the graph provided in part (a) and **LABEL** the direction with the correct crystallographic nomenclature, $< hkl >$. (5 pts)

c) It is difficult to get 100% pure iron because there are often some impurity elements in the material. One common impurity element is hydrogen, which is present as an interstitial element in iron.

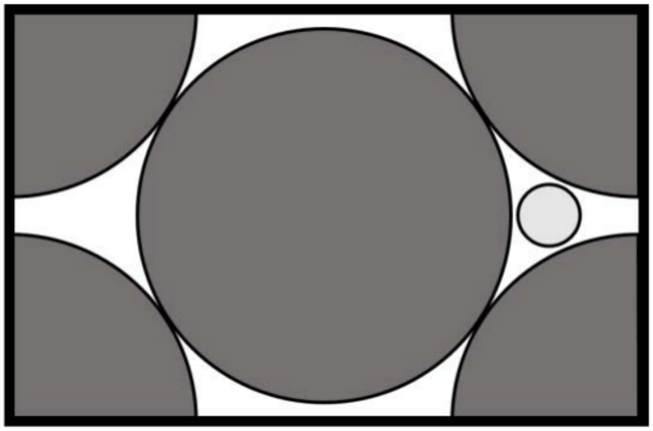
CIRCLE the image below that accurately shows an interstitial hydrogen atom in the (110) plane of iron. (3 pts)



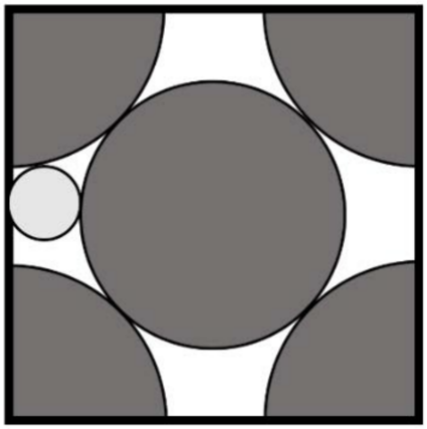
**Images are not to scale.*



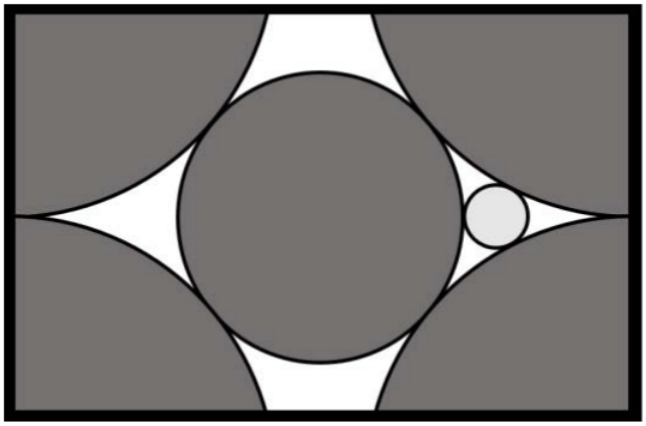
A



B



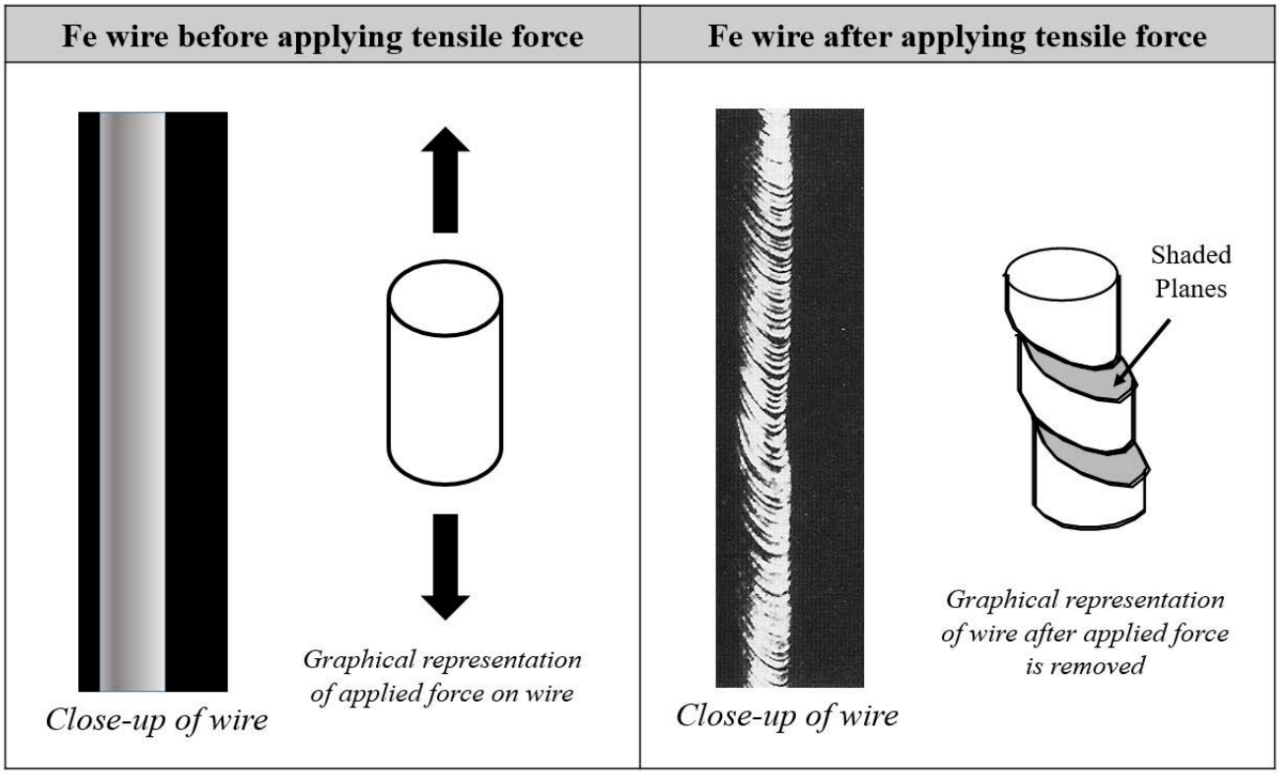
C



D

d) Iron has a radius of 1.24Å. Calculate the density of Fe in $\mathrm{g/cm^3}$? (1 atomic mass unit $= 1.66 \times 10^{-24}$ grams, $1\text{Å} = 10^{-8}\ \mathrm{cm}$) (6pts)

You decide to run a tensile test on an Fe wire. After the experiment, you look at the part of the sample that has deformed and see the following:



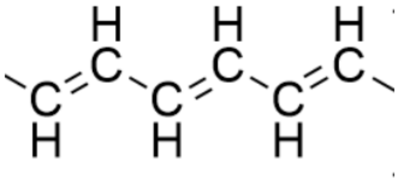
e) In ONE sentence, explain what is special about the **shaded planes** in the diagram above. (4 pts)

Problem 4 (20 POINTS)

We've talked a lot about semiconductors, but we haven't mentioned one interesting class of semiconductors - organic semiconductors. Professor Grossman will be using organic LEDs for horticultural lighting on the spaceship, so it's important to understand them!

LEDs can be used to grow plants in space!

a) One example of an organic semiconductor is polyethyne (PE). A portion of its structure is shown below. Circle the repeating unit. (2 pts)



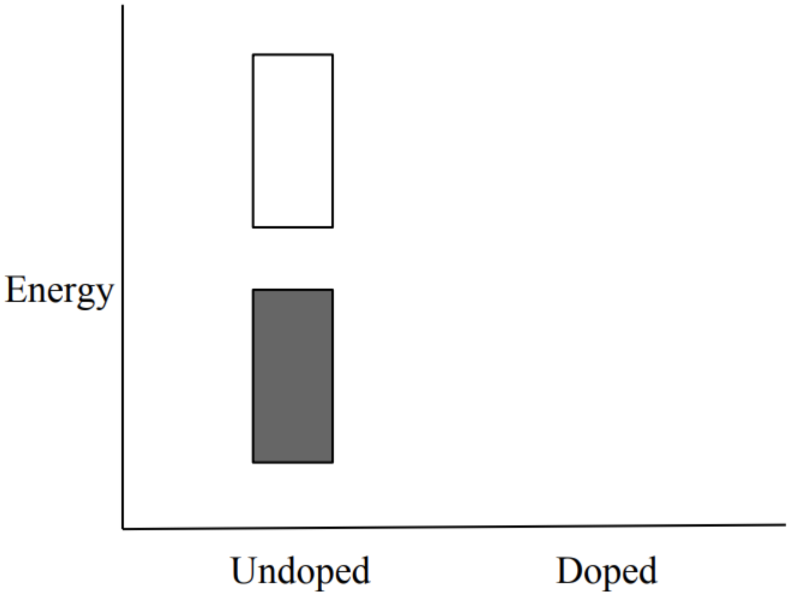
b) Polyethyne is a semiconductor because its resonance structures allow electrons to move. One is structure shown above; draw one repeating unit of another polyethyne resonance structure. (3pts)

c) To enhance conductivity to useful levels, polyethyne needs to be doped — but the dopants behave differently from inorganic semiconductors. When doping with bromine, two electrons are removed from the polymer per bromine molecule:

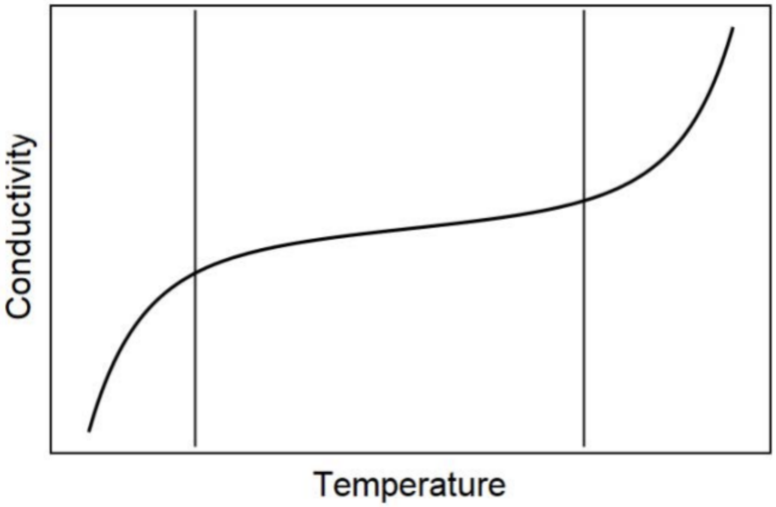
$$\mathrm{PE} + \mathrm{Br}_2 \rightarrow (\mathrm{PE})^{2+} + 2\mathrm{Br}^-$$

In this case, is bromine acting as a p-type dopant or n-type? Briefly explain your answer. (Conduction occurs through the polymer chains; the bromine ions do not contribute significantly, and for this question you can assume that they are present only to keep total charge neutral) $(3\mathrm{pts})$

d) The band diagram for neutral polyethyne is shown below. Sketch the band diagram for Br_2- doped polyethyne on the same axes. (4 pts)



e) Certain organic semiconductors follow the same trend of temperature vs. conductivity as inorganic semiconductors. A schematic is shown below.

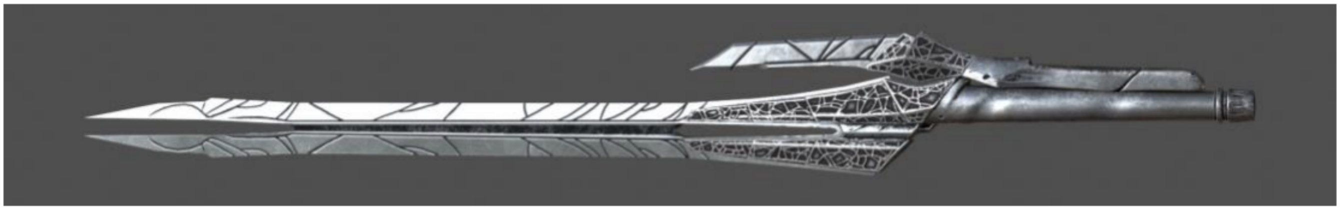


i. What causes the near-zero slope of temperature dependence in the intermediate temperature regime? (4 pts)

ii. Theoretical studies have shown that polyethyne could exhibit near-zero temperature dependence from 100 K up to about 450 K; however, the glass transition temperature of your PE is near 400 K. What is one thing you could do to increase the glass transition temperature of your PE semiconductor so that it can be used over a wider temperature range? (4 pts)

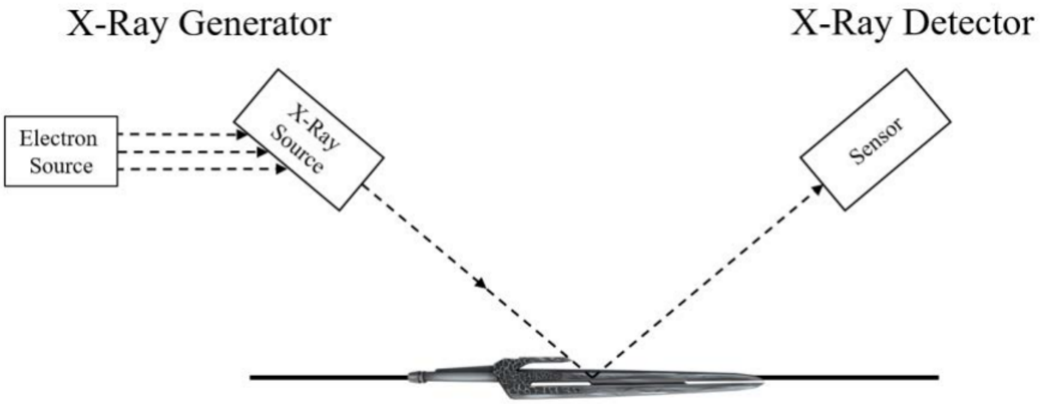
Problem 5 (21 POINTS)

An alien sword of a PURE METAL has fallen from space onto MIT's campus! As an expert materials scientist, you're called in to investigate its properties.



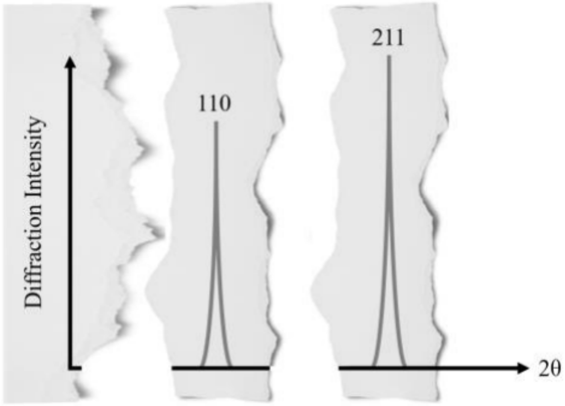
An alien sword! Who knows what it's made of… oh wait, we can find out using x-rays. :)

a) First thing's first - let's figure out what crystal structure the material in this sword has! You stick the sword into your **x-ray diffraction (XRD)** machine and wait for some results.



(Note: It's a little different in real life.)

Unfortunately, the alien sword releases a blast of ~alien energy~ during the experiment! Not only does it damage your XRD machine, but your results get all ripped up. You manage to salvage some **PIECES** of the XRD graph, shown below:



Based on the salvaged XRD graph, what are ALL of the **possible cubic crystal structures** the sword could have? (4 pts)

b) You still don't know what the sword is made of! Luckily, the **x-ray generator** part of your million-dollar XRD machine hasn't been damaged. Undeterred, you decide to make the sword the **source** of x-rays by accelerating electrons at it to generate an **x-ray spectrum**.

Draw an x-ray spectrum. Label the horizontal and vertical axes, the Brehmsstrahlung radiation, $\mathrm{K}_\alpha, \mathrm{K}_\beta, \mathrm{L}_\alpha$, and L_β. (6 pts)

c) You can figure out what material your sword is by analyzing its x-ray spectrum!

In the resultant x-ray emission spectrum, you observe a L_α peak at a wavelength $\lambda = 2.383 \times 10^{-9}$ meters. What is the metal the sword is made of? Assume the screening factor, sigma (σ), for $\mathrm{L}\alpha$ radiation is 7.4.

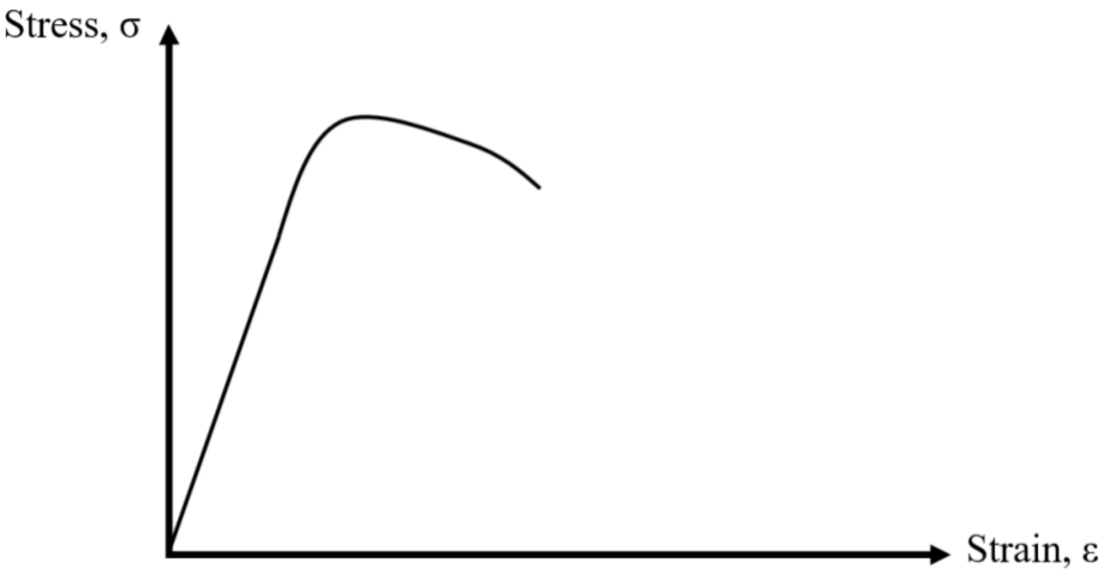
Use the equation $E = 13.6 * (Z-\sigma)^2 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$, where σ is the screening factor. (3 pts)

d) Unfortunately, you got so absorbed in your work that you don't notice shooting accelerated electrons at the sword has heated it up! The sword has been at 600K for the 3 hours you spent analyzing your data. In other words, the sword has been **ANNEALED**.

In ONE sentence, explain how this might change at least two mechanical properties of the sword. (4 pts)

e) The graph below has a stress-strain curve for the sword BEFORE your experiments.

i. Draw the stress-strain curve for the sword AFTER your experiments, i.e. after it was **ANNEALED** and has been returned to room temperature. (4 pts)



Problem 6 (19 POINTS)

You're working in Professor Grossman's lab and have been given the following solutions:

Solution 1: 0.0334grams of $\mathrm{CaF_2}$ in 2 L of water
Solution 2: 0.0334grams of $\mathrm{CaF_2}$ in 3 L of water
Solution 3: Solution $2+1$ L of $5^*10^{-5}\mathrm{MPbF_2}$

a) Assuming the ionic solid completely dissolves to create a saturated aqueous solution, what is the $\mathrm{K_{sp}}$ of $\mathrm{CaF_2}$ in Solution 1 ? (3 pts)

b) The concentration of Solution 2 is $1.43^*10^{-4}\mathrm{M}$, and the $\mathrm{K_{sp}}$ of $\mathrm{PbF_2}$ is 3.7^*10^{-8}.

i. What are the concentrations of each ion in Solution 3? (4 pts)

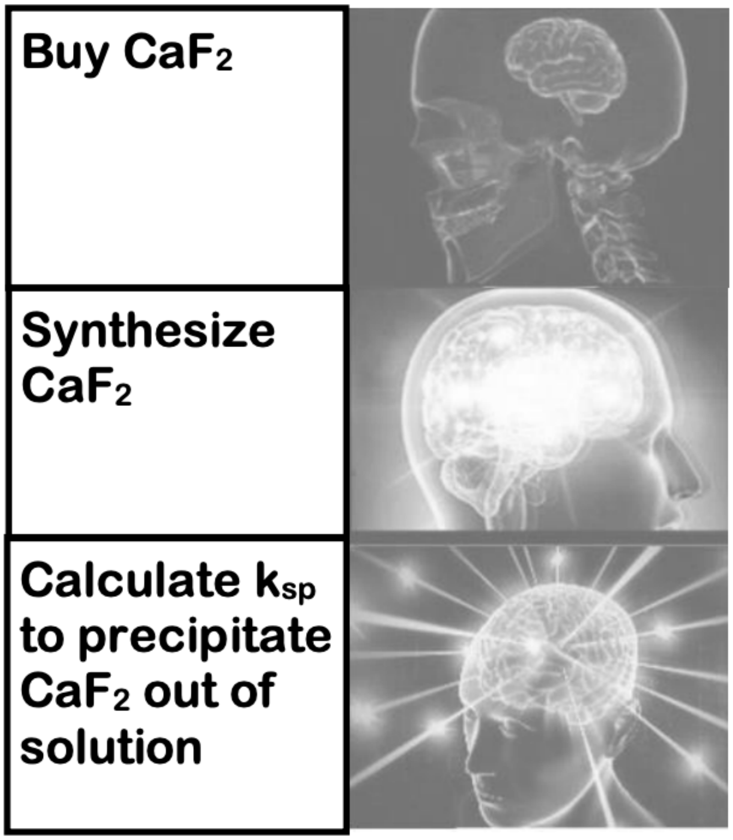
ii. Write out the $\mathrm{K_{sp}}$ expressions for both $\mathrm{CaF_2}$ and $\mathrm{PbF_2}$. (2 pts)

iii. Use the expressions from b)ii. to show why there wouldn't be any precipitates. (4 pts)

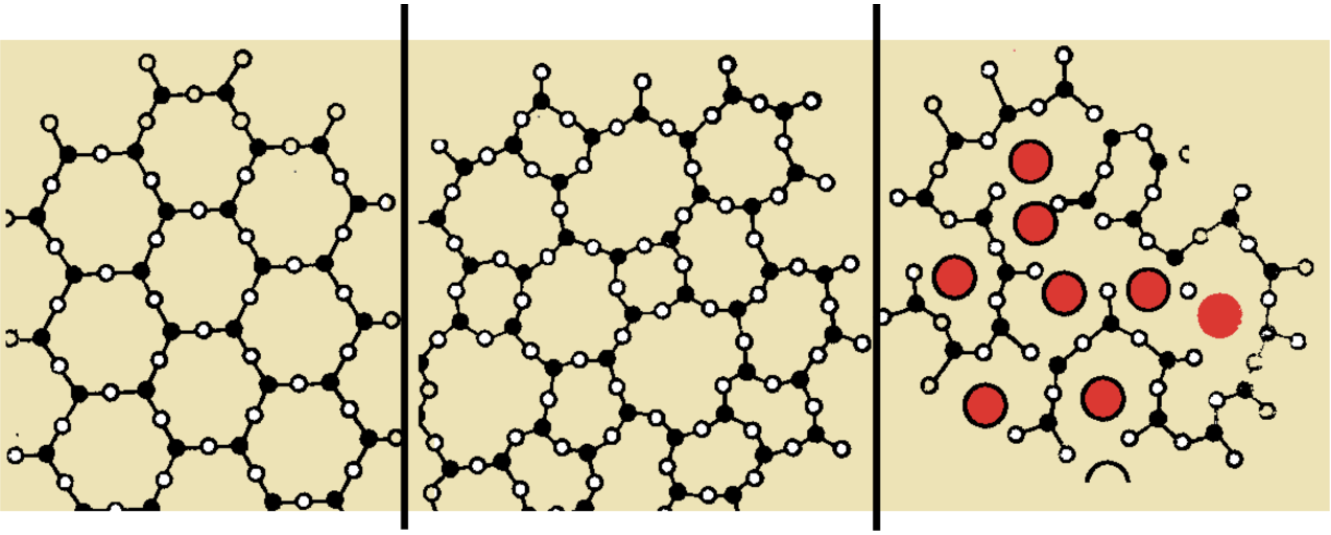
c) Now, consider Solution 2 alone. You want to precipitate the $\mathrm{CaF_2}$ out of solution using one of the following chemicals in your lab: $\mathrm{PbI_2}$, CaS, and $\mathrm{MgF_2}$.

i. Name one chemical you could use to precipitate $\mathrm{CaF_2}$. (there may be multiple correct answers) (2 pts)

ii. How many moles of the chemical that you chose for part c) i. are necessary to precipitate the original $4.28 * 10^{-4}$ moles of $\mathrm{CaF_2}$ out of the solution? (4 pts)



PROBLEM 7 (25 POINTS)



i. ii. iii.

Above are sketches (from three different textbooks) of three samples of silicon dioxide. One of the samples contains Na_2O as a network modifier.

a) Which sample contains Na_2O? (2 pts)

b) Which sample is crystalline quartz? (2 pts)

c) Plot the molar volume vs temperature curves of the three materials on the same plot. Be sure to label your axes. (6 pts)

d) Na_2O and CaO are both network modifiers. Network modifiers are added when the glass is in a liquid state. You know that the rate law for the dissolution of CaO in liquid silica is rate $_{CaO} = 4[CaO]$.

Write a similar rate law for the dissolution of Na_2O in liquid silica and use it to fill in the following table. The Na_2O reaction is **second order in terms of** Na_2O and **independent of the silica concentration**. Please determine **the value of the rate constant**, and write the units for $[Na_2O]$ and rate.

Fill in the units row and find the rate of trial 2 (8pts):

	$[Na_2O]$	rate
Unit		
Trial 1	2×10^{-5}	1.2×10^{-9}
Trial 2	4×10^{-5}	

Rate law: $\text{rate}_{Na2O} =$ ________________________

e) What are the units of the rate constant in:

i. the CaO rate law (2pts)

ii. the Na_2O rate law (2pts)

f) Thinking about the size of Na vs. Ca ions, explain in ONE sentence why it makes sense that the sodium oxide reaction occurs at a faster rate than the calcium oxide reaction. (3 pts)

Problem 8 (24 POINTS)

You're interested in understanding the diffusion of hydrogen gas through a palladium (Pd) filter to make sure the concentration of H doesn't get too high in the living quarters of the rocket.

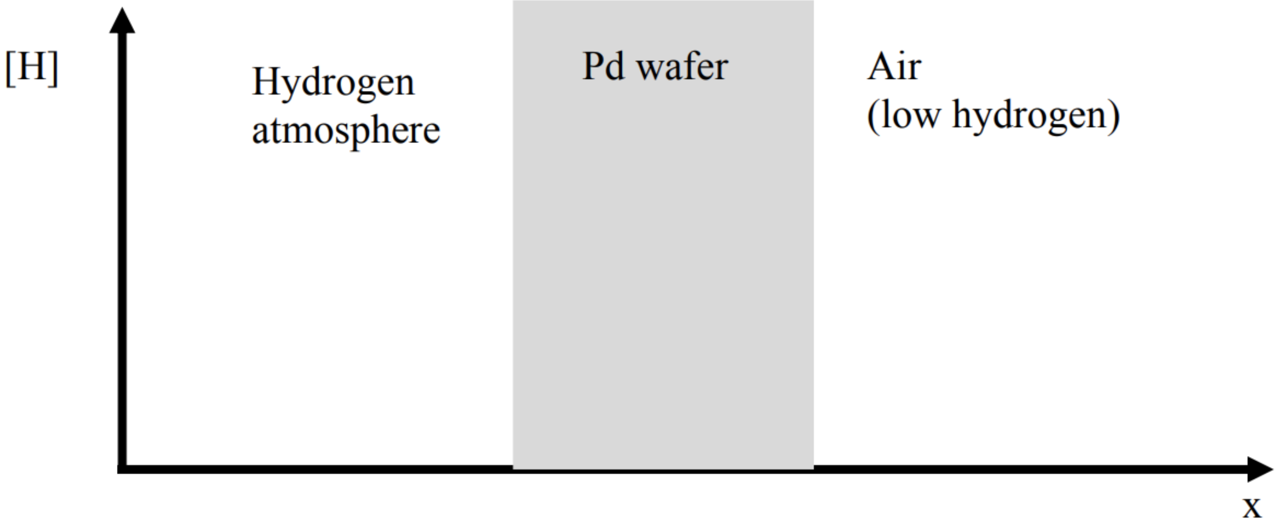
Modified astronaut sleeping. Original image is in the public domain (source: NASA).

a) Calculate the original number of Pd vacancies in a $1\,\mathrm{mol}$ sample of Pd, assuming a vacancy activation energy $= 0.7\mathrm{eV}$, $\mathrm{T} = 300\ \mathrm{K}$, and the entropic constant $\mathrm{A} = 1 (5\mathrm{pts})$

b) Does hydrogen diffuse through the palladium lattice through **interstitial sites** or through **substitutional sites**? Use Hume-Rothery rules to justify your answer in ONE sentence. (3 pts)

c) The diffusion coefficient of hydrogen through palladium at $300\ \mathrm{K}$ is $3.2 \times 10^{-10}\ \mathrm{m}^2/\mathrm{s}$. You expose one side of the wafer to a hydrogen atmosphere with concentration $0.0446\mathrm{M}$and the other to air with a hydrogen concentration of $2.23 \times 10^{-8}\mathrm{M}$. What is the flux of hydrogen atoms through this Pd crystal at $300\ \mathrm{K}$? The Pd wafer is $2.7\ \mathrm{mm}$ thick. Hint: 1 liter is $0.001\ \mathrm{m}^3$. (5 pts)

d) Draw the concentration profile of hydrogen atoms across this crystal at $300\mathrm{K}$. (3 pts)



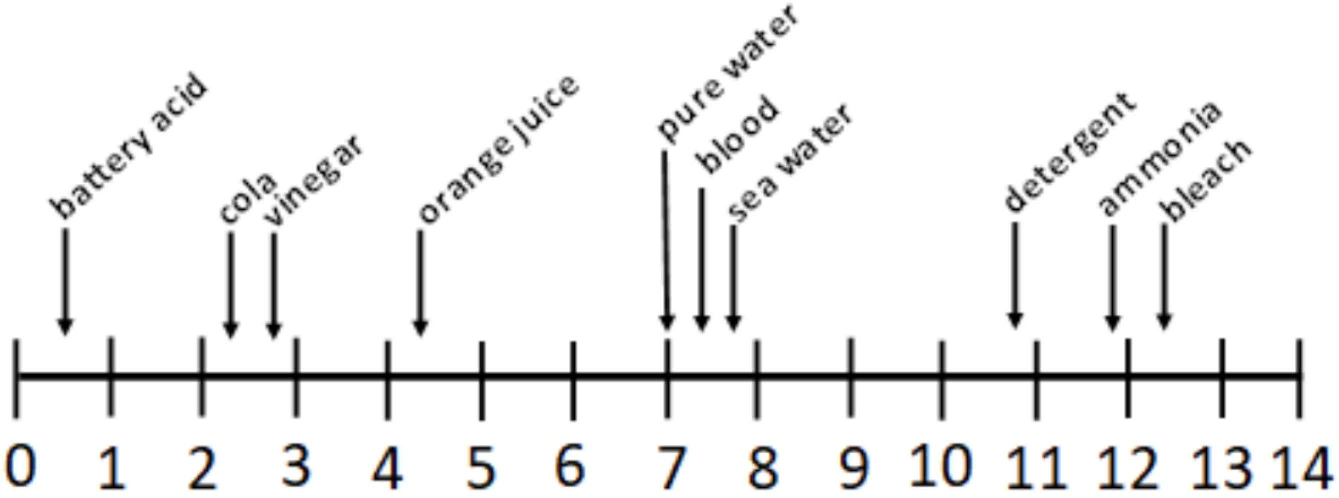
e) At 400 K, the diffusion coefficient is $\mathrm{D}(400\ \mathrm{K}) = 3.51 \times 10^{-5}\ \mathrm{m}^2/\mathrm{s}$.

i. Assume that diffusion follows the Arrhenius law: $\mathrm{D} = \mathrm{D}_0 * \exp(-\mathrm{E_a}/(\mathrm{k_B T}))$. What is the activation energy $\mathrm{E_a}$ of the diffusion of H through Pd? (4 pts)

ii. At what temperature should we hold the Pd such that the flux of hydrogen atoms through the Pd filter is $1.38 \times 10^{-4}\ \mathrm{mol}/\mathrm{m}^2\ \mathrm{s}$? Hint: use the information from part c. or part e. to determine D_0.(4 pts)

Problem 9 (19 POINTS)

The following diagram shows the pH of some common substances:



a) From the scale above, name:

- i. The strongest acid (1 pt)
- ii. The weakest base (1 pt)
- iii. A neutral substance (1 pt)

The acidic ingredient in vinegar is acetic acid $(\mathrm{CH_3COOH})$. You bought a bottle of vinegar and measured the pH of your solution is around 2.4, and the molar concentration of acetic acid in vinegar is around $0.85\mathrm{M}$.

b) Write the acid reaction of acetic acid with water. Label the conjugate acid and base pairs. (4 pts)

c) What is the hydronium ion $\left(\mathrm{H_3O^+}\right)$ concentration of our $0.85\mathrm{M}$ solution of acetic acid? (3 pts)

d) Based on the information given and your answer to parts b) and c), determine the value of the acid ionization constant, $\mathrm{K_a}$, for acetic acid. (3 pts)

e) What is the hydronium ion $\left(\mathrm{H_3O^+}\right)$ concentration of a $0.010\mathrm{M}$ solution of acetic acid? (3 pts)

f) What is the pH of a $0.010\mathrm{M}$ solution of acetic acid? (3 pts)

Problem 10 (13 POINTS)

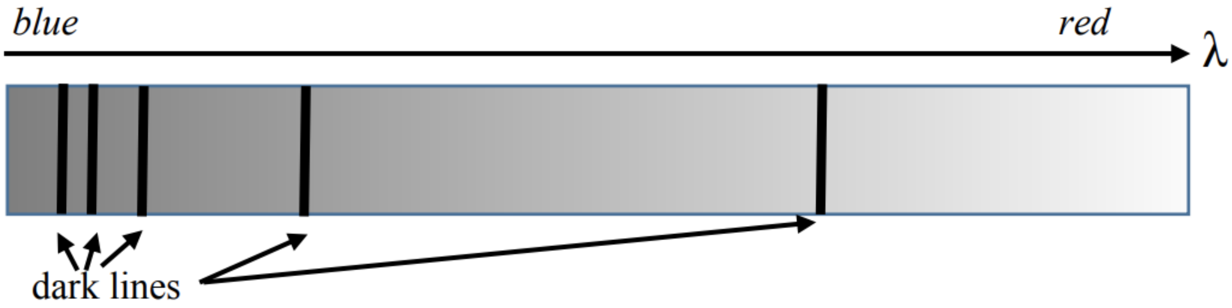
As the universe cooled after the big bang, ionized hydrogen $(\mathrm{H+})$ combined with free electrons $(\mathrm{e-})$ to form hydrogen gas.

a) Write a balanced equation for this reaction. (2 pts)

b) When $\mathrm{H+}$ and $\mathrm{e-}$ combine, a photon is emitted as the electron relaxes to the ground state, essentially reversing the process of ionization from the ground state.

- i. What is the energy of this electronic transition? (2 pts)
- ii. What is the wavelength of the photon that is emitted? (3 pts)

c) We can learn about the elemental composition of stars by observing which wavelengths are absorbed by the star.



i. Explain in ONE sentence why absorption spectra have dark lines (as shown in the figure above). [Note – to save money at CopyTech we printed this in greyscale, but it was originally a spectrum going from blue to red.] (3pts)

ii. Explain in ONE sentence why the shorter-wavelength dark lines are closer together than the longer-wavelength dark lines (3pts)

Modified image of astronaut waving © original source unknown. All rights reserved. This content is excluded from our Creative Commons license. For information, see https://ocw.mit.edu/fairuse.

CHAPTER OVERVIEW

5: CHEM ATLASes

5.1: CHEM ATLAS_1
5.2: CHEM ATLAS_2
5.3: CHEM ATLAS_3

5.1: CHEM ATLAS_1

What is This?

The purpose of this document is to serve as a guide and resource that gives you a quick overview of each lecture. For each lecture, there is a summary of the main topics covered, the Why This Matters moment, and the new Why This Employs section, plus a few example problems. These handouts will be given by "Unit," which is the content that goes into each exam. There's also a Concept Map at the beginning of each Unit, to show how the various materials are connected together.

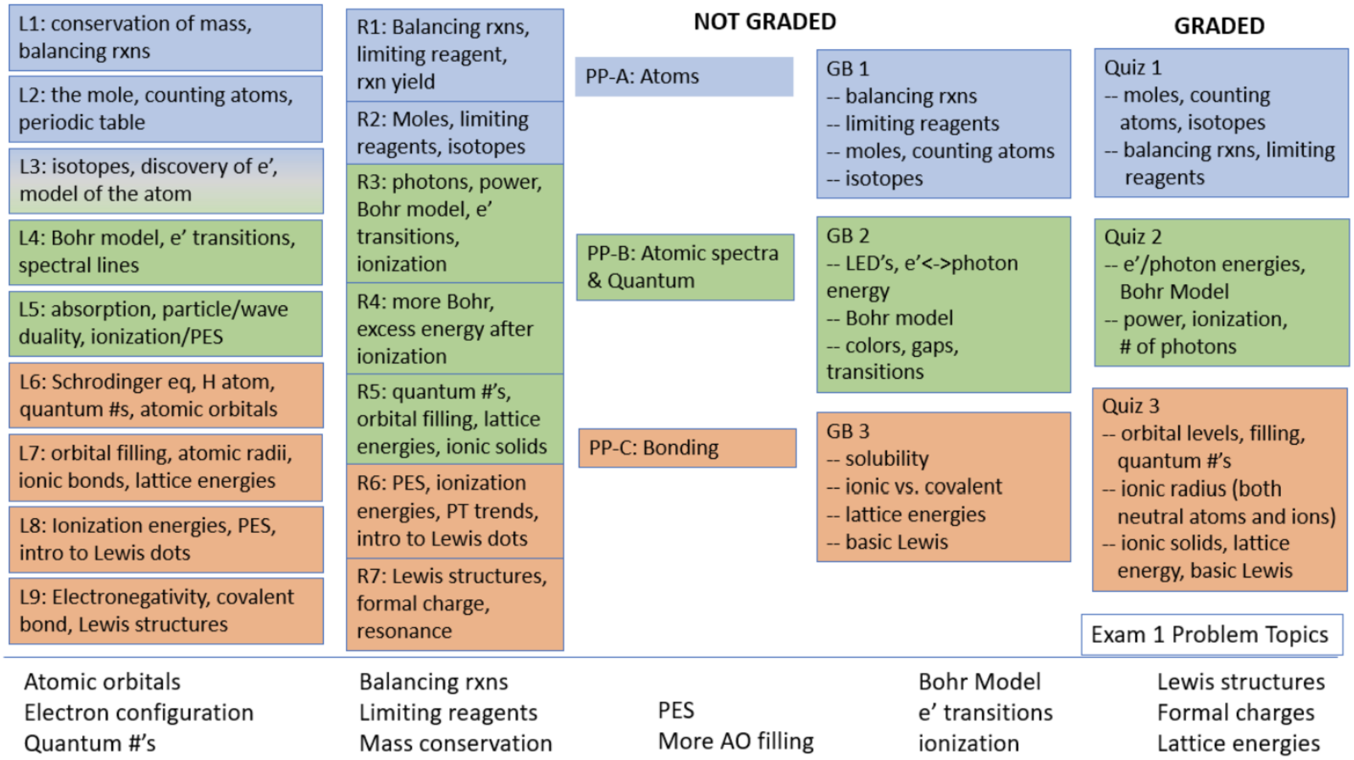
So why did we make this? We hope it's useful to get a good snapshot of any given lecture. Whether you couldn't make it to a lecture or you couldn't stop thinking about a lecture, this is a way to quickly get a sense of the content. It also gives me a chance to provide additional details that I may not have time for in the Why This Matters example, and also it lets me try out the Why This Employs section, which I certainly will not have time to discuss much in the lecture. Hopefully you find it useful, and as with anything else in this class, any and all feedback is most welcome!

One point about these lecture summaries. Please note that the lecture summaries are not meant to be a substitute for lecture notes. If you were to only read these summaries and not go to lecture, yes you'd get a good sense of the lecture from a very high level view, but no, you wouldn't get enough out of it for it to be your only resource to learn the material!

How This Connects: Unit 1, Lectures 1-9

In this class we have 36 lectures, 20 recitations, 9 goodie bags, and 12 problem sets, all tightly integrated and each one designed to contribute to your overall 3.091 learning experience. These different resources come together in the Celebrations of Learnings throughout the semester, including 9 quizzes, 3 midterms, and a final exam. For each unit, defined as the content that goes into a midterm, we have created a Concept Map to elucidate connections between the different class components so that you can see clearly the context of each.

Below is an image of the Exam 1 Concept Map. This demonstrates how each of the aspects of the course fit together: you have lots of resources! The Practice Problems, Recitations, Goodie Bags, and Lectures are ungraded resources to help you prepare for the quizzes and exams. All of the material listed on this concept map is fair game for Exam 1.



NOT GRADED

L1: conservation of mass, balancing rxns

L2: the mole, counting atoms, periodic table

L3: isotopes, discovery of e', model of the atom

L4: Bohr model, e' transitions, spectral lines

L5: absorption, particle/wave duality, ionization/PES

L6: Schrodinger eq, H atom, quantum #s, atomic orbitals

L7: orbital filling, atomic radii, ionic bonds, lattice energies

L8: Ionization energies, PES, intro to Lewis dots

L9: Electronegativity, covalent bond, Lewis structures

R1: Balancing rxns, limiting reagent, rxn yield

R2: Moles, limiting reagents, isotopes

R3: photons, power, Bohr model, e' transitions, ionization

R4: more Bohr, excess energy after ionization

R5: quantum #'s, orbital filling, lattice energies, ionic solids

R6: PES, ionization energies, PT trends, intro to Lewis dots

R7: Lewis structures, formal charge, resonance

PP-A: Atoms

PP-B: Atomic spectra & Quantum

PP-C: Bonding

GB 1
-- balancing rxns
-- limiting reagents
-- moles, counting atoms
-- isotopes

GB 2
-- LED's, e'<->photon energy
-- Bohr model
-- colors, gaps, transitions

GB 3
-- solubility
-- ionic vs. covalent
-- lattice energies
-- basic Lewis

GRADED

Quiz 1
-- moles, counting atoms, isotopes
-- balancing rxns, limiting reagents

Quiz 2
-- e'/photon energies, Bohr Model
-- power, ionization, # of photons

Quiz 3
-- orbital levels, filling, quantum #'s
-- ionic radius (both neutral atoms and ions)
-- ionic solids, lattice energy, basic Lewis

Exam 1 Problem Topics

Atomic orbitals
Electron configuration
Quantum #'s

Balancing rxns
Limiting reagents
Mass conservation

PES
More AO filling

Bohr Model
e' transitions
ionization

Lewis structures
Formal charges
Lattice energies

Lecture 1: Introduction and the chemistry of the periodic table

Summary

“Never trust an atom, they make everything up,” is a classic chemistry joke that also happens to be so true, but if we want to know which elements comprise our materials of interest, then we need to know how these elements interact with one another, how they are structured, and how the material was processed to achieve this structure. To truly answer these questions, investigators in the last few centuries have made use of the **scientific method**. This involves asking questions, gathering and examining evidence, identifying explanations, and re-testing.

One of the most exciting questions in the history of chemistry was that of the **atom**—Democritus and Leucippus hypothesized indivisible building blocks of the universe (though now we know that atoms can be broken down into even smaller “subatomic particles”). Robert Boyle, in his quest to identify different atoms, studied metal ores (naturally occurring rocks containing metal impurities) and succeeded in separating a large number of elements, including many metals. As the list of discovered atoms grew, scientists also began studying their categorization. For example, Antoine Lavoisier named four property-based categories for the 33 elements he identified: Gases, Non-Metals, Metals, and Earths. John Dalton identified 36 different elements, and designed a graphical symbol to represent each of them.

In this lecture we introduced the concept of **chemical reaction balancing**, which involves adding coefficients to the reactants and/or products in the reaction to ensure that there are equal numbers of each type of atom on the left- and right-hand sides of the arrow. This is necessary because of the **law of conservation of mass**, which states that nothing is created or destroyed at the atomic level, so the mass of the reactants equals the mass of the products. Rather, atoms can be rearranged to form different molecules. The first chemical reaction we balanced was a **combustion reaction**, which is a reaction in which a carbonaceous material burns in the presence of oxygen. We found the **limiting reagent** for this reaction, which is the reacting species (atom or molecule) that is used up first. The **yield** of the reaction is the amount of product formed.

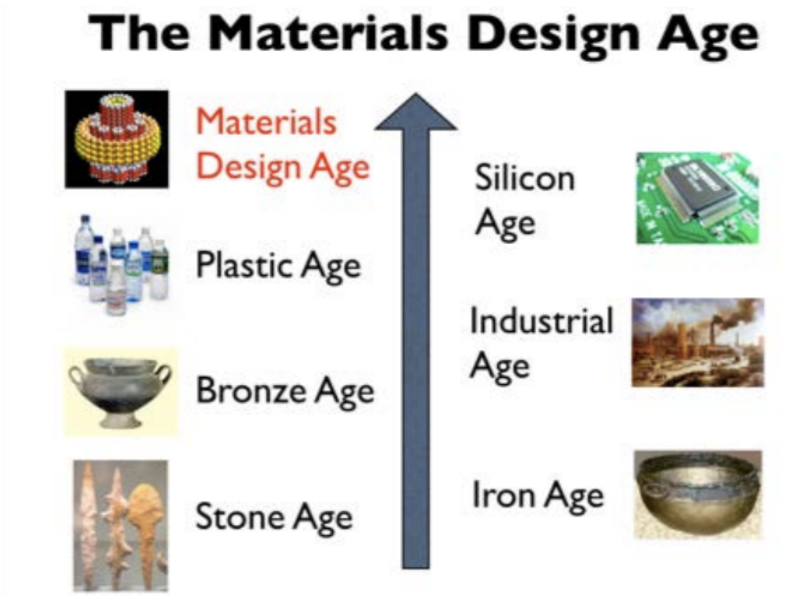
Dalton stated that atoms of a given element have a particular weight and other distinguishing characteristics. He proposed the law of multiple proportions, which says that when two elements react to form a series of compounds, the ratios of masses of the 2nd element per gram to the 1st can be expressed as ratios of integers.

Why this matters

In this first lecture, we started talking about the discovery of the elements. Well, I don’t mean to give anything away, but there aren’t going to be all that many of them in the end. In fact, to date we’ve got 118 on the official roster, but if we consider which ones we can use to make stuff for humans that number is lower, more like 80 or 90. How many elements do you think there are in your cell phone? It depends on the phone, but in mine there are 64 different elements!

That’s more than two thirds of all of the ones we could even have used and it’s incredible to think about. Because of this massive design potential, the world we live in has completely changed.

As a Materials Scientist, I love that we have this tradition (shout out to Danish scholar Christian J. Thomsen) of naming the age we live in by the material that mattered most during that age. But as a Materials Scientist, I also love that we’ll never be able to do that again. The reason is that we truly live in a new era, one where we can realize the dream of Richard Feynman, who in his famous speech “There’s Plenty of Room at the Bottom” put forth the vision for atomicscale design and nanotechnology 30 years ahead of its time. Today, we routinely control both the choice of elements as well as their structure as they come together to make materials do things we never thought possible even just 10 years ago! In other words, we control their chemistry at the atomic scale.



Images of stone arrows, bronze pot, industrial age, plastic bottles, silicon chip © sources unknown. This content is excluded from our Creative Commons license. For information, see https://ocw.mit.edu/fairuse. Image of atomic design is in the public domain.

This gets to why this is so cool (and, you guessed it, why it matters). You see, so many of our current global challenges – whether in energy, health, or the environment – have a bottleneck that occurs because of the material that makes up a central part of the technology (in some devices it's called the "active layer"). That means that by "simply" choosing or making a different material, one has the potential to completely change the properties, cost, and manufacturability of the technology. This is unlike a previous revolution around silicon where we went from a cost of $1 per transistor in 1965 to $0.00000001 per transistor in 2015. Talk about a learning curve! That was primarily due to advances in processing of the same element, silicon, to get to smaller and smaller components. More than a billion transistors now fit nicely on a single chip. Unlike this dramatic age of silicon, many of the next technology revolutions will rely on changing the material itself: in some cases, completely. We now live in the Materials Design Age, which has come just in time since it converges with very pressing challenges on a global scale that will rely on new materials to be solved. And this is why the discovery of these elements matters so much. They are our playground and the basis from which we will make the next set of technologies to change the world for the better.

Why this employs

In this section, we'll discuss how the material in each lecture connects to real jobs. I'm trying it out this year for the first time, and since I likely won't have time to spend on it in lecture, this document is the only place you'll find it. In Why This Matters, I passionately believe that each lecture can and should be connected to some larger-scale challenge, or innovation, or inspiration. In Why This Employs, my goal is to connect each lecture with a possible field of employment. Similar to Why This Matters, this is not meant to be exhaustive but rather illustrative, to give you another way in which the material you're learning has value beyond the classroom and connects to something, in this case a job.

We spent half of this first lecture talking about the class structure, not just administratively (what's graded, what's not, etc) but also pedagogically (the different components, how they come together to provide a learning experience, etc.). Thinking about how to teach better, and how students learn, and how new technologies should or should not be a part of this, is a wonderfully rich area of employment. If you're interested in learning more, check out MIT's Teaching and Learning Lab or some of the cool initiatives in education like EdX, NEET, or the "superUROP" programs.

Another employment direction related to this lecture is the discovery of new elements. Here, we examined how the earliest chemists attempted to identify elements. This came down to smashing, burning, boiling, reacting, etc. It turns out that's still a thing, only in modern times all this reacting occurs with much bigger pieces of equipment and much larger teams of people. The next element yet to be discovered (at the time of writing, that would mean the 119th known element) will likely not have a very long lifetime, and will be very difficult to make in large quantities. But pushing the boundaries between what we have found naturally and what we can make synthetically as it relates to the fundamental building blocks of the universe. . . well, that's a pretty exciting thing to do. And given the prediction by some that an “island of stability” exists for heavier elements that have yet to be made, it’s possible that an entirely new era of chemistry awaits such discoveries.

The last example I’ll give for employment relates to the idea of the metal ores that I mentioned earlier in this lecture. Remember that this is where Dalton and many others were discovering those new elements. Basically, you take a rock and carefully break it up and viola, you get Fe out of it (ok, it’s a bit more complicated than that, but that’s the idea). It turns out that quite often the metal atom is locked up pretty tightly in the form of an “oxide” (yes, that means bonded to oxygen, but we’ll get to that in a few lectures). The point is that extracting metals like aluminum from rocks takes an enormous amount of energy, which means it requires a lot of burning of fossil fuels. What if you could come up with a new, much “greener” way to get metals or minerals in their pure form out of the rocks from which they originate? This would be a very big deal. Mining metals and minerals involves massive teams of engineers who cover a wide array of jobs from figuring out where to mine, to characterization of the starting materials, to optimizing extraction chemistry, to working on new ways to do that more efficiently.

Example Problems

1. In this lecture, you witnessed my passion for pyrotechnics.

a) Write and balance the chemical reaction for a similar process, the combustion of propane ($\mathrm{C_3H_8}$).

Answer

$\mathrm{C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O}$

b) If you have $500\mathrm{g}$ of propane, how many moles do you have? How many molecules?

Answer

First, find the molar mass of propane.

$$3 * 12\ \mathrm{g/mol} + 8 * 1\ \mathrm{g/mol} = 44\ \mathrm{g/mol}$$

Use the grams given and the molar mass to convert to moles:

$$500/44 = 11.36\ \mathrm{mol}$$

Lecture 2: Counting Atoms and Organizing the Elements

Summary

This chapter, we introduced the concept of the **mole**. This is a constant number, also referred to as **Avogadro's number**, equal to 6.0221409×10^{23}. The **atomic mass units** (AMUs) assigned to an element are equal to the mass in grams of a mole of atoms of that element. Just as Avogadro's number is just a number, the AMU is just a mass, and $1\mathrm{AMU}$ is equal to 1.67377×10^{-24} grams. Just like the mole, an AMU is another special unit that chemists use to connect the very small world of atoms with the comparatively large world of things we work with. This link between the macro and atomic worlds means that by simply measuring the mass of a substance, we can know how many atoms of that material we have.

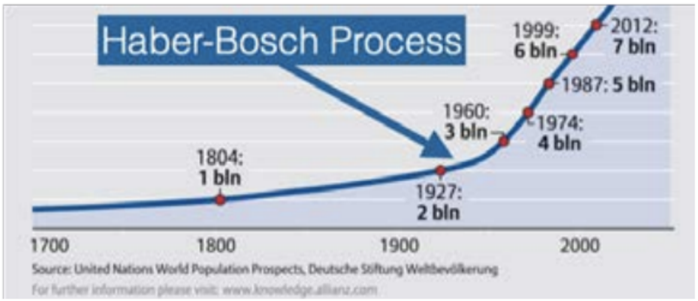
In class we used the example of the combustion of a candle, otherwise known as the nicely balanced reaction $\mathrm{C_{25}H_{52} + 38O_2 \rightarrow 25CO_2 + 26H_2O}$. We used this example to emphasize how the concept of the mole gives us a link between the atomic and macroscopic worlds, between grams and atoms. We also used this example to re-emphasize the concepts of limiting reagent and yield.

Next, we focused on organizing the periodic table. Unlike in the last chapter, here organization means more than coming up with a naming scheme or a simple categorization of the elements, as Dalton, Lavoisier, and many others had already done. In this lecture what we mean by organization is really pattern recognition. Scientists were starting to see patterns emerging among the elements, and the more elements were discovered, the more effort was put to understanding these patterns.

Dmitri Mendeleev developed the precursor to today's periodic table. His big breakthrough was that he arranged the then-known (63) elements not just by their mass, but also by the repeating (periodic!) patterns he observed in their properties. This led him to leave gaps in the periodic table that would later be filled with newly discovered elements. Because of the periodicity in properties, he could even predict the properties of many as-of-yet undiscovered elements. The rows of your periodic table are called periods, and the columns are called **groups**. The **Main Group Elements** are those in periods two and three. There is a general trend from metallic to non-metallic elements along the periods. The **Transition Elements** are in groups 3-12 and periods 4 and 5 .

Why this matters

The population of humans on this planet has seen a dramatic, exponential growth. Let’s zoom in on where the growth really started to kick into high gear. See that uptick, around the early 1900’s? Notice the massive change in slope. That’s when we figured out how to make nitrogen in a way that plants can use.



People vs. time plot © Population Reference Bureau. All rights reserved. This content is excluded from out Creative Commons license. For information, see https://ocw.mit.edu/fairuse.

In other words, with the discovery that is now known as the Haber-Bosch process (named after the German chemists Fritz Haber and Carl Bosch), the world was able to make fertilizer in the abundance needed to feed billions. The key comes down to something called "fixing" nitrogen. Plants need nitrogen to grow, but most plants cannot use any of that plentiful 78% N_2 that's in the air. Instead, they need it in a form that serves up single N atoms, like ammonia (NH_3). SO how can we go from N_2 to NH_3? Easily, with the following chemical reaction:

$$N_2 + H_2 \rightarrow NH_3$$

Ah, sorry, let’s balance that:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

That’s better. What Haber and Bosch actually did was develop a catalyst and process that allowed this reaction to be carried out much more efficiently than previously. But catalysis is getting a little ahead of ourselves. For now, let’s focus on the balanced reaction and count some atoms.

In 2019, 500 million tons of nitrogen is produced for fertilizer each year using the Haber-Bosch process. Half of the protein in all human beings on this planet comes from nitrogen that was fixed by this process! So here's my question: how long can we continue fixing nitrogen this way? And since the reaction tells us we need both N_2 and H_2, which one would be the limiting reagent?

From all of our discussion so far in this lecture we know that we can use the periodic table to determine that 1 mole of NH_3 is 17 grams. Just for simplicity, suppose in the future we continue needing to make the same amount we're making today, namely 500 million tons of NH_3 per year. There are roughly a million grams per ton, so 500 million tons per year $500 \times 106 \times 106$ grams per year. Dividing by 17 grams per mole, this means we need to make roughly 30×10^{12} moles of NH_3 /year. Given the balanced reaction above, this means we'll need as input to the reaction 15×10^{12} moles of N_2 per year. Now, the mass of the atmosphere is about $5.15 * 10^{21}$ grams, of which 78% is N_2, so that makes about 4×10^{21} grams of N_2 in the air. And since the atomic mass for a nitrogen atom is 7 , then it's 14 for N_2 which means there are 14 grams per mole of N_2. So the number of moles available in the atmosphere is 4×10^{21} grams of $N_2/14$ grams / mole $= 3.5 \times 10^{20}$ moles of N_2 in the atmosphere. Well that's good news! Taking 3.5×10^{20} moles of N_2 total and dividing that by 15×10^{12} moles of N_2 needed per year, we find that we could keep at it with the Haber-Bosch process of fixing nitrogen from the atmosphere for more than 20 million years or so before using it all up.

That’s just cool. Think about this: we just went from atom to macroscopic world and it’s all because we have this concept of the mole. But we never really answered the question, namely which one is the limiting reagent in the reaction, the N_2 or the H_2? We now know how long N_2 will last us if we were to use it all up in this reaction, so what’s left is to do the same thing for H_2. Speaking of which, where will we even get H_2? Certainly not from the air. I’ll let you all work through this but here’s a hint: the oceans contain a whole lot of water, like more than 10^{18} tons. Maybe you don’t even need to do any calculations to figure this out!

Why this employs

How does counting or organizing atoms lead to a job? Well, for one thing we're talking about order, precision, and measurement. After all, Mendeleev's success relied on combining careful measurement of properties with precise ordering. This skill is needed for many different jobs. One place with measurement as its mission is the National Institute of Standards and Technology (NIST). Check out the tag line in their Materials Measurement Laboratory: "MML serves as the national reference laboratory for measurements in the chemical, biological and material sciences. Activities range from fundamental and applied research to the development and dissemination of certified reference materials and data to assure the quality of measurement results." And that's just one of their many divisions.

Another job that comes to mind is one related to the fertilizer discussed in our Why This Matters. The three fundamental constituents of commercial fertilizers used throughout the world are nitrogen, phosphorus, and potassium. As we know, nitrogen requires fixing. Potassium must be obtained in other ways. For example, it comes nicely with chlorine as potassium chloride (KCl), but we'd prefer not to have chlorine in the soil since it can lead to toxicity in the crops and high acidity and salinity in the soil. However, getting potassium in other forms is expensive and requires, as you might guess, chemistry. To make matters more complicated, both the natural sources for potassium and the specific soil needs are highly dependent on geography. For farmers in tropical regions in Brazil and some countries in Africa, the soil and rock compositions require fertilizers that better match the chemical needs of plants than are currently available. As a solution, more fertilizer is added to achieve as much crop yield as counterparts in the north, but many of the basic ingredients, especially the potassium, are produced in more northern regions and therefore are much more expensive in the Southern Hemisphere. The need for local, sustainable fertilizing solutions to increase yields is urgent! But this is starting to sound more like a second edition of Why This Matters and less like a Why This Employs. My point is that the development of fertilizers is a problem of chemistry, and the world is in desperate need of new solutions. In terms of jobs, this could mean becoming something called an "Analytical Chemist" which means you apply the principles of chemistry to figure out what stuff is made of, what the precise compositions are, how to monitor it, modify it, etc. This could also mean working at a company or research lab that develops cutting edge ideas (like recent work on using electrochemistry to make potassium).

Extra practice

1. Solar cells sometimes contain a titanium (Ti) coating that stops the cell from short-circuiting. The Kroll Process for making titanium metal out of titanium oxide is:

$$\mathrm{TiCl_4 + Mg \rightarrow MgCl_2 + Ti}$$

a) Balance the reaction.

Answer

$$\mathrm{TiCl_4 + 2Mg -> 2MgCl_2 + Ti}$$

b) If you have 50 g of both $\mathrm{TiCl4}$ and Mg, what is the limiting reagent in the reaction?

Answer

Molar mass of Mg: $24.3\ \mathrm{g/mol}$
Molar mass of $\mathrm{TiCl_4}$: $189.9\ \mathrm{g/mol}$

Find the moles of each reactant by dividing $50\ \mathrm{g}$ by the individual molar masses:

$$50\ \mathrm{g}/24.3 = 2\ \mathrm{molMg} \qquad 50\ \mathrm{g}/189.9 = 0.3\ \mathrm{molTiCl_4}$$

Use the mole ratio from the balanced reaction $(1\ \mathrm{molTiCl_4}/2\ \mathrm{molMg})$ to see how much $\mathrm{TiCl_4}$ could be used up with the amount of Mg you have available:

$$(2\ \mathrm{molMg\ available})/(2\ \mathrm{molMg}/1\ \mathrm{molTiCl_4}) = 1\ \mathrm{molTiCl_4}$$

$1\ \mathrm{molTiCl_4}$ would be used up if we had an endless supply of it with the amount of Mg we have. This amount of $\mathrm{TiCl_4}$ is more than the amount we actually have available, meaning that the $\mathrm{TiCl_4}$ will run out before the Mg. $\mathrm{TiCl_4}$ is therefore the limiting reagent.

c) What is the yield of the reaction in grams?

Answer

To calculate the Ti yield of the reaction, we use the ratio of Ti to $\mathrm{TiCl_4}$ (because these two have a 1:1 molar ratio) and then convert from moles to grams of Ti:

0.3 moles of $\mathrm{TiCl_4}$ are being used (it's the limiting reagent, so it will be used in its entirety) and because of the 1: 1 molar ratio we know that 0.3 moles of Ti will be produced. Multiply this number by the molar mass of Ti:

$$0.3 * 47.9 \text{ g/mol} = 14.37\text{g Ti}$$

d) Plot the yield of Ti (g) as a function of increasing Mg available for reaction.

Answer

The plot of Ti grams (on the y axis) vs. Mg grams (on the x axis) starts at 0 and increases linearly until the Ti grams reach 14.37 g at which point we run out of $\mathrm{TiCl_4}$ and the reaction will stop.

Lecture 3: The Discovery of the Electron and the Structure of the Atom

Summary

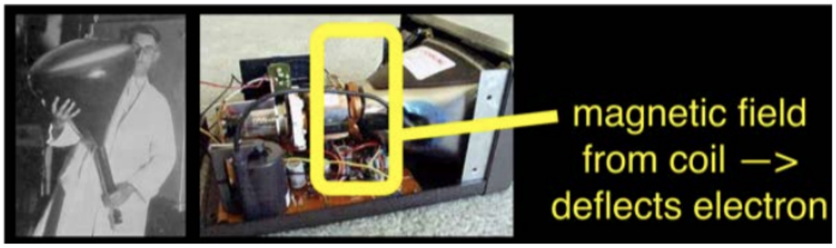
This lecture began with discussion of ground-breaking experiments that brought the scientific community closer to understanding the structure of the atom. These included J.J. Thomson's experiments with the cathode ray tube (CRT), which allowed him to find the charge-to-mass ratio of **electrons**, which he realized were negatively charged particles found in all atoms. Robert Millikan was able to ascertain the mass *and* the charge of the electron using his oil drop experiment. The atom was not the most fundamental particle after all, rather it was made of smaller particles like electrons, and as we learn next those smaller things that make up atoms have a structure to them. The electronic structure.

Building on the radiation studies of Marie and Pierre Curie, Ernest Rutherford was able to identify three types of particles found in radiation: **alpha particles**, which were large and positively charged, **beta particles**, which were small and negatively charged, and **gamma rays**, which didn't deflect or interact with the photographic plate in Rutherford's experiment at all. Rutherford then conducted the gold foil experiment, which showed that atoms have positive charge that is localized in the core of the atom rather than dispersed among the negative charge, as Thomson had proposed. This positively charged center of the atom is called the **nucleus**. The positively charged particles in the nucleus are called **protons**. For any neutral atom, the number of protons present must equal the number of electrons present. This number is called the element's **atomic number**, which is denoted by the letter Z. Except for the case of a neutral hydrogen atom composed of only one proton in its nucleus and one electron, all atoms also contain **neutrons** in their nuclei, which are, as the name might suggest, neutrally charged particles. To obtain the **mass number** of a given atom, the number of protons and neutrons in that specific nucleus are added together. Atoms of the same element can have different numbers of neutrons. This makes them different **isotopes** of the same element. To obtain the mass given for each element in your periodic table, a weighted average is taken of the mass numbers of that element's naturally occurring stable isotopes. The weight is assigned according to the isotopes' percent abundance in nature.

After Rutherford's experiments, there remained the question of how an atom structured in this way could be stable. Niels Bohr was the one who postulated that the angular momentum of the electrons in atoms must be quantized, which means that it takes on discrete values. This meant that the electron's energy and distance from the nucleus were quantized as well—the electron can only occupy certain orbits.

Why this matters

The discovery of the electron led to a profound new understanding of the atom, which in turn led to an entirely new theory (quantum mechanics), which in turn led to orbitals, bonding, and the building blocks for all of modern chemistry, as we'll see soon. But the discovery of the electron also led to a new capability that revolutionized the world: the ability to paint with electricity. The phosphor screen that was on the end of Thomson's cathode ray tube was the precursor to television, and the beginning of a technological revolution that changed almost every aspect of our lives. TV wasn't invented by Thomson himself, but Thomson's discovery of this new fundamental paint brush – the electron itself – was crucial for the concept to take off. Look at what the man on the left in this image is holding: it's an early version of a TV, which you can now recognize as a giant cathode ray tube! John Logie Baird was one of the first to commercialize television sets, selling his first one in 1925. You can see the inside of an early TV in the middle picture: note that it was comprised of a CRT plus a coil to induce a magnetic field – essentially the same setup that Thomson used in his groundbreaking experiments.



Man with CRT & open TV images © sources unknown. This content is excluded from our Creative Commons license. For information, see https://ocw.mit.edu/fairuse.

If electrons were scanned across the phosphor screen fast enough, an image could be painted so many times per second that it looked like motion to the human eye. This was easy to do, because changing a magnetic field quickly and precisely (to position electrons on the screen) can be achieved with simple electronic circuitry. Over the next generation, electrons became a dominant way to exchange visual information. The chemistry of the screen itself is also essential. A ‘screen’ is actually a phosphor coating that was often put on a piece of glass and was the target of the electron beam. Phosphor is a broad term for materials that emit light in response to a stimulus. This act of emitting light is called luminescence. It can get confusing since the term “phosphorescent” means that the material slowly emits light over time after being stimulated. A good example of a phosphorescent material would be glow-in-the-dark toys, where the stimulus is light, and the phosphor can keep glowing for many hours. On the other hand, a “fluorescent” material also emits light in response to a stimulus, but as a quick flash lasting nanoseconds. The term phosphor can refer to either of these, but the coating on the CRT screen and in those early televisions is the fluorescent kind. You can imagine why: if it didn’t emit light quickly,, the image would have afterglows that lasted for hours, which wouldn’t exactly make for a nice movie-watching experience.

To make matters even more confusing, the term phosphor (which as we just established can refer to materials that are phosphorescent or materials that are fluorescent), is not to be confused with the element phosphorus. Phosphorous also emits light, but of a different nature entirely, since its glow comes from a chemical reaction (a process called “chemiluminescence”). So, to sum up: the screen we’re talking about uses a phosphor which is fluorescent, not phosphorescent, and doesn’t have any phosphorus in it. Great.

Chemically speaking, what are these phosphors? There are so many different materials that are phosphors that it would take an entirely separate book to go through them all. They can be small molecules, complex solids, or liquids. They can emit light in response to many different stimuli, from light to heat to electric fields to the electrons we’re discussing here in our CRTs. The first television screens were black and white, so the goal was simply to use phosphors that glowed white when they were struck by electrons. Powders made from zinc, cadmium, and sulfur and a dab of silver were early ingredients. In order to achieve color TV, blue, green, and red phosphors were needed. The electron beam could be pointed at whichever ones were needed to make a given color, again using the magnetic field to guide the electrons with fantastic precision. It turned out the green and blue phosphors were pretty straightforward to make, zinc-sulfide with a touch of copper for green, and silver for blue. But red was a different story: for red phosphors it took additional decades’ worth of research to find anything that worked. This is the reason why color television didn’t come on the scene until the mid-1960’s, a full 40 years after black white television was introduced! The red phosphor challenge was finally solved by using a complex mixture of yttrium, oxygen, sulfur, and a bit of europium for good measure.

Since we’ve listed yttrium, I have to mention that it is one of four – yes four! – elements that were discovered in the same cave in the same town, Ytterby, Sweden. Yttrium, terbium, erbium, and ytterbium are all named after this town. We’re still waiting for cambrium or bostonium.

Now, it’s only your parents or grandparents who will remember what watching TV on a CRT was like. That’s because TVs nowadays work on a different principle, namely light emitting diodes (LEDs). But in the end, it’s still painting with electrons! An LED emits light using the cascade of electrons from high energy to low energy in a solid material. We’ll learn all about that material (it’s called a semiconductor) and why electrons can make light this way a little later in the semester. The light that comes out of an LED in your TV (or phone or tablet) still often passes through a phosphor, since the phosphor can be used to fine-tune the color of light we see. In this case the phosphor is stimulated by light instead of electrons, but the outcome is the same: light and color are produced using electrons and chemistry.

Why this employs

How can we get a job based on the discovery of the electron? That’s kind of like asking how we can get a job related to the knowledge of atoms – in other words, electrons and atoms make up everything so anything would qualify, at least if it has any reference to matter in the employment description. But how about if we go back, specifically, to that first beam of electrons that Thompson made to discover their very existence. . . what jobs might involve beams of electrons. We already discussed painting with electrons in the topic of displays in Why This Matters, but it turns out there’s a whole lot more you can do with a beam of electrons than just make pictures. To do so, though, we’ll need more power. A lot of power.

If you crank up the power of that electron beam enough, and you keep it in a vacuum (just like Thompson did) to make sure they don’t scatter off of anything, then you can use the electron beam to create very localized heat, enough to melt any material. If it’s done to join two materials together in a precise manner we call it welding. Electrons have a lot of advantages in welding because they can be focused to very small areas using magnetic fields, and the power can be dialed in to whatever the job requires (and there’s almost no limit to how powerful you can make a beam of electrons). On the higher end, for industrial welding, electron beams can get up to much as 10,000,000 Watts per mm^3 which can heat up a metal at a rate of 1,000,000,000 Kelvin per second!

Electron beam welding is a big industry, and there are many jobs associated with it. You could weld metal parts together at GE for its aviation business, and I mention that company specifically because it was James Russel who invented electron beam welding while he was at GE, back in the 1950’s (as a fun side note, he also invented the first CD). If you do a search for electron beam welding you’ll find huge numbers of listing for companies that provide it as a service to other companies. Bodycote, for example, states that they are, “the world’s leading provider of heat treatments and specialist thermal processing services,” and with 5,700 employees in 26 countries they have a lot of jobs. But there are many smaller scale operations that hire people who like to shoot massively high energy electrons at metal parts, like the family-owned Roark in Brownsburg, IN, which boasts one of the largest electron beam welding chambers in the U.S., or Precision Technologies, Inc., which has a cool-sounding 5-axis electron beam welder that goes up to 150 kV, “capable of welding parts as small as a few grams up to ones weighing several tons,” or how about Fraunhofer FEP which develops customized electron beam technologies and states, “Using electrons we improve your materials and products!” Cool.

Extra practice

1. Your friend Wonder Woman tells you that her bracelets are made of a metal, Feminum (this is legit, it was in the '70 s TV show), only found on her home island. Feminum (symbol Fm) has atomic number 120 and atomic mass 285.47. The element has 2 isotopes, $^{285}\mathrm{Fm}$ and $^{X}\mathrm{Fm}$. The natural abundance of $^{285}\mathrm{Fm}$ on the island is 77%.

   a. What is the other isotope, and what is its natural abundance?

   b. How many protons and neutrons does each isotope have?

Answer

77% abundance of one isotope implies 23 percent abundance of the other, since we know there are only two isotopes. The atomic mass is the weighted avg. of the two isotopes. Solve the weighted average equation to obtain the missing mass number:

$$(0.77)(285)+(0.23)(x)=285.47 \qquad x=287.04, \text{ rounds to } 287$$

2. The number above the Li symbol on the periodic table (on the right) is the number of protons in a lithium nucleus. What is the number below the symbol? How do you calculate it?

Answer

The number below the atomic symbol is the atomic mass. It's not specific to the atom-it's a weighted average of the element's stable (non-radioactive) isotopes, with weights given according to the isotopes' abundance in nature.

For example, lithium's atomic mass is 6.94, and its two stable isotopes are $7(92.4\%$abundance) and $6(7.6\%$abundance)

3. Assuming all the protons (red) and neutrons (blue) are visible, use proper notation to write out the atom that corresponds to each of the following nuclei:

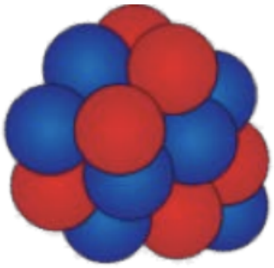


Image courtesy of CK-12 Foundation, License: CC BY-NC.

Answer

a) mass : 13 , atomic : 6 , atomic symbol: C
b) mass : 7 , atomic : 3 , atomic symbol: Li

Lecture 4: The Bohr Model and Electronic Transitions

Summary

The **Bohr model** is a framework used to describe the **quantized** nature of atoms. By assuming that electrons orbited around atomic nuclei-like planets around the sun-Bohr showed that the electrons bound to atomic nuclei can only exist in discrete energy levels. By equating the attractive force of the Coulomb interaction between the negatively charged electron and the positive nucleus, $F_{Coulomb} = -Ze^2/r^2$, and the repulsive force due to rotation, $F = mv^2/r$, and substituting the quantized angular momentum, $L = mvr = nh/2$, we find formulas for the quantized radius and the quantized energy. The energy of an electron in the nth energy level of an atom which has Z protons is

$$E = -13.6Z^2/n^2 \quad [eV]$$

The integer n, which can have any positive value ≥ 1, is called a quantum number because it makes it so that the energy can only take on certain, discrete values as opposed to a continuum of possibilities. The state $n = 1$ is the **ground state**, and higher energy levels are called **excited states**. When an electron goes from a state with a lower quantum number to one with a higher quantum number, the energy of the electron becomes less negative: it gains energy. We know that energy must be conserved, so the energy gained in such a transition must come from somewhere. In fact, a photon with exactly the $\Delta\mathrm{E}$ between two energy states in the atom can be **absorbed**, exciting the electron. Similarly, if the transition happens in the opposite direction, the excess $\Delta\mathrm{E}$ can be **emitted** in the form of a photon.

The kinds of photons capable of being absorbed or emitted by a Bohr model atom or molecule can be equivalently characterized by their energy, frequency, or wavelength. Einstein taught us that light can also be quantized in his work on the photoelectric effect: the energy of the photon can take discrete values:

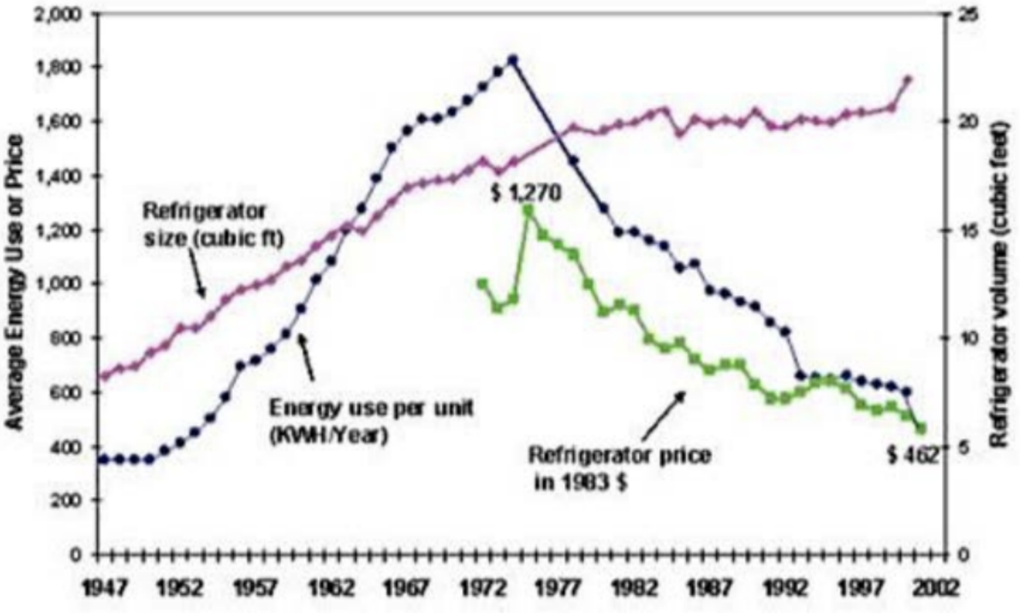
$$E = hf = hc/\lambda$$

Where f is frequency, λ is wavelength, h is Planck's constant, c is the speed of light, and the second equality is true because $\mathrm{c} = \mathrm{f}\lambda$. The wavelength of light that can interact with a particular energy transition can be found by equating the two expressions above. With this in mind, we see that light can be used to probe what electronic transitions are happening in an atom or molecule, and therefore what energy levels are present in a material. The Bohr model fit the spectral lines of stars observed previously by astronomers; in particular, the discrete wavelengths emitted by hydrogen gas that had been observed by spectrometer finally had an explanation.

There are a few limitations to the Bohr model. We now know that electrons are not really orbiting the nucleus (although their angular momentum is quantized as predicted). Further, the Bohr model can only be used to describe electronic transitions with a single electron, such as $\mathrm{H_{He}He^+}$, or $\mathrm{Li^{2+}}$. However, the key takeaways hold: if the energy states in an atom or molecule are known, the wavelengths of light that can be emitted or absorbed by the material are also determined. Likewise, if the discrete wavelengths emitted or absorbed by an atom or molecule are observed, the energy levels available to an electron are also known.

Why this matters

How does absorption of photons by electrons that are transitioning from one energy level to another matter? One application this principle is connected to is the refrigerator(!) That might not seem obvious at first, but let's see why. Take a look at the average energy used by a fridge in the U.S. over a 55-year period. It's interesting to note that the average size of a refrigerator grew steadily for 35 years and then plateaued in the 1980's.



Average energy use vs. time © source unknown.

This, it turns out, was not because people didn't want more fridge, but rather because they couldn't fit anything larger through the kitchen door. More to the point, note that the energy use per unit increased along with the size for 30 years, until suddenly it started decreasing rapidly in the 1970's, even though the size continued to increase. This is because during that time there was also an oil shortage and people were starting to get concerned about energy use. Some of these people had important titles like President of the United States (Nixon, Ford, and Carter), and a whole lot of legislation aimed at energy conservation happened because of them. For example, President Ford signed the first law ever on this topic in 1975, the Energy Policy and Conservation Act, which led to the establishment of fuel economy standards for cars and efficiency standards for appliances. After that, more laws were signed that created incentives to lower energy consumption (towards a goal of making the U.S. an energy independent nation by 1985), with Carter presenting a plan to congress stating that, "conservation is the quickest, cheapest, most practical source of energy," requiring federal agencies to develop energy conservation plans, and creating the Department of Energy (DOE).

In this Why This Matters, I want to emphasize the importance of government policy. It was the government stepping in that led to the technological innovation that led to greater efficiency and lower costs. In 1992, the Energy Star program was introduced which led to even greater reduction in the energy consumption of appliances and critically increased consumer awareness. Not only did refrigerators themselves become cheaper because of this innovation, but the energy they used continued to decrease. In 2019 in the U.S., we save about $20 billion annually on energy consumption alone for our refrigerators compared to the 1970's. Sadly, since 2017, the Trump administration has been trying to eliminate the Energy Star program, which many consider to be one of the most successful voluntary energy efficiency programs in the world. It has saved Americans $430 billion in energy costs across hundreds of appliances, not to mention the lower CO2 emissions that have resulted.

Now we still haven't connected back to our chemistry lesson, and while I could do that for the energy savings alone, there's another example involving a fridge-related policy decision that very clearly brings Bohr back to the table. That is the Montreal Protocol, which was signed in 1987 and was the first treaty to be ratified by all countries in the world. It represented universal agreement to protect the stratospheric ozone layer by phasing out both production and consumption of ozone-depleting chemicals, like chlorofluorocarbons (CFCs). Taking this action led to the recovery of the earth's ozone layer that protects life from harmful UV radiation. Millions of lives have been saved as a result. But what is it about CFC's that makes them deplete ozone? And why is ozone so important for blocking UV radiation? The answer, of course, comes from chemistry.

Ozone is a molecule consisting of three oxygen atoms, O_3, and a common CFC molecule consists of a carbon atom, three chlorine atoms, and a fluorine atom, $\mathrm{CCl_3\,F}$. Occasionally, the CFC molecule breaks down and gives up one of its Cl atoms, like this:

$$\mathrm{CCl_3\,F(\,g) \rightarrow CCl_2\,F(\,g) + Cl(g)}$$

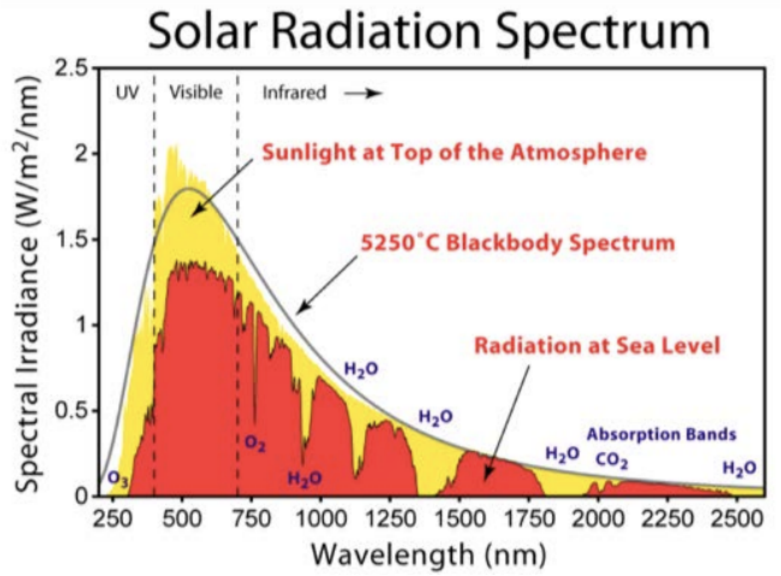
Note the "(g)" subscripts are included to show that all this is happening in the gas phase. Once a chlorine atom is freed up, it can then react with ozone, like this:

$$\mathrm{O_3}(g) + \mathrm{Cl}(g) \rightarrow \mathrm{ClO}(g) + \mathrm{O_2}(g)$$

And so each CFC molecule can deplete one ozone molecule. But it doesn't stop there. A third reaction takes place, since there are also oxygen atoms in the stratosphere. When an oxygen atom interacts with the ClO molecule, it reacts with it to make O_2, like this:

$$\mathrm{ClO}(g) + \mathrm{O}(g) \rightarrow \mathrm{Cl}(g) + \mathrm{O_2}(g)$$

And therein lies the real problem: the Cl atom is now free again and ready to attack another ozone molecule. Because of this catalytic cycle, one single CFC molecule can lead to the destruction of 100,000 ozone molecules!



Solar radiation spectrum by Robert A. Rohde as part of the Global Warming Art project. License: CC BY-SA. Source: Wikimedia Commons.

That brings us to the second question from above: why does losing ozone lead to more UV radiation? This is where electron transitions come in. Check out the plot in this figure of the solar spectrum. The x-axis is the wavelength of light coming from the sun, covering only the UV, visible and infrared (so it is just a sliver of the full EM spectrum we showed a few pages back). The y-axis is the intensity of light at a given wavelength, in Watts per area. A Watt is a measure of power, which is energy per time, or Joules/s. In plain words, this is a plot showing the power of sunlight as a function of its color.

The first thing to point out on the plot is that solid black curve, which corresponds to a theoretical prediction of the black body radiation emitted by an object at the temperature of the sun. This temperature varies a lot depending on where in the sun it's measured, but near the surface, $\mathrm{T} = 5250^{\circ}\mathrm{C}$ is a decent approximation. Note that it's a nice continuous spectrum, and it has a shape typical of black body radiation (remember, that's the kind of radiation we mentioned earlier - the kind that Planck introduced the concept of quantization to explain).

Next, there's the yellow shaded parts that correspond to the actual measured power from the sun before it interacts with our atmosphere. It follows the black body radiation quite well, which validates the prediction. And then, there's the red shaded region. This is the power from the sun as measured on earth, so the only difference between the red and the yellow is that the red is a measurement of photons from the sun that have passed through the atmosphere. It follows the yellow pretty well in general, except that now there are gaps in the spectrum: discrete wavelengths where there is no light observed on earth at all! The plot shows the reason why: next to some of the larger gaps, there is a molecule. $\mathrm{H_2O}$ is listed in several spots. One gap is attributed to $\mathrm{O_2}$ and another to $\mathrm{CO_2}$, and one of those gaps is due to our nice, friendly, no-longer-getting-depleted ozone molecule, $\mathrm{O_3}$. It's the gap all the way over on the left side of the plot, and it's right where the UV light would have been shining down on us. We can see that it does indeed shine down on us outside of the atmosphere (the yellow), but not at the earth's surface (the red).

This tiny sliver of absence of UV light due to the O_3 molecule is absolutely essential for life on earth as we know it, and it's all thanks to electrons being pumped up in energy from one state to another. In this case it happens in a molecule, not an atom, but the same principle we learned in this lecture for electron transitions according to the Bohr model applies. There are discrete energy states where electrons are allowed to be in the $\mathrm{O_3}$ molecule, and transitions between these energy levels can happen when an electron either absorbs or emits a photon. Just like the Bohr model for the hydrogen atom, the discrete nature of electronic transitions in molecules means that absorption of light occurs only at distinct points in the spectrum. For ozone, there just happens to be an energy difference between two electron states that has the energy of a UV photon, which is why this particular molecule absorbs well in the UV.

Why this employs

I was thinking about mentioning jobs in spectral astronomy, since the Bohr model explained the observation of spectral lines from hydrogen and other light elements out in space. The same type of analysis, using basically just a (much) fancier version of the spectroscope you got in your Goodie Bag, is used today to understand the stuff that makes up distant stars, nebulae, galaxies, quasars, all sorts of other intergalactic matter, including whether exoplanets have earth-link atmospheric compositions.

But instead of going down that outer space route, I'd like to pick up here on the point I made in Why This Matters, regarding how solving the ozone depletion problem is a beautiful example of how important science policy can be in making the world a better place. What employment opportunities are there along such lines? "Science policy" is a broad term that can apply to a wide array of jobs and activities, from deciding how science is funded to how it can (or cannot) be translated into commercial products, to how science impacts human health to protecting the health of the environment. The jobs that result from this direction often involve a connection to politics and Washington (if in the U.S.) but they don't necessarily have to. One way to get involved is through fellowships, where students can engage with policy-makers in DC for a summer or a semester.

There are a number of options along these lines, like the AAAS Diplomacy fellow (check out https://www.aaas.org/programs/scienc...cy-fellowships), or fellowships at the Science and Technology Policy Institute, or the White House Office of Science and Technology Policy (OSTP). And then beyond such general ones there are many specialized fellowships in science policy that go by the sub-field, like the American Geophysical Union Congressional Science Fellowship, or the various NOAA Sea Grants for ocean-related policy, or the John Bahcall Public Policy Fellowship for astronomy. And many more.

Beyond fellowships there are tons of jobs out there, like at science policy centers, think tanks or other organizations, from the Union of Concerned Scientists, to the RAND Corporation, to UNESCO, to the Federation of American Scientists, to the Center for Science in the Public Interest, to University-based centers like Arizona State's Consortium for science policy and outcomes. These are only a very few examples – there are so many more. You could get involved directly with the science funding agencies like the NSF, DOE, or NIH (if you become a program manager at any of those please give me a call). Science policy is an incredibly important part of what science is, what it can become, and how it can be used most effectively, wisely, and for the good of the world.

Extra practice

1. What is the energy associated with the ground state in a lithium ion?

Answer

$$E_n = -R_y \frac{Z^2}{n^2} = -13.6 \frac{3^2}{1^2} = -122.4 \mathrm{eV}$$

2. If a light wave has the same magnitude of energy as the lithium ground state, what are the frequency and wavelength of this light?

Answer

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

$$122.4[\mathrm{eV}] = \frac{\left(4.14x10^{-15}[\mathrm{eVs}]\right)\left(3\times 10^{8}[\mathrm{~m/s}]\right)}{(\lambda[\mathrm{m}])}$$

$$\lambda = 9.9\times 10^{-7}[\mathrm{~m}]$$

Lecture 5: Wave-Particle Duality and Quantum Mechanics

Summary

This chapter, we continued our discussion of ionization. We restricted our examples to ionization of hydrogen atoms in order to use Bohr's model of the atom. An electron in the ground state, or lowest energy state, of a hydrogen atom has an energy of $-13.6\mathrm{eV}$. Therefore, this electron's ionization energy, or the energy required to free it from the nuclear pull and effectively transition it to energy level $\mathrm{n} = \infty$, is $13.6\mathrm{eV}$. The ionization energy of an electron in an atom with atomic number Z can be found with the following formula:

$$\Delta E_{\text{ionization}} = -13.6Z^2 \quad \frac{1}{n_f^2} - \frac{1}{n_i^2}\Bigg)(eV)$$

Ionization energy can be thought of in terms of Einstein's **photoelectric effect**. In his groundbreaking experiment, Einstein shone light (streams of photons) of different energies onto slabs of metal. The photons had to reach a minimum threshold energy in order to ionize the metal atoms. It makes sense that metals with higher first ionization energies will be better able to hold on to their electrons. In other words, light with higher frequency will be necessary to ionize metals with higher first ionization energies. **Photo-Electron Spectroscopy (PES)** is a characterization technique that involves ionizing materials with photons and measuring the removed electrons' kinetic energies. The energy of the bound state of each removed electron can be calculated by finding the difference between the incoming photon's energy and the resulting kinetic energy of the freed electron.

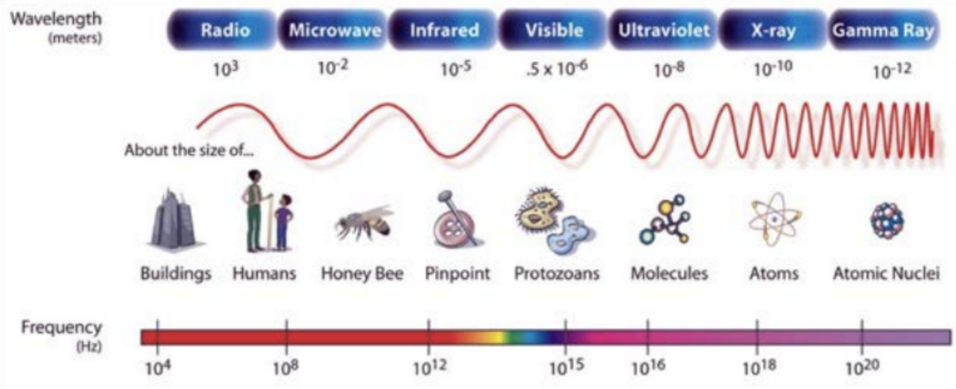
The Bohr model couldn't explain quantization of electron levels; they were imposed in the model, but not understood. Through a series of experiments in the early 20th century, **wave-particle duality** was demonstrated. This meant that light waves were shown to behave as particles, and particles were shown to behave as waves. The most famous of these experiments was the doubleslit experiment, where electrons were shown to act like both waves and particles. Louis de Broglie showed that *all* matter acts like a wave and has a corresponding wavelength (λ). This wavelength can be found using the de Broglie relation, where p is the object's momentum, which is equal to its mass times its velocity, and h is Planck's constant:

$$\lambda = \frac{h}{p}$$

Erwin Schrödinger, with **The Schrödinger Equation**, described the relation between a wavelike particle's spatial distribution and its allowed energies. In the Schrödinger equation, quantization is a natural consequence of solving for a standing wave. This wavefunction ψ does not have direct physical meaning, at least that we know of, but its square $|\psi|^2$ corresponds to the probability of finding the particle at any given location. Solving the Schrödinger equation for an electron in an atom gives a set of wavefunctions that correspond to the electron's energy levels and spatial probability distributions. Note the dramatic difference from the Bohr picture: now the electron can be anywhere there is a nonzero $|\psi|^2$ which is almost everywhere. The concept of exact position does not apply in the quantum world, since particles cannot have their position and momentum specified exactly, in accordance with the Heisenberg Uncertainty Principle.

Why this matters

Let's apply the de Broglie wavelength equation to an electron. We know the mass of an electron is $9\times 10^{-31}\mathrm{~kg}$. Now put the electron in an electric field caused by a voltage of $100\mathrm{~V}$. We know this will cause the electron to accelerate and gain some momentum. Specifically, the energy of the electron is: charge* voltage $= \mathrm{e}^{*}\mathrm{~V} = 100$ volts $*1.6\times 10^{-19}$ Coulombs $= 1.6\times 10^{-17}$ Joules. This is because the unit volts is equal to units of $\mathrm{J/C}$. So now we have an energy of the electron accelerated across $100\mathrm{~V}$, and from that we can get its velocity, $v6\times 10^{6}\mathrm{~m/s}$. Next we can get its wavelength: $\lambda = h/mv = 6.6\times 10^{-34} J^{*} s/\left(9\times 10^{-31}\mathrm{~kg} * 6\times 10^{6}\mathrm{~m/s}\right)$, which when we realize the units of $J = [\mathrm{kg}]\left[\mathrm{m}^{2}\right]/\left[\mathrm{s}^{2}\right]$ we see gives us $\lambda = 1.2\times 10^{-10}\mathrm{~m} = 0.12\mathrm{~nm}$ for this electron.



This figure is in the public domain (created by NASA).

Remember the electromagnetic spectrum from last chapter? That's light covering orders of magnitude of wavelength, only a sliver of which lies in the visible range (400-750 nm). But in order to use this light to see things, we must use a wavelength of light that is either equal or smaller in size to what we're trying to see. Otherwise the light simply won't pick it up (you can check out the physics of diffraction for more info on this, but for now, you can take my word on it). The correlation between the limit of what we can see and the wavelength of light we use to see it is why I like this other electromagnetic spectrum picture. On it is superimposed examples of objects the size of the given wavelength. If we want to use a type of light to see, say, a human, then we'd need to stay at or below wavelengths of 1 m since humans are about 1 m in size. That doesn't mean we can see in the microwave region, but that's just a limitation of our eyes not of what is possible with a type of light. With better eyes than ours, we'd be able to use microwaves to see people, but we wouldn't, for example, be able to use radio waves since they have a longer wavelength than the thing we're trying to see.

Now let's go to the atomic scale: at the x-ray part of the spectrum, we'd need to use x-rays or gamma rays to see objects at that scale. But it turns out that not only can our eyes not see in that part of the spectrum, but even the devices and detectors we've built cannot see all that well. We can take x-rays and do so all the time, but only to see images on the mm resolution as opposed to nm. For the latter, we'd need to see an x-ray reflecting off of a nm-sized object and be able to measure it with precision, something we're not able to do. That said, we do use x-rays to get atomic-scale information, but that's a different thing all together and it has to do with the spacing between atoms in solids. We'll learn all about that later in the semester. But here we're still trying to actually "see" the object and the object is an atom. We can't use x-rays—even though they're at the right wavelength—and forget about gamma rays, because they're even harder to detect. But what else could we use?

That's why we did the electron wavelength calculation to start this Why This Matters section – using the fact that an electron is a wave, and by giving it the right velocity, we can make an electron have exactly the wavelength needed to see at the atomic scale. Electrons can be our "flashlight"! It also turns out they're a lot easier to capture and use to construct images than x-rays. This discovery jump-started the whole field of electron microscopy and changed the way we see matter. It was Don Eigler and Erhard Schweizer who showed in 1989 that by seeing individual Xe atoms, they could arrange 35 of them to spell their company's logo. This is definitely an expensive way to write a logo, but the point is that the accomplishment realized Richard Feynman's dream of being able to put an atom wherever you want.

Speaking of Feynman, he was an incredible scientist and a masterful teacher. If you want to see an amazing lecture entirely devoted to the double-slit experiment, find and watch Feynman's 1959 speech, "There's Plenty of Room at the Bottom," and you won't regret it. This is where he laid out the dream of putting atoms anywhere you want, and that was truly the first vision of the field we now call nanotechnology. The reason it took 30 years to realize Feynman's dream is that we were working in the dark, literally. If you can't see atoms and molecules, it's hard to control them or at least know that something you've done led to an atomic-scale control that you wanted. This type of control led to the nanotechnology revolution and it was entirely enabled by the ability of scientists to see materials at the nm scale, which as you now know was made possible by the wave nature of the electron.

Why this employs

It is true that we put humans on the human without resorting to quantum mechanics, evidence to how powerful and useful the classical view of the world is. But in order to truly understand the world, from the atom to the oceans and mountains to the universe to life itself, the quantum nature of it all must be understood and in some cases quantum effects completely dominate. Electrons and their interaction with light fall into this category: without a quantum description there’s no hope in explaining the interactions that take place. So let’s talk about jobs related to lasers.

Stimulated emission (first discussed in a paper by Einstein in 1917) involves the interaction between a photon and an atom that has electrons in an excited state. If the photon has just the right wavelength when it hits the excited atom, then the atom emits a second photon identical to the first. The LASER is “Light Amplification by Stimulated Emission of Radiation,” and it is entirely and only described by quantum mechanics since it relies on knowing the discrete energies levels of electrons in the atom. And by the way, any time you’re online, you’re using a laser since that’s how information travels through fiber optic cables.

There are so many job postings for “laser engineer” that it wouldn’t be possible to even begin to list (one site I just checked has 7000+ listing!). The reason is that lasers are used today in every walk of life. There are jobs with lasers in medicine, like in eye surgery, to industry where lasers cut and weld, to tracking systems for all sorts of applications, to research in new types of spectroscopy, to so many many more. So if you want a job that uses wave-particle duality to make coherent light, then that’s an awesome first step, but the next step would be to get more specific.

Take LIDAR as an example: this stands for Light Detection and Ranging, which is a remote sensing method that uses laser pulses to measure distances. LIDAR has completely revolutionized the ability of robots, like self-driving cars for example, to see. It's inside those bulky boxes on top of a self-driving car that spins continuously, giving 360 degrees of visibility as well as extremely accurate depth information (to $+/-2\text{ cm}$). It's still expensive ($\$75\text{ K}$ a pop for the car-top systems!), but because of how enabling LIDAR is, and how much the demand for this technology will grow, there are many jobs opportunities. These range from jobs at big player companies like Velodyne that's already selling systems to many markets, to smaller companies trying to innovate the technology like Luminar that promises a $\$500$ LIDAR system in the size of a soda can. There's a whole range in between including self-driving car companies themselves like Waymo that have decided to build their own LIDAR systems. And this was just one tiny example of the vast number of LASER-based job opportunities.

Example Problems

1. You observe hydrogen electrons transitioning from $\mathrm{n}=3$ to $\mathrm{n}=1$.

a) What is the energy change in this transition? Is it absorption or emission?

Answer

The electron is falling to a lower energy state from a higher energy state, so it must be emission.

$$\Delta E=-13.6 Z^{2}\left(\frac{1}{3^{2}}-\frac{1}{1^{2}}\right)=-12.09 \mathrm{eV}$$

We can double check our intuition: since the energy value we found is negative, the transition must correspond to emission.

b) What color light do you observe?

Answer

$$\lambda=\frac{h c}{10.2[e V]}=1.22 \times 10^{-7} \mathrm{~m}=102.6 \mathrm{~nm}$$

This transition is in the UV.

c) How many possible transitions could an electron falling from $=3$ to $n=1$ complete? Which transition is responsible for the orange color?

Answer

There are two possible paths: straight from $n=3$ to $n=1$ or $n=3$ to $n=2+n=2$ to $n=1$.

Next, calculate the wavelength of the three possible photon emissions. We already know that from $\mathrm{n}=3$ to $\mathrm{n}=1$, the wavelength of the emitted photon was $102.6\mathrm{~nm}$

From $\mathrm{n}=2$ to $\mathrm{n}=1$:

$$\Delta E = -13.6Z^2\left(\frac{1}{2^2} - \frac{1}{1^2}\right) = -10.2\text{eV}$$

$$\lambda = \frac{hc}{10.2\text{eV}} = 1.22\times10^{-7}\text{ m} = 122\text{ nm}$$

This transition is also in the UV.

From $\text{n}=3$ to $\text{n}=2$:

$$\Delta E = -13.6Z^2\left(\frac{1}{3^2} - \frac{1}{2^2}\right) = -1.89\text{eV}$$

$$\lambda = \frac{hc}{1.89\text{eV}} = 6.57\times10^{-7}\text{ m} = 657\text{ nm}$$

This transition corresponds to orange light.

2. A red laser, a green laser, and a blue laser shine on different pieces of the same kind of metal, and detectors are set up to measure the presence of emitted electrons. For the red laser, no electrons are detected. For the green laser and the blue laser, electrons are observed flying off of the metal. Which of the following statements must be true?

i) The number of electrons emitted from the metal using the blue laser is greatest

ii) The kinetic energy of electrons emitted from the metal using the blue laser is highest

iii) The red laser would lead to electron emission if the laser intensity was increased

Answer

ii) is true, because the blue light has higher energy than green and red light, and the energy of electrons emitted is proportional to the energy of the photons hitting the metal surface

i) and iii) are incorrect because the number of electrons is related to the number of photons = light intensity, and light intensity does not affect energy of electrons emitted.

Lecture 6: The Atomic Orbital and Quantum Numbers

Summary

One of the main limitations of the Bohr model is that it can only describe an atom with a single electron. To find the properties of multiple electrons in an atom, it is necessary to solve the **Schrodinger equation**, $(K+V)\psi = E\psi$, where K is kinetic energy, V is potential energy $(-1/r$ for an electron in an atom), E is the total magnitude of energy, and ψ is the **wavefunction**, or **orbital** of the electron. The solution to the Schrodinger equation for an electron in a hydrogen atom has three separate components: $\psi = R(r)P(\theta)F(\psi)$. The full form of the solution form has three big implications:

1. Electrons don't really orbit around atoms, at least in the sense that planets orbit around the sun. The solution to the Schrodinger equation yields a wavefunction, which when squared, gives an expression $|\psi|^2 = 1$ for the probability distribution of the electron's location in relation to the nucleus. Further, though each electron has some radius it is most likely to be found, there is also a chance that it is much closer to or much further from the nucleus. For example, while Bohr model electrons with $n=1$ live at exactly 0.529Å from the nucleus, the wavefunction for a real electron in the hydrogen atom has occupational probability peaked at 0.529Å and smeared out on either side of that value. As the principle quantum number increases, the number of **nodes** - forbidden regions - increases, giving distinct bands around the atom where the electron is likely to be.

2. Four quantum numbers are necessary to fully describe a particular solution. The principle quantum number, n is primarily responsible for the energy level of the electron. Just like in the Bohr model, n can take any integer value from 1 to infinity. As n gets larger, the total energy gets less negative (bigger). An electron is equivalently referred to as being in the n^{th} energy level and the n^{th} shell; the remaining quantum numbers describe subshells. The angular momentum quantum number, l, is primarily responsible for the shape of the orbital. The values that l can take on depend on which shell the electron is in: the range goes from 0 to $(n-1)$. The magnetic quantum number, m_l, is responsible for the orientation of the orbital in space. Its values depend on both n and l, and the range of m_l goes from $(-l)$ to (l). Finally, the spin quantum number, m_s can have one of two values: $+1/2$ or $-1/2$, which is equivalently referred to as up or down.

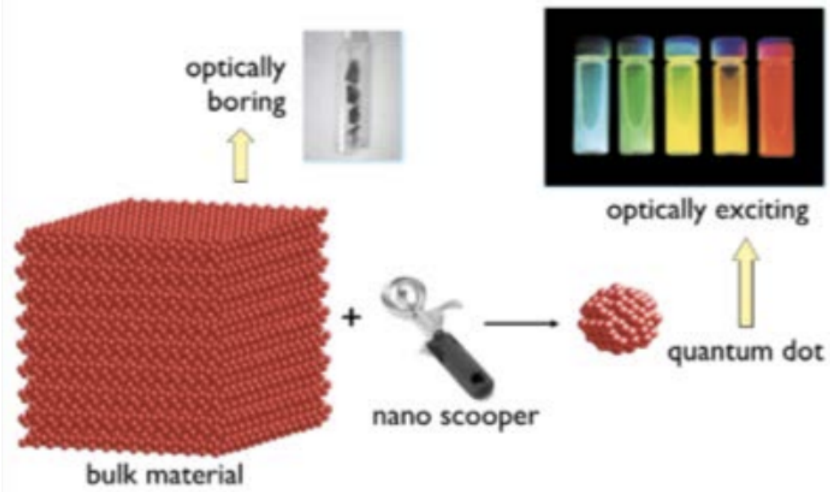
3. Electrons that solve the Schrodinger equation are distinct from Bohr electrons. While there is only one electron per shell in the Bohr model, the Schrodinger equation gives degenerate solutions: as n increases, there are more and more orbital levels. Further, the Bohr model gives a fixed allowed radius for the electron to live, while the Schrodinger equation gives a distribution of probability that an electron is at a given distance from the center (and some forbidden zones!). Finally, though the Bohr model could only describe the behavior of one-electron atoms, the Schrodinger equation is much more broad: it can describe the electronic structure of an atom with any number of electrons.

We also discussed how the values for the l quantum number get the letter names $\mathrm{s}, \mathrm{p}, \mathrm{d}$, and f corresponding to $l=0,1,2,3$, respectively. If we say an electron is in the $2s$ orbital, then we know it corresponds to the quantum numbers $n=2, l=0, m_l=0$, and spin could be up or down. Other examples of sets of quantum numbers and the corresponding orbitals were covered and these hydrogen orbitals were shown as the building blocks of chemistry. That's because to describe an atom and its properties, we fill these orbitals from lowest energy up, with the number of electrons Z in the atom. This occupation follows a general trend that is the topic of the next lecture, but in this one we covered a very important rule: the Pauli Exclusion Principle. This rule states that no two electrons can have the same set of quantum numbers, meaning that two electrons and *only* two electrons can occupy any given orbital.

Why this matters

Quantum weirdness is one of the most important reasons why nanotechnology has gotten so much attention recently. Now, there has been quite a bit of press about nanotechnology over the last two decades, but one of my all-time favorite articles appeared long ago in the U.K. Telegraph: “How Super-Cows and Nanotechnology will Make Ice Cream Healthy.” I always remember that piece because of the way they define nanotechnology: they describe a company as “experimenting with nanotechnology, or the science of invisibly tiny things.” I suppose I like this quote because of how ridiculous it is, since first of all there are many different realms of science and engineering associated with tiny things we cannot see (nanotechnology is one of them, but how about nuclear physics with its quarks and gluons, or solar wind with its hot plasma particles that reach our earth only to be deflected by our planet’s magnetic field, or dark matter?). Second of all, I like this quote because it shines a spotlight – albeit incorrectly – on one hold-up in nanotechnology development, which was not being able to observe what was happening. This changed once we could use electrons as a way to illuminate matter, as discussed in last chapter’s Why This Matters.

The main point is that nanotechnology holds great promise. Not so much for the reasons that gave it fame in the early 2000’s (healthy ice cream being the least of it, we were supposed to have a space elevator by now!), but rather because of the chemistry that’s “under the hood” of nanotechnology. What does nanotech even mean, and why do we have a whole name for it? Let’s answer that with an example directly related to today’s lecture.



Images of bulk semiconductors, ice cream scoop, quantum dot © sources unknown.

We’ve been talking about orbitals of electrons in atoms and how the orbital is the probability cloud for the electron. Well what if we take that cloud, and we squeeze it? Or in other words, confine it so that it can’t take up the same volume as it typically would. There’s a name for that: quantum confinement. And when we confine quantum things, like in this case an electron in an atom, new properties emerge. Take color as an example. For a piece of bulk material, where “bulk” here just means it’s not nanosized, I might have something that's kind of optically boring. It's just a piece of gray material. But then I take out my nano-ice-cream-scooper and I make a little tiny chunk of the material. Suddenly, without changing anything except the size, I can tune the color to pretty much anything I want!

The fact that changing the size of this material allows us to tune a given property is quite incredible. Imagine if I were to take one of those strips of metal from your first Goodie Bag and break it into two pieces: you wouldn't expect the color of the metal to change. But if you could break just a tiny piece of it off, like one with just 10-20 atoms in it, then that piece would change color. How weird is that? It's because of this electron cloud running out of real estate when the amount of matter is small enough. When it's nanoscale, the confined probability cloud changes the energy of the electron, which in turn changes the color of the material. We talked about electrons changing their energy levels in atoms as a way to either absorb or emit a photon corresponding to that energy shift. Well here we've got a new way to shift the starting and terminating levels themselves, simply by changing the size of the material. That's an example of why nano is such a big deal.

The ability to control the properties of a material is one of the foundations of our modern era. As we've already learned, understanding the periodic table of the elements and all of the differences between the behavior of these elements gave scientists and engineers knowledge of the basic ingredients that are used to build our world. Going nano is kind of like adding a whole other dimension to the periodic table: it's like each element can now do new things, take on new properties, and be utilized in new applications.

Why this employs

Quantum computing has gotten a lot of attention recently, and for good reason. Over the past decade, we have reached the point where quantum bits, or qubits, can be made and controlled experimentally. The computers we use today manipulate information in the form of individual bits, which are the famous 1's and 0's of the last 50+ years. But in a quantum computer, the quantum mechanical phenomena that we've been learning about in this chapter are used to manipulate information.

It's qubits that hold the key since those are the keepers of quantum states, which have quantum numbers just like the electron states in an atom. When two qubits interact with one another we get much more than just 1's and 0's, instead we get all possible superpositions. It's like being able to harness the probability cloud as a computing cloud where all possible answers are computed at once.

Quantum computing is getting a lot bigger and a lot more exciting, with many companies predicting commercial quantum computers by 2025. The Why This Employs idea for this lecture is to take those quantum states we've just discussed and run with them. . . all the way to Google's Artificial Intelligence Lab, or to the team at IBM Q, or to D-Wave, or to the folks at Intel working on their Qubit Chips, or to any of the 63 companies currently listed at Wikipedia under "Companies worldwide engaged in the development of quantum computing." A list that is growing rapidly. And that doesn't even include doing research on this topic in a lab here at MIT :)

Example problems

1. Write the quantum numbers for each electron in a neutral carbon atom.

Answer

Note: the spin signs are selected arbitrarily, so it would be just as correct to flip them all. For

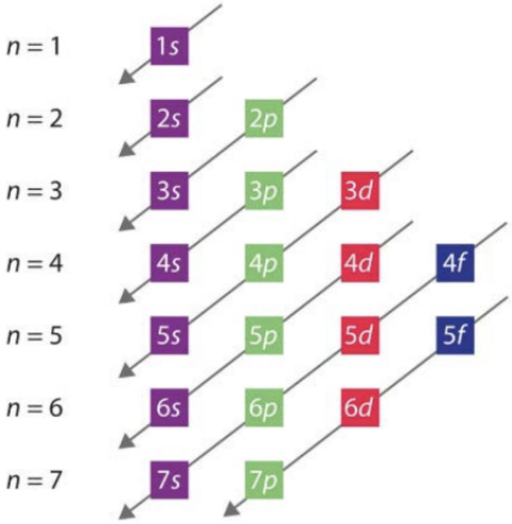
n	l	m	m_s
1	0	0	$1/2$
1	0	0	$-1/2$
2	0	0	$1/2$
2	0	0	$-1/2$
2	1	-1	$1/2$
2	1	0	$1/2$

the 2p electrons, they must have the same spin due to Hund's rule.

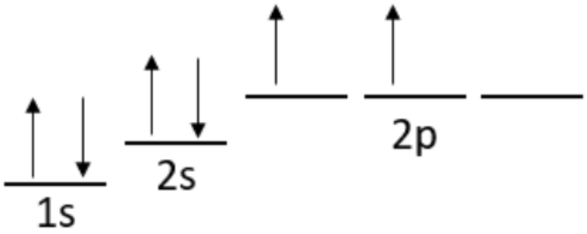
Lecture 7: Filling the Periodic Table and Our First Bond (it’s Ionic)

Summary

The **Aufbau principle** is a tool used to remember the (typical) order in which subshells are filled in a multielectron atom. Electron interactions complicate which subshells are filled first: shielding and orbital penetration affect which combination of electron energy and shape (quantum numbers n and l, respectively), is the next-most-stable state. The Aufbau principle is often represented visually. Though the Aufbau principle generally gives the order that electrons fill in the subshells, it doesn't tell the full story. Previously, we learned that each orbital can hold two electrons: one spin up and one spin down. We also learned that each value of l, written here as $\mathrm{s}, \mathrm{p}, \mathrm{d}$, and f, can have a different number of subshells based on the allowed values of m_l. The **electronic configuration** of any atom can be written using these guidelines: for example, potassium is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$. Often, the electronic configuration is shortened to include only the nearest fully occupied noble gas atom and the valence electrons: in this case, potassium is [Ar] $n = 4s^1$.



When an atom has only a partially filled shell, **Hund's rule** comes in to play: all of the orbitals in the partially-filled subshell must be singly occupied before any are doubly occupied. For C, which has 6 electrons and electronic configuration $1s^2 2s^2 2p^2$, Hund's rule tells us that the electrons are distributed as shown in the diagram below.



If the elements are arranged by increasing number of electrons (and protons), **periodic trends** start to emerge, and electron filling explains the organization of the Periodic Table with blocks that correspond to the subshell being filled. The s- and p-blocks are “main group” elements while those in the d-block are “transition elements” and “f-block” are “inner transition elements.” A larger principal quantum number n corresponds to bigger orbitals and therefore bigger atoms: from this, we can predict that atomic radius should increase down a period in the periodic table. On the other hand, having more protons pulls electrons in towards the atom, so atomic radius gets smaller going from left to right across a row. If an atom loses an electron, its radius decreases: this kind of atom is called a “cation.” Similarly, if an atom gains an electron, the “anion” is bigger.

Finally, we learned that ionic bonds are the electrostatic attraction between two oppositely charged ions: they're formed by the transfer of one or more electrons between the ions. The strength of an ionic bond can be approximated by a Coulomb interaction: $E = kQQ/r$. If the distance between two ionically bonded atoms is greater, the bond will generally be weaker! Just by looking at the size of the ions that make up the bond, we can infer a lot of information about the corresponding ionic solid.

Why this matters

We just made our first bond in 3.091, and it's a strong one! Take a look at this table of lattice energies (in $\mathrm{kJ/mol}$) for a bunch of ionic solids. The range of ionic bond strength spans an order of magnitude in this chart, but even the weakest solid listed (potassium iodide, KI, at $649\ \mathrm{kJ/mol}$) is still really strong with a melting temperature of $681^{\circ}\mathrm{C}$.

Cation	Anion				
	F-	Cl-	Br-	I-	O2-
Li+	1,036	853	807	757	2,925
Na+	923	787	747	704	2,695
K+	821	715	682	649	2,360
Be2+	3,505	3,020	2,914	2,800	4,443
Mg2+	2,957	2,524	2,440	2,327	3,791
Ca2+	2,630	2,258	2,176	2,074	3,401
Al3+	5,215	5,492	5,361	5,218	15,916

The strongest ionic solid listed in this table is aluminum oxide, formed by combining $2\mathrm{Al}$ atoms for every 3 O atoms (this balances charge with Al being 3^{+} and O being 2^{-}). Aluminum oxide melts at a whopping $2,072^{\circ}\mathrm{C}$, and its widely used for its hardness and strength. For example, $\mathrm{Al_2O_3}$ is used as an abrasive, including as a much less expensive substitute for diamond, and in many types of sandpaper or cutting tools. Because of its strength, it's used as an additive in many applications, including toothpaste! For this Why This Matters moment, I'd like to focus on an unfilled need rather than an established solution. This is a problem where a harder material with the right properties and in the right structure could change millions of lives.

Hemodialysis is a process to purify the blood of a person who has kidneys that don't work correctly. A typical patient will have to go in 3 times per week, sit in a chair that looks something like this for about 4 hours per session, totaling 600 hours of their time and a cost of $\$80,000$undergo hemodialysis, and this number has been growing steadily over the past 30 years. It is expected that, as the incidence of cardiovascular diseases such as diabetes and hypertension increase, the population of individuals needing dialysis will grow as well. That machine on the left of the chair in the picture is a hemodialysis machine. During the process blood is removed from the body through an access point in a patient's vein, and passed through the machine which removes toxins and excess fluids, after which the filtered blood is returned to the body through another access point back into circulation. Here's Why This Matters.

If that machine could be shrunk down to a much smaller size and made portable, then patients would be able to do this at home or while traveling or wherever they are, which would seriously improve their quality of life. But current filters don’t work well enough to make the device small and portable, so people who need hemodialysis treatment are stuck. That is, unless a new filter could be invented, one that satisfies three key criteria: 1) the material must be biocompatible, 2) it must allow for selective filtration so it can remove some things but not others, and 3) it must provide efficient and fast filtration. Such a filter does not currently exist. Current filters are cellulose-based porous membranes with highly variable pore size, meaning that molecular selectivity is difficult to control. The pores in current filters also overlap a lot, making tortuous paths that slow the fluid motion, increasing the amount of time it takes for the blood to flow through. Current filters are easily clogged, they’re delicate and tough to clean, so at best they’re single-use only and at worst they get clogged so much so quickly that even achieving a single use is difficult.

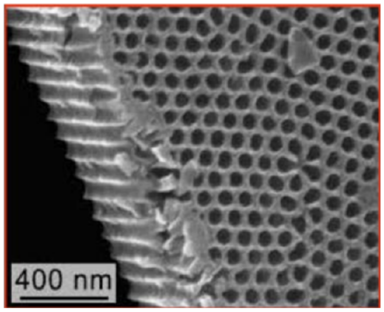


Image of alumina filter by Assaud, L. et al. Beilstein Journal of Nanotechnology 5 (2014): 162-72. License: CC BY.

Here we can consider the strong ionic bonds we learned about in this lecture. Here's a picture of a new filter made out of Al_2O_3. Note from the scale bar that the pores are seriously small, only 10 s of nanometers in diameter. They're also aligned in the same direction (so none of that tortuous flow slowing things down), which means the flow through them will be fast and efficient. And note that the pores are all roughly the same size, which gives the filter the ability to sharply reject the targeted toxins. And of course, since it's a strong ionic solid, this filter can be cleaned very aggressively with pretty much whatever cleaning chemicals or thermal treatment you care to throw at it. There's still much work to be done, like reducing the cost of making such filters, and they're still a bit too brittle, but in general ionic solids hold tremendous potential as next-generation filters!

Why this employs

That example of a new type of ultra-resilient filter is only one of many where new high strength materials are needed. And it's not just the material itself but also the way it's processed. And because of how badly resilient new materials are needed, many of the larger chemical companies like Dow, Saint-Gobain, BASF, Sinopec, LG Chem, Arkema, or Mitsubishi Chemical, to name just a few of the giants (all of these have annual sales in the $10's of billions.

And all of these companies have large teams working on making high strength materials. Sometimes it's high strength steel, sometimes it's plastic, and of course other times, ionic materials. All of these companies have job postings, but an excellent way to explore career interest is to do internships, and all of these companies also have internships for students. You could go directly to the company web site, or you could also check out the resources we have here at MIT. There are a lot of them.

For example, take a look at the web page capd.mit.edu, where if you click on "Jobs and Internships" you'll get all sorts of support and resources. Definitely worth checking out!

Example Problems

1. Rank the following atoms in terms of size, ionization energy, and electronegativity:

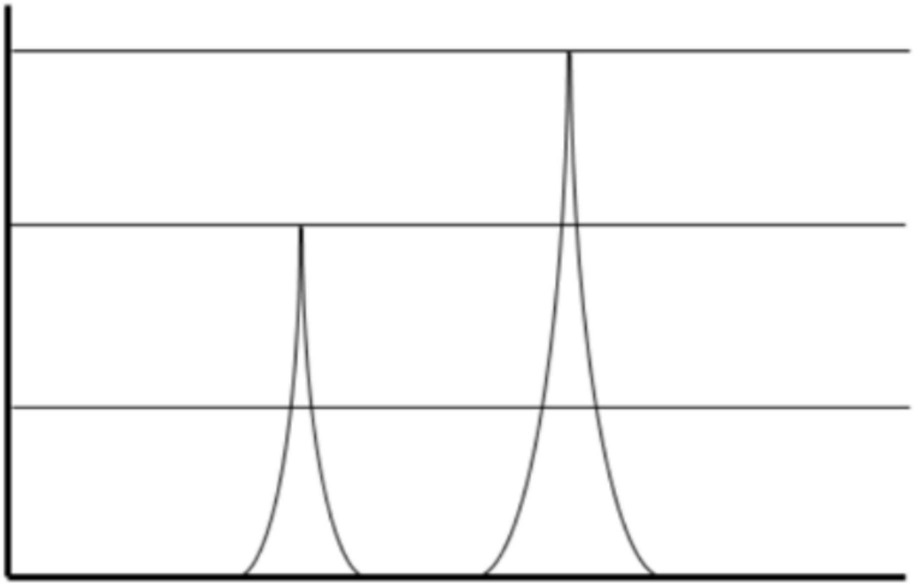
$\text{Ge} \qquad \text{Rb} \qquad \text{Sn} \qquad \text{I}$

Answer

As the period increases down the periodic table, electrons are more and more shielded from the nucleus, so atomic size increases. Additionally, as the group number increases across the periodic table, there are more and more protons and therefore increased attraction from the nucleus, so atomic size decreases.

(smallest) $\text{Ge} \qquad \text{I} \qquad \text{Sn} \qquad \text{Rb}$ (largest)

2. Below is a PES spectrum for the outer electrons of a mystery element. Label the axes and the direction of increasing ionization energy.



a) If the configuration of the inner electrons of the mystery element are the same as neon, identify the element.

Answer

Phosphorous: its electronic configuration is $[\mathrm{Ne}] 2\,\mathrm{s}^2 3\mathrm{p}^3$

b) Separately, while you were taking PES spectra for carbon in a vacuum, the seal on the vacuum machine broke and let in an unknown gas. You observe the following on the contaminated spectrum:

i. There are 6 peaks total (including the carbon peaks)

ii. Five peaks are the same height

iii. One peak is three times higher than the others

What is the contaminating element? Explain your reasoning.

Answer

The electronic configuration of carbon is $1\,\mathrm{s}^2 2\,\mathrm{s}^2 2\mathrm{p}^2$. Since there are 2 electrons in each shell, these three peaks must be the same height. The additional peaks must therefore belong to $1\,\mathrm{s}^2 2\,\mathrm{s}^2\,2\mathrm{p}^6$, since one of the peaks is three times higher than the rest. The contaminating gas is Ne.

Lecture 8: Ions, Ionization, and Valence

Summary

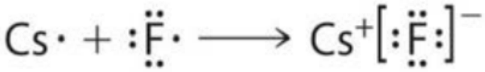
This lecture we continued our discussion of ionization energy. We saw that, similar to Li and Be in the last lecture, the ionization energy for the elements along the periods (from left to right on the periodic table) in the p and d block increases due to a higher number of protons leading to an increased nuclear pull. It makes sense that more energy is necessary to free them. On the other hand, going down the groups (from the top to bottom on the periodic table) the ionization energy decreases because the increased shielding and distance from the nucleus is more significant than the increased nuclear pull due to added protons.

The reason for increasing ionization energies for electrons closer to the nucleus is that these electrons are more tightly bound. For example, Li’s first ionization energy is 5.4 eV, while its second ionization energy is 122 eV. This second electron experiences less shielding than the first. This ionization energy information can be viewed on a **Photo-electron Spectroscopy** (PES) plot. This is a plot showing ionization energy versus relative intensity for a given element. PES involves shining enough energy on an atom to ionize all of its electrons, measuring their kinetic energy, with the difference being equal to how much energy the electron was bound by. PES is a simple, powerful technique to directly measure electron occupation.

Another periodic trend discussed was **electron affinity**, or the change in energy that accompanies an additional electron. The halogens (group 17 on the periodic table) have the highest electron affinity, because an additional electron would result in a full octet and complete filling of the subshell. Electron affinity increases along the periods of the periodic table up until the halogens.

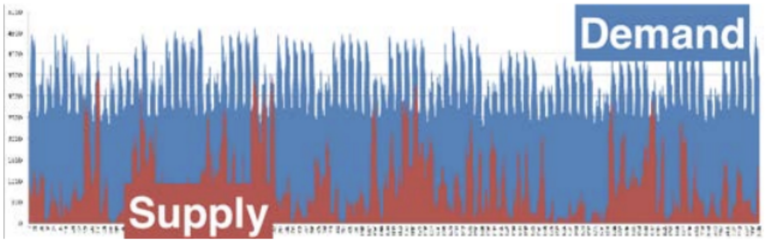
This lecture also laid out the idea of **valence electrons**. These are the electrons that occupy orbitals beyond the highest filled noble gas core. For example, carbon and silicon both have 4 valence electrons. Carbon's highest filled noble gas core is [He], while silicon’s is [Ne]. Valence electrons are what drive chemical bonds. Valence electrons on atoms are depicted using **Lewis Dot Diagrams**, which are the chemical symbols of the elements with dots surrounding them that represent the valence electrons. Lewis Dot Structures are helpful in visualizing the **octet rule**, which states that atoms (ignoring the transition metals for now) are at their lowest and most stable energy state with 8 electrons in their valence.

In this lecture we began applying Lewis Dot Structures to ionic bonds. Cations are depicted with plus signs on their top right corner, and anions with negative signs, as shown below.



Why this matters

In this lecture, we’ve been focusing on atoms that lose or gain electrons, also called ions. Now we’ll discuss how this topic relates to renewable energy solutions.



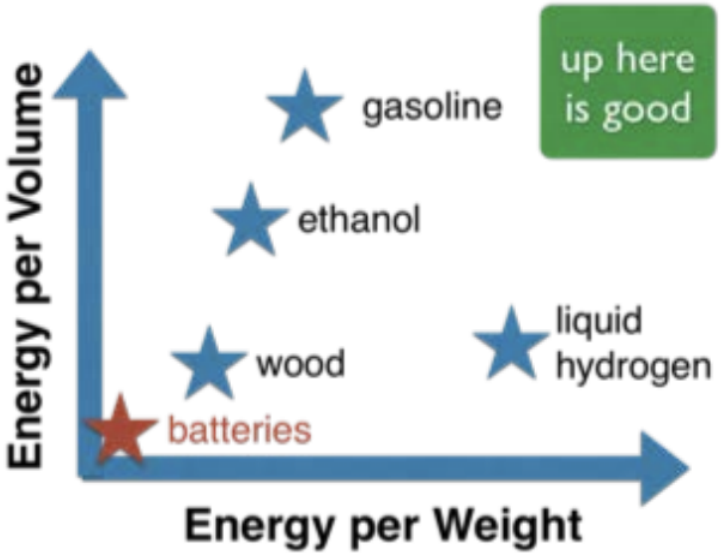
Take a look at this plot of the demand of electricity (in blue) vs. supply of electricity from a wind farm (in red), recorded over a two and a half month period in 2013 in Denmark. Notice that on the demand side, there’s some variability, but there’s also a lot of regularity. The 5-day work week draws more energy than the weekends, and the amount of energy needed doesn’t really vary much from week to week. Now contrast that with the supply of electricity from a wind turbine farm. Even if you put the turbines in a known windy area, there’s still a huge amount of variability. Wind energy is not that expensive to produce, but the biggest challenge isn’t cost, it’s steadiness of supply. If you think about how to build enough of this type of unreliable supply to meet the consistent demand, you’d need to overbuild capacity by a factor of at least 10 (and even that wouldn’t be enough on some days)! That of course isn’t going to be economically feasible, so the real solution, if we want to expand how much energy we get from intermittent renewables like wind and solar, is to be able to store the energy for when it’s needed. If we have reliable storage, then the supply can be quite unreliable and we’d still be able to meet a steady demand, as long as on average the supply can meet it.

One of the easiest ways to store energy is to push something up a hill and then let it roll back down. Push a ball up a hill and then hold it there, and when you want the stored potential energy back as kinetic energy, simply let it go. We pump water up hills, called “pumped hydro,” which is currently one of the only viable technologies that can scale up to the size (meaning, power) of actual electricity grids. A massive amount of water is pumped up a hill when there’s excess energy supply, and then rolled back down to turn a turbine to generate electricity when there’s excess demand. Although this is a relatively cheap storage solution, there are all sorts of problems with scaling up any further than it is today, primarily because of the low energy we get from gravitational energy and therefore how much land is required. There’s a great post that explains why it will be hard to increase pumped hydro as an energy storage technology at dothemath, which is a cool site in general if you haven’t seen it: https://dothemath.ucsd.edu/2011/11/p...p-the-storage/.

So what else can we pump up a hill to store energy? This is where our ions come into the picture! Ions are the key ingredient in batteries. Think of a battery as an electronic hill, and when the battery is charged the ions are getting pumped up. Cations in particular, like Li+, get pushed up the energy hill, and the lower energy state (down at the bottom of the hill) would be one in which it can get that electron back and become neutral again. When the circuit is closed, the cation falls down the energy hill to meet up with the electron, which goes around the circuit doing work along the way. In this case instead of mechanical work like the water, the electron is doing electrical work directly. This is one of the great advantages of electrochemical storage (a nice way of saying a battery), namely that we're storing directly the kind of energy we mostly need, electrical energy. Stored mechanical or thermal energy later often needs to be converted into electrical at great efficiency loss.

But how good are batteries today, really? Could they ever be used to store the massive amounts of energy needed at "grid scales"? For reference, the U.S. uses 3 TW on average, or 3×10^{12} Watts $= 3 \times 10^{12}$ Joules/second of energy, so you get a sense of what it means to be at the scale of the grid. Let's make sure we're straight on energy vs. power: a Watt is a Joule/second which is energy per time, which is power. That's an important metric since we need to be able to access energy at a given pace. The total amount of energy is power multiplied by time, so for the U.S. if our average power draw as a nation is 3TW, then our daily energy use is 72TW-hours (TWh) and our yearly energy use is $26,280\text{TWh}$ Just to give you a sense of how big this number is, a typical AAA battery stores about a single Wh of energy. That means if we wanted to store the U.S. energy needs all we would need to do is build a storage facility containing $26,280,000,000,000$AAA batteries! In case you're wondering, that's about a million times the number of AAA batteries sold in the U.S. each year.

And therein lies the problem with batteries, namely their low energy density. But as I hope you're seeing in this class, such problems are often opportunities for chemistry to come in and make a game-changing difference.



This figure shows the energy per weight vs. energy per volume for a few different storage materials. Note that batteries are in the lower left, which isn't so good. You can see why gasoline is so unique: it's got a very high energy density both by weight and by volume, and on top of that it's safe and easy to transport and extremely cheap. The competition is tough.

One liter of gasoline stores 33 megajoules (MJ) of energy, or about 9 kWh if you prefer those units. That liter costs about a dollar. Now take one MIT Professor, who can output about 60 W or 60 J/s on a good day. This means that the professor can generate the same amount of energy as in a liter of gasoline, 33MJ, in roughly 153 hours. Given the average pay of an MIT professor of $\$10/\text{hr}$, it would cost $\$1530$ to get the energy from the professor. Compared to about $\$1$ to get the same amount of stored energy from the gasoline. Batteries need to start looking a lot more like gasoline and a lot less like an MIT Professor if they're going to be competitive grid-scale energy storage technologies.

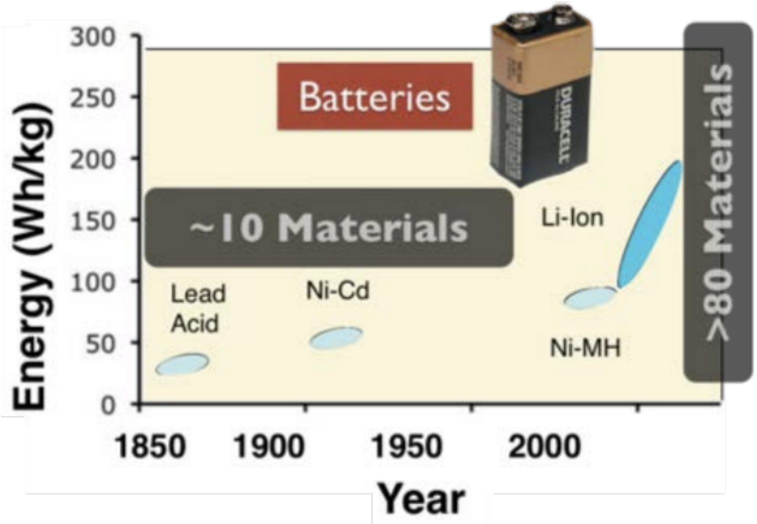


Figure energy vs. year © source unknown. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/fairuse.

The good news is that there has already been tremendous progress in just the last 10-20 years. Check out this plot of energy density vs. year for batteries. Notice the very slow progress for about 150 years, with a doubling of energy density occurring roughly every 60 years. Then the slope of progress changes, and the reason is simple: chemistry. Specifically, the rapid improvements are happening because we've reached an era wherein we can make energy hills for ions with many more types of materials than ever before. I've added to the plot the number of materials cathodes are made of: historically only about 10 different cathode materials were used during those slow-paced first 150 years, but now we can and do make cathodes out of over 80 different materials, and the number is growing by the week. This explosion of materials possibility is due to a deeper understanding of ions and new ability to design materials with more efficient energy landscapes for them to traverse. So yes, there's a lot of work to do to make batteries competitive in grid-scale energy storage, but the time is absolutely ripe to get it done.

Why this employs

Knowledge of ions can get you all sorts of jobs. But since I focused on the battery field in Why This Matters, let's focus on that same topic here. The global battery market is already enormous and its projected growth is stunning. Here's a chart from a report from Deutsche Bank from 2016 showing the projected near-term growth in battery production by some of the top companies that make batteries. All of these companies are hiring thousands and thousands of scientists and engineers, techno-economists (predicting tech trends is not easy!), packaging and mechanical design experts, and much more, all to work on various aspects of one thing: the ion. And there are many more jobs than that. Big battery companies like those listed in the chart are investing heavily in hiring people to work on batteries, but so are little companies. And so are many research teams at universities, who are spinning out companies based on new concepts.

Not only are there many different battery chemistries that have been around for a while and are being greatly improved, from lithium-ion to nickel-metal-hydride to lead-acid, but there are also so many exciting completely new directions for batteries. All of these future battery technologies involve jobs, and while it's hard to list them all because of how much the field has grown, here are a few cool directions companies are pursuing:

- Silicon-based anodes (replacing the currently used graphite) which would increase energy density by a factor of 3
- Using metal nanowires in the electrolyte to prevent breakdown, making the battery last 10 or 100x longer
- Making the electrolyte a solid instead of the current liquid, which would make the battery more stable and allow much faster charge times •
- Throwing graphene into the battery since, anyway, what problem can graphene not solve? (ok, but in all seriousness, graphene has been shown to allow for much faster charge/discharge)
- Making batteries out of foam metals
- Making batteries foldable (paper-thin but that won't break) and also stretchable
- Aluminum air batteries that have demonstrated a 1,100 mile range in an electric car
- Powering the charging of batteries with various means, from wi-fi signals (not inductive wireless, which is something else), to ultrasound, to amino acids, to urine. Batteries made from sodium, zinc, sulfur, magnesium, and so many other

materials!
- Making batteries that can never catch fire

Example problems

1. Choose the larger atom from the following pairs:

a) Rb, Rb^+

Answer

Rb is larger, because it has an additional shell $\left(\mathrm{Rb}^+\right.$ loses its 5 s^1 electron)

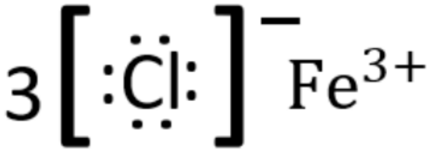
b) Rb^+, Kr

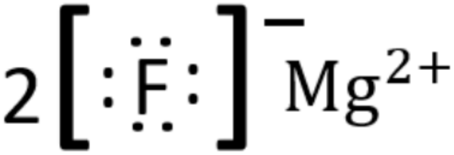
Answer

Kr is larger, because it has one less proton than Rb^+, so the nucleus pulls less on the electrons

2) Draw the Lewis dot structures of $\mathrm{FeCl_3}$ and $\mathrm{MgF_2}$.

Answer





Lecture 9: Lewis Structures, Covalent Bonds, and Resonance

Summary

Covalent bonds are created via the sharing of electrons rather than through electrostatic attraction between cations and anions, as an ionic bonds. The shared electrons in covalent bonds achieve a lower and more stable energy state by interacting with two nuclei instead of one. Lewis Dot Structures represent the two electrons in a covalent bond with lines, as shown for $\mathrm{H_2}$ to the right.

1. Connect atoms, central often less electronegative
2. Determine total number of valence electrons
3. Place bonding pair of electrons between adjacent atoms
4. Starting with terminal atoms, add electrons to each one to form octet (2 for H)
5. If electrons are left over, place on the central atom
6. If central atom hasn't reached octet, use lone pairs from terminal atoms to form multiple bonds to the central atom to achieve octet

It is possible to have more than one Lewis structure that doesn't valuate the octet rule. For these instances, we calculate the formal charge. The sum of the formal charge must equal the overall charge on the molecule or ion. To calculate formal charge, follow these steps:

1. Nonbonding electrons are assigned to the atom on which they are located.
2. Bonding electrons are divided equally between the bonded atoms.

3. Then, the formal charge can be computed for each atom as follows:

$$\text{formal charge } = \text{valence } e^{-} - \left(\text{nonbonding } e^{-\prime}s + \frac{\text{bonding } e^{-\prime}s}{2}\right)$$

In addition to stability, formal charge tells us about the structure's electronegativity—atoms with negative formal charge should be more electronegative, and those with positive formal charge less electronegative.

It's also possible to have two different Lewis structures with the same formal charge. This indicates that the actual molecule is a combination of its most stable resonance structures, as with the ozone example in class, where we have on average 1.5 bonds on either side of the center oxygen.

We also discussed the concept of **polarity** - a measure of how unequally electrons are shared between two atoms in a bond. In nonpolar covalent bonds, the electrons are shared equally, as in H_2.

In polar covalent bonds, the sharing is unequal. **Electronegativity** (χ), the tendency of an atom to attract a shared pair of electrons toward itself, can be used as a measure of polarity in a bond. In a completely nonpolar bond, the two atoms will have identical electronegativities, meaning $\Delta\chi = 0$. In a strong ionic bond, there is a large difference in electronegativities. In CsF, using Pauling's scale, $\Delta\chi = 3.98 - .79 = 3.19$.

Finally, we named some ways that the octet rule can be broken. Some elements, like boron, can have fewer than 8 electrons. Others, like sulfur, can have an **expanded octet**.

Why this matters

Speaking of the CO_2 molecule and its formal charges and stable structure, that's the focus of this Why This Matters. Let's get this done up front: after a century and a half of experiments and data collection, the scientific community has established with enormous consensus that carbon dioxide emissions are the primary cause of climate change. Other theories such as solar cycles or volcanic activity do not correlate with observed temperature changes, and there is now only one consistent explanation for rising global temperatures and our changing climate: anthropogenic greenhouse gases, led by carbon dioxide.

By the way, if anyone (say, I don't know, a politician?) were to tell you something like, "There is tremendous disagreement as to whether the earth is round. The debate over the earth's shape should be encouraged - in classrooms, public forums, and the halls of Congress," you would call such a remark either obliviousness or a lie. This is the same kind of lie told by many people about the facts of climate change. A great deal of media coverage focuses on how to define such "alternative facts," but categorizing the remark is beside the point. Regardless of what we call it, this type of statement is a threat to the very foundations of science, to reason-based argument, and therefore to society. Politicians may live in a "post-fact" world, but scientists do not, and cannot. There is no "post-fact science."

Ok, back to our molecule. Why is this particular molecule so important for climate change and global warming? CO_2 is called a "greenhouse gas" because of its ability to absorb infrared radiation, which in turn warms the planet. Take a look back at the plot of intensity of solar radiation hitting the planet as a function of frequency, from Why This Matters in lecture 4. Yellow is what strikes the upper atmosphere and red is what hits earth's surface, so the difference between the yellow and red curves is where some of that solar energy is being absorbed. Small molecules in the atmosphere, like ozone, water, and carbon dioxide, are what absorb that incoming solar energy. You can see where CO_2 is absorbing, out towards the right in the infrared part of the spectrum, while ozone is over on the left in the UV, and water is everywhere. It's the strength of IR absorption that makes CO_2 such an effective greenhouse gas.

About 25% of the solar radiation that hits the earth (so 25% of the integrated red in the plot) gets reflected back out to the universe. But what is reflected is not what is absorbed: instead, most of the energy that is reflected is in the longer wavelength, infrared part of the spectrum. Since CO_2 absorbs efficiently in that part, it acts like a blanket, keeping some of that reflected energy from escaping and redirecting it back to the atmosphere and surface. This blanket keeps us at a cozy $15^{\circ}C$ instead of $-18^{\circ}C$, which is what the average temperature on earth would be if all of that reflected solar energy were able to escape.

As an aside, the term "greenhouse gas" is a bit of a confusing name that has unfortunately stuck. The effect of absorbing long wavelength radiation on the planet's temperature has nothing to do with the effects of warming in a greenhouse used to grow plants, the latter relying mostly on preventing air convection from carrying heat away.

Here's the connection back to our Lewis structures and formal charge. That efficient absorption of CO_2 in the infrared I mentioned, that is directly related to how the atoms in the molecule vibrate. The photon is absorbed because it gets transferred into vibrational energy, so the specific way atoms jiggle around is extremely important to what photons it can absorb and how efficiently it does so. If the CO_2 molecule were to have a triple bond and a single bond, which is a valid Lewis structure but with higher formal charge, then its patterns of vibrations would change dramatically compared to the more stable double-bond case (with formal charge $= 0$), which in turn would make it much less efficient at absorbing all the infrared energy!

Why this employs

Today's lecture has been about the covalent bond, a convenient way to represent it with Lewis structures, and what we can learn about molecules from these structures. It's hard to come across a job in any engineering or science field that doesn't require at least some understanding of the covalent bond since it's so ubiquitous. This also makes it hard to zero in on a specific job market for Why This Employs. That's why I'm going to focus way down to a single material – carbon – and the jobs you could find related to its covalent bonds.

In a few lectures we'll be learning about molecular orbitals and as an example you'll see just how flexible carbon can be in its bonding environment. It's one of the most flexible elements in the whole PT in that it likes single, double, and triple bonds as well as anything in between (read: resonance structures and delocalization). Let's pick one of the many forms carbon takes to focus on here: the aromatic ring. The term aromatic does have its origins in the fact that aromatic molecules can have a sweet fragrance to them, but in fact benzene—the classic aromatic molecule— has no such smell. Instead, the way the term is used in chemistry is that the electrons in a ring of carbon have lowered their energy by delocalizing (yes, resonance structures!). Most often this occurs for a ring that has alternating single and double bonds, which then form an average over its resonance structures. Benzene is the classic example of this, as it is the simplest aromatic ring one can make.

And you've probably heard of benzene before, but what you may not know is just how many ways benzene can be modified to make or do something useful. Check out this chart of only a very small fraction of benzene derivatives, where the ring has some addition(s) to give it a specific property or functionality. This massive variation of the chemistry of a single molecule is possible largely because of that covalent bond that carbon makes.

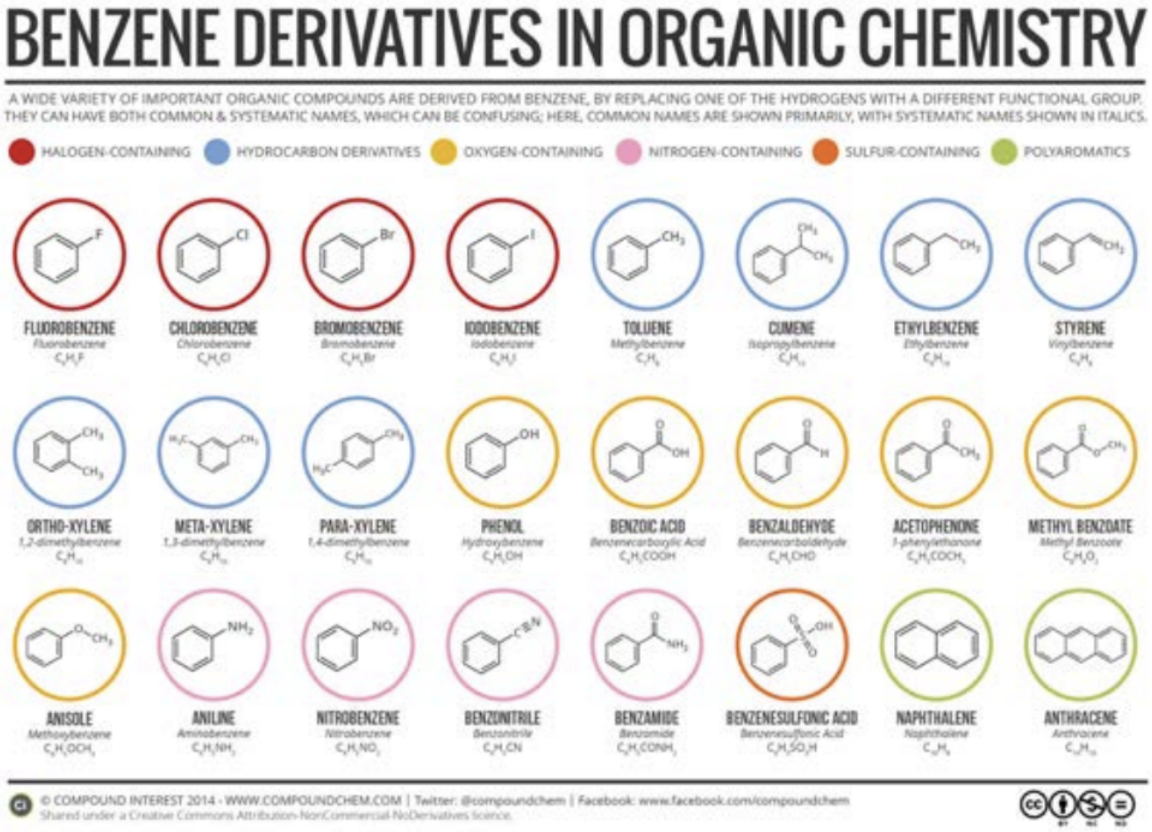


Figure of benzene derivatives by Compound Interest 2014 - www.compoundchem.com. License: CC BY-NC-ND. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/fairuse.

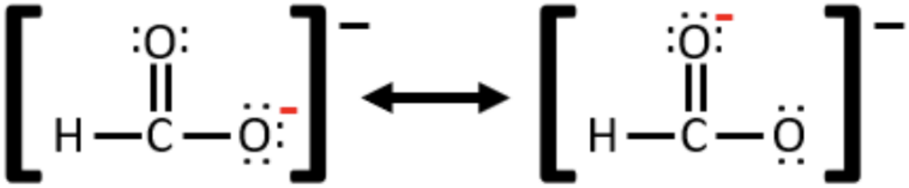
Many materials we encounter on a daily basis are manufactured from derivatives of benzene. Polystyrene, for example, is a polymer formed by connecting styrene molecules together, and billions of kilograms of polystyrene are produced each year. So, certainly jobs in companies that involve manufacturing, recycling, or utilizing plastics like polystyrene are related (I'm thinking a senior chemist position at BASF, a chemical manufacturing company, for example). But the uses of benzene derivatives go far beyond plastics. For example, industries use benzene to make resins, nylon and many different synthetic fibers, as well as lubricants, rubbers, dyes, detergents, drugs, and pesticides. Take medicine as another example: here's the acetaminophen (Tylenol) molecule – it's a benzene derivative!

So the pharmaceuticals industry is also a great place to take your knowledge of benzene (I'm thinking Johnson and Johnson, Pfizer, Novartis, and so on). These companies invest billions and billions of dollars every year to fund research on the development and testing of new medicines, many of which have at their core a resonant Lewis structure.

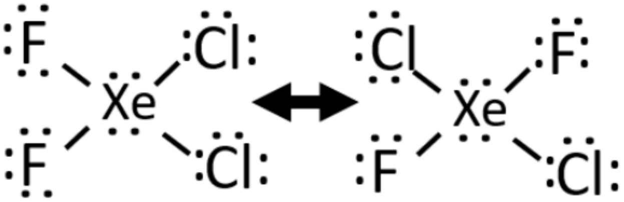
Example Problems

1. Draw the resonance for CHO_2^- and assign formal charges to each atom.

Answer



2. True or false: The following picture shows two resonance structures of a molecule



Answer

False. The two structures aren't resonant structures because the atoms move around.

Further Reading

Lecture 1: Introduction and the chemistry of the periodic table

- History of atoms (not tested):

  https://courses.lumenlearning.com/trident-boundless-chemistry/chapter/history-of-atomic-structure/

- Balancing reactions and limiting reagent:

  https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_(Inorganic_Chemistry)/Chemical_Reactions/Limiting_Reagents

Lecture 2: Counting Atoms and Organizing the Elements

- The mole and molecular weight:

  https://opentextbc.ca/chemistry/chapter/3-1-formula-mass-and-the-mole-concept/

- More info on careers in food science and agricultural chemistry:

  https://www.acs.org/content/acs/en/careers/college-to-career/chemistry-careers/agricultural-and-foodhtml

Lecture 3: The Discovery of the Electron and the Structure of the Atom

- Review of isotopes:

  https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Atomic_Theory/Isotopes

- Plum pudding recipe (not tested):

  https://www.epicurious.com/recipes/food/views/superb-english-plum-pudding-20010

Lecture 4: The Bohr Model and Electronic Transitions

- More on Black Body Radiation, quantization, and a cool video on the photoelectric effect:

  https://chem.libretexts.org/Courses/University_of_Arkansas_Little_Rock/Chem_1402%3A_General_Chemistry_1_(Belford)/Text/6%3A_The_Structure_of_Atoms/6.2%3A_Quantization%3A_Planck%2C_Einstein%2C_Energy%2C_and_Photons*

- Summary of emission and absorption spectra:

  http://physicsnet.co.uk/a-level-physics-as-a2/electromagnetic-radiation-quantum-phenomena/ line-spectra/

- Science in context—Einstein and other prominent scientists fled Nazi Germany (not tested):

  https://physicstoday.scitation.org/do/10.1063/PT.6.4.20180926a/full/

Lecture 5: Wave-Particle Duality and Quantum Mechanics

- More on wave-particle duality and the quantum atom:

  https://www.khanacademy.org/science/physics/quantum-physics/quantum-numbers-and-orbitals/ a/the-quantum-mechanical-model-of-the-atom

- Photoelectron spectroscopy:

  https://www.khanacademy.org/science/chemistry/electronic-structure\-of-atoms/electron-configurationsa/photoelectron-spectroscopy

Lecture 6: The Atomic Orbital and Quantum Numbers

- Quantum numbers:

  https://courses.lumenlearning.com/cheminter/chapter/quantum-numbers/

- The Schrodinger Equation and Particle in a Box (not tested):

  http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/schr.html

- Quantum mechanics crash course:

  https://www.youtube.com/watch?v=qO_W70VegbQ&list=PL8dPuuaLjXtN0ge7yDk_UA0ldZJdhwkoV& index=45

- Introduction to Quantum Mechanics by David J. Griffiths, available here or at your local MIT library:

  https://www.cambridge.org/core/books/introduction-to-quantum-mechanics/990799CA07A83%20/%20FC5312402AF6860311E

Lecture 7: Filling the Periodic Table and Our First Bond (it's Ionic)

- Electronic configurations:

  https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Electronic_Structure_of_Atoms_and_Molecules/Electronic_Configurations/Electronic_Configurations_Intro

- Periodic trends:

  https://opentextbc.ca/introductorychemistry/chapter/periodic-trends-2/

- Ionic bonds:

  https://www.youtube.com/watch?v=zpaHPXVR8WU

Lecture 8: Ions, Ionization, and Valence

Photoelectron Spectroscopy (PES):

https://www.khanacademy.org/science/chemistry/electronic-structure-of-atoms/electron-configurations\ -jay-sal/a/photoelectron-spectroscopy

Lecture 9: Lewis Structures

- Drawing Lewis Dot Diagrams: Extra practice:

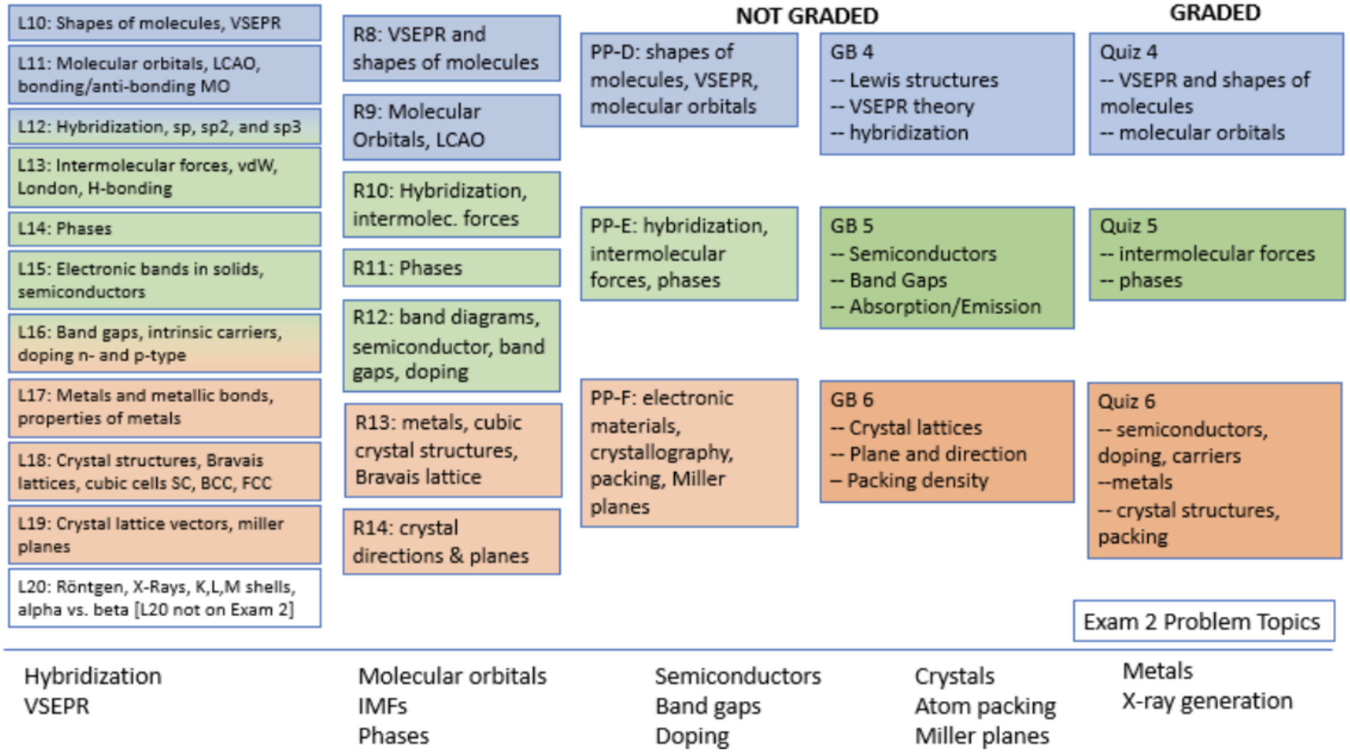
  http://www.chem.ucalgary.ca/courses/351/Carey5th/Ch01/ch1-3depth.html

- Video tutorial:

  https://www.youtube.com/watch?v=ulyopnxjAZ8

5.2: CHEM ATLAS_2

How This Connects: Unit 2, Lectures 10-20



L10: Shapes of molecules, VSEPR

L11: Molecular orbitals, LCAO, bonding/anti-bonding MO

L12: Hybridization, sp, sp2, and sp3

L13: Intermolecular forces, vdW, London, H-bonding

L14: Phases

L15: Electronic bands in solids, semiconductors

L16: Band gaps, intrinsic carriers, doping n- and p-type

L17: Metals and metallic bonds, properties of metals

L18: Crystal structures, Bravais lattices, cubic cells SC, BCC, FCC

L19: Crystal lattice vectors, miller planes

L20: Röntgen, X-Rays, K,L,M shells, alpha vs. beta [L20 not on Exam 2]

R8: VSEPR and shapes of molecules

R9: Molecular Orbitals, LCAO

R10: Hybridization, intermolec. forces

R11: Phases

R12: band diagrams, semiconductor, band gaps, doping

R13: metals, cubic crystal structures, Bravais lattice

R14: crystal directions & planes

NOT GRADED

PP-D: shapes of molecules, VSEPR, molecular orbitals

PP-E: hybridization, intermolecular forces, phases

PP-F: electronic materials, crystallography, packing, Miller planes

GB 4
-- Lewis structures
-- VSEPR theory
-- hybridization

GB 5
-- Semiconductors
-- Band Gaps
-- Absorption/Emission

GB 6
-- Crystal lattices
-- Plane and direction
– Packing density

GRADED

Quiz 4
-- VSEPR and shapes of molecules
-- molecular orbitals

Quiz 5
-- intermolecular forces
-- phases

Quiz 6
-- semiconductors, doping, carriers
--metals
-- crystal structures, packing

Exam 2 Problem Topics

Hybridization
VSEPR

Molecular orbitals
IMFs
Phases

Semiconductors
Band gaps
Doping

Crystals
Atom packing
Miller planes

Metals
X-ray generation

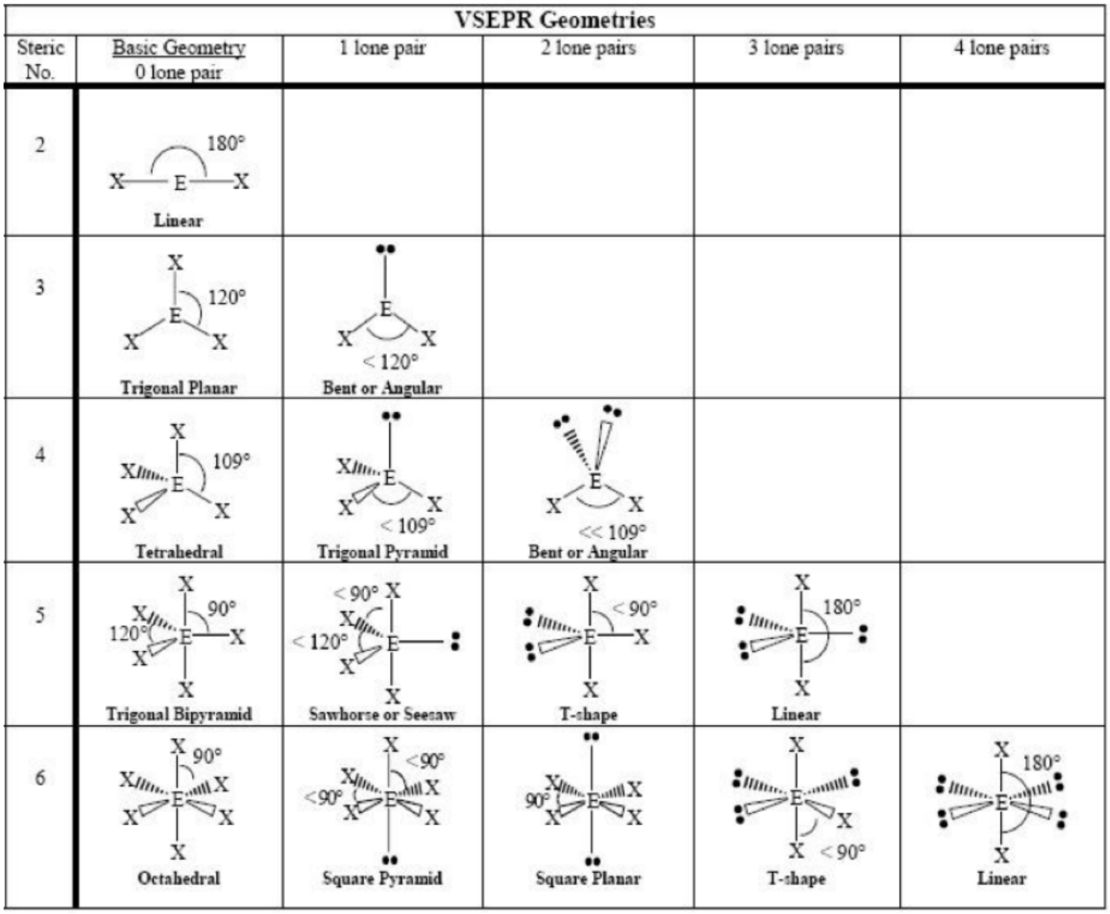
Lecture 10: Shapes of Molecules

Summary

This lecture focused on the Valence Shell Electron Pair Repulsion (VSEPR) model. This model allows us to predict the shapes of molecules—a precursor to more fully understanding their properties. VSEPR is based around electron repulsion, and gives the most stable structures as those that minimize these repulsions. To find the VSEPR representation of a molecule, follow these steps:

1. Write Lewis structure
2. Classify each electron pair as bonding or nonbonding
3. Maximize separation between domains
4. Give more space to non-bonding domains and to bonding domains with higher bond order

A bonding pair (BP) of electrons is any two electrons that take part in a bond. A double bond is made up of 2 BPs, and a triple bond is made up of 3 BPs. A lone pair (LP) of electrons is any two electrons that are not part of a bond. The strength of repulsion between electron pairs, in ascending order, goes as follows: BP-BP, BP-LP, LP-LP. Also, the repulsion of a single BP is less than that of 2 BPs or 3 BPs.

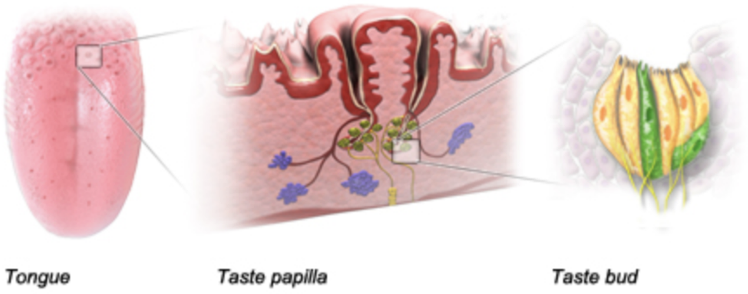


VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal Planar	< 120° Bent or Angular			
4	109° Tetrahedral	< 109° Trigonal Pyramid	<< 109° Bent or Angular		
5	90° 120° Trigonal Bipyramid	< 90° < 120° Sawhorse or Seesaw	< 90° T-shape	180° Linear	
6	90° Octahedral	<90° <90° Square Pyramid	90° Square Planar	< 90° T-shape	180° Linear

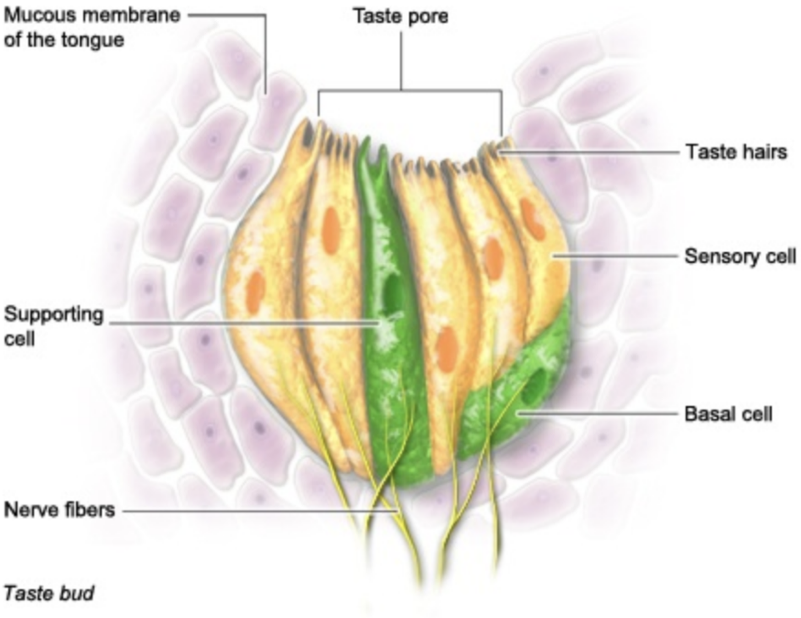
VSEPR Geometries by Boundless Chemistry. License: CC BY-SA. This content is excluded from our Creative Commons license. For information, see https://ocw.mit.edu/fairuse.

Why this matters

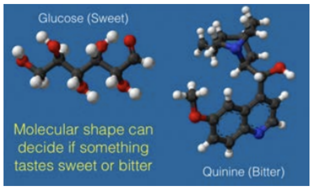
The average human can discriminate between 4,000 and 10,000 different odors. (Before we get excited about how awesome that is, consider that a dog can smell between 10 and 100 thousand times better than a human!). But what is smell, from a chemistry perspective? Taste and smell are related, and thinking about what's behind them goes back to the ancient Greeks. None other than our friend Democritus (atomism!) speculated that the taste of a substance was due to the shape of its component particles. He thought that acidic particles would be sharp, since they felt like they attacked your mouth, while sweet stuff was made of nice cuddly soft shapes. While his reasoning was quite simple, the idea that taste and smell were governed by shape was amazingly prescient.



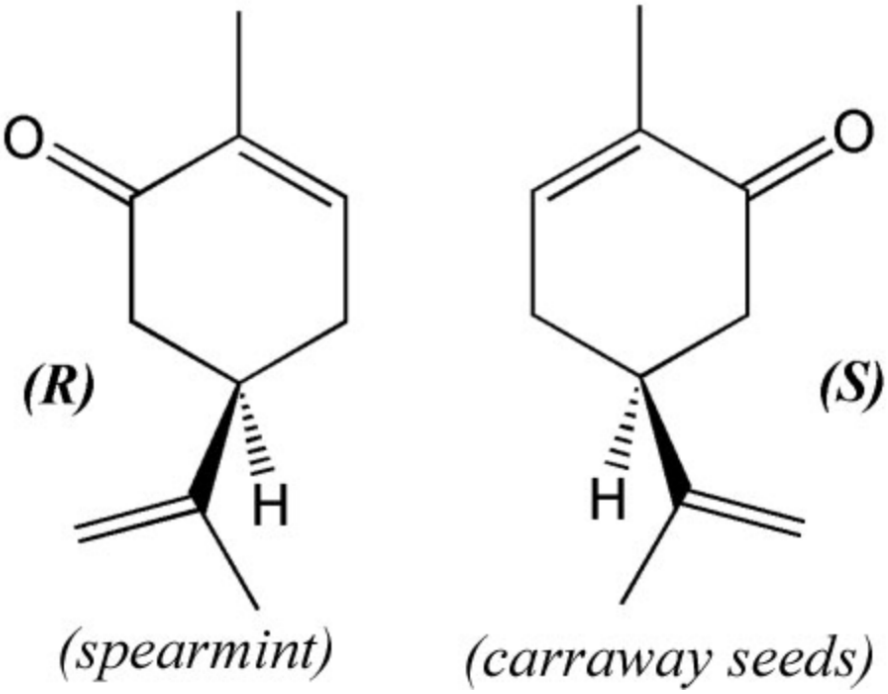
Fast forward 2500 years and we now know that the ability to taste and smell works through “receptor sites” in the tongue and nose. Here’s the tongue broken down, showing the receptor site on the right, and below that is a larger view of receptor site with various parts labeled. Note that the receptor site is also what we call a taste bud. Signals that get sent from this receptor site to the brain through the nerve fibers determine what you taste, and the signal is deeply dependent not just on the composition of the molecule itself, but also on its shape.



Take a look at the two molecules below, glucose which tastes sweet, and quinine which tastes bitter. Their chemistries are different and the way the chemistry of the molecule bonds to the sensory cell is crucial, but the way the shape fits into the pore itself and impacts the orientation of the molecule on the sensory cell can be equally important. If we didn’t know the shapes of these molecules, we’d write them out as simple 2D Lewis structures, but it’s those 3D shapes that you see in the figure that distinguish their tastes!

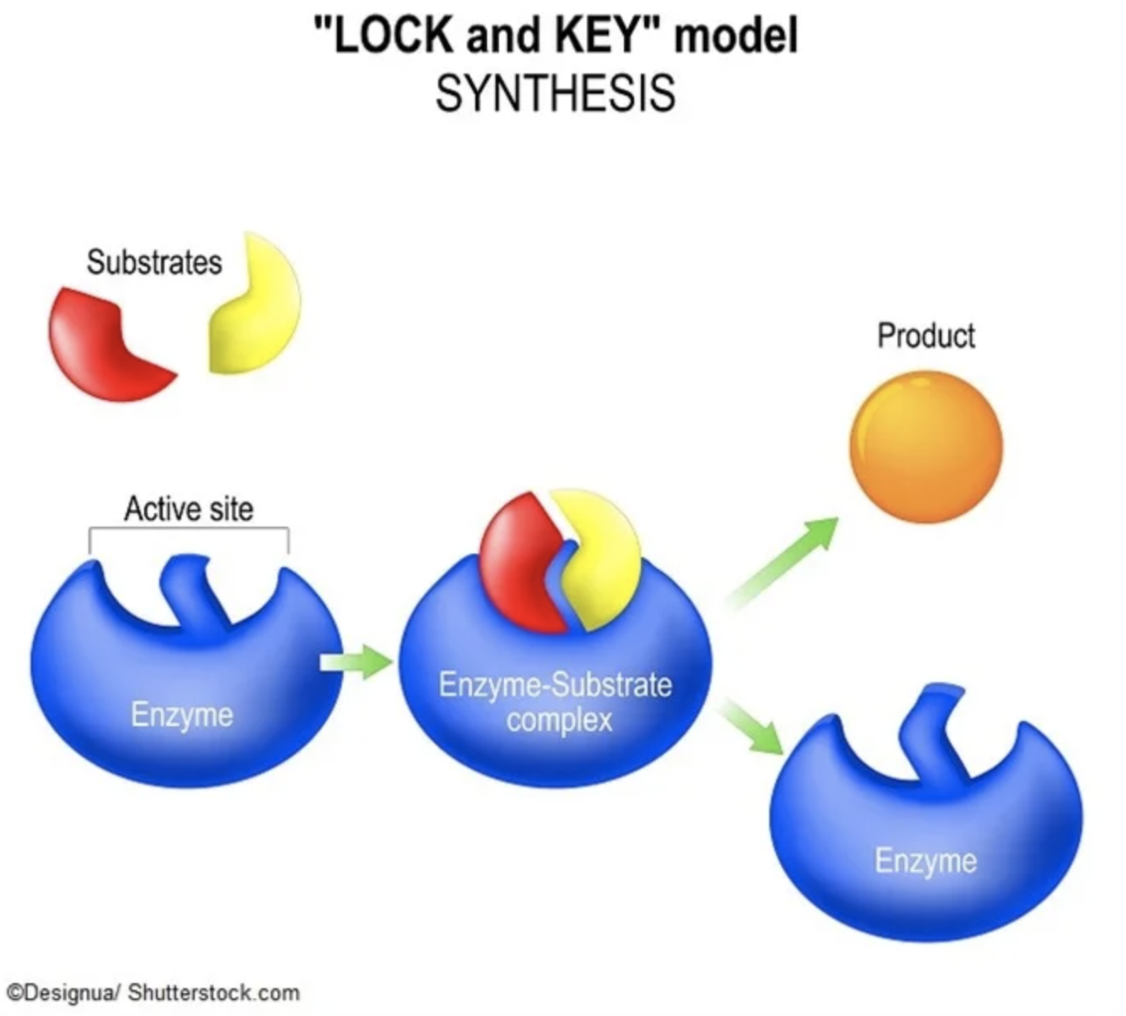


In the case of the carvone molecule, or $C_{10}H_{14}O$, we have an even more striking example of the role of shape on smell. This molecule forms two mirror images, denoted R and S in the figure below. The R form smells like spearmint while the S form smells like caraway seeds. Same exact chemistry, different shape, different smell. Many molecules can take on two forms like this with mirror symmetry but that aren’t the same, and such pairs are called enantiomers. Actually, beyond molecules, enantiomers can be anything. Your hands, for example, are enantiomers. If you hold them up facing one another you’ll see they have mirror symmetry, and if you try to rotate one around the other you’ll see you can’t superimpose them. For this reason, the property of having mirror symmetry but not being superimposable is called handedness, or chirality. The fact that the two enantiomers are perceived as smelling different shows that those receptor cells must contain chiral groups, allowing them to respond more strongly to one enantiomer than to the other. Thus, both for the molecule being smelled and for the molecules used to do the smelling, molecular shape holds the key!



Why this employs

It’s about time we talk about enzymes. These are molecules, often proteins, folded into a specific (and complicated!) shape, that speed up chemical reactions in your body. Enzymes are absolutely essential for so many crucial functions of our body, including respiration, digestion, muscle and nerve function, and many more. In digestion, the role of an enzyme molecule can speed up a needed reaction by a factor of a million times! That lets you digest your dinner in hours rather than, well, a thousand years.



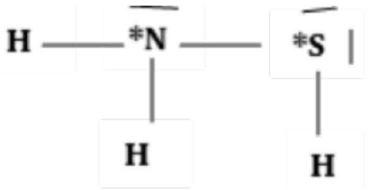
Enzymes work by binding to molecules in a specific way, and you may have already guessed that shape is crucial. In fact, way back in 1894 it was the Nobel Laureate Emil Fischer who came up with the ”lock and key” model to explain how enzymes work. The idea in this model is pretty much how it sounds: an enzyme’s active site is a specific shape, and only the substrate will fit into it, like a lock and key. Here’s a cartoon to illustrate how the enzyme perfectly fits, because of its shape, into a substrate, giving the substrate the power to make reactions happen faster (also called catalysis). The model has been updated over the past 100 years, for example to include the fact that the substrate and enzyme itself are dynamic and can change shape when they interact, or that the effects of the surrounding solvent are important, but the key feature that shape is crucial remains the foundational principle upon which enzymes operate.

As you may have noticed by just going to the grocery store, there’s a big market for new foods with new enzymes. There are so many enzymes involved in digestion, like lipases that help digest fats in the gut. amylase helps change starches into sugars. Maltase breaks the sugar maltose into glucose (it’s in potatoes, pasta, and beer, for example). Trypsin breaks proteins down into amino acids. Lactase breaks down lactose, the sugar in milk, into glucose and galactose, and on and on. Which brings me to the job market: here, specifically the food industry. The synthesis and use of new enzymes in the preparation of food have seen tremendous growth not only in digestion but also in the taste and texture of the food, as well as possible economic benefits. There are many jobs related to food science (check out this article in the NatureJobs pages, which is a cool site in case you haven’t seen it: *https : //www.nature.com/naturejobs/science/articles/10.1038/nj7422 - 149a?WT.ecid = NATUREjobs* - 20121106). But jobs related to enzymes having to do with food also relate to the future of humanity itself. How will we feed our population in the future? Will all protein need to be plant-based? Or will we eat insect-meat? Or meat grown in a lab? Will food be 3D-printed, and will it be served by robots? All of these topics have recently received vast amounts of attention, research funding, led to start-ups, and a lot of interest from larger companies, and all of that spells jobs. Specifically, jobs involving knowledge about enzymes, which in the end only function because of their shape (VSEPR!).

Example Problems

1. Draw the Lewis structure of H_2N-SH and determine the VSEPR geometry around (a) the nitrogen atom, and (b) the sulfur atom.

Answer



a) Geometry around the nitrogen atom: trigonal pyramidal

b) Geometry around the sulfur atom: bent

2. Determine the VSPER geometry for each of the following and predict whether each will be polar or nonpolar

a) BF_3

Answer

BF_3: Difference in N-F electronegativity: polar bonds. Trigonal planar: dipoles cancel! Nonpolar

b) FOF

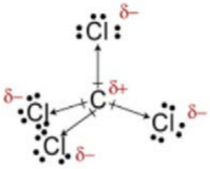
Answer

FOF: Difference in $O-F$ electronegativity: dipole moment: polar

c) CCl_4

Answer

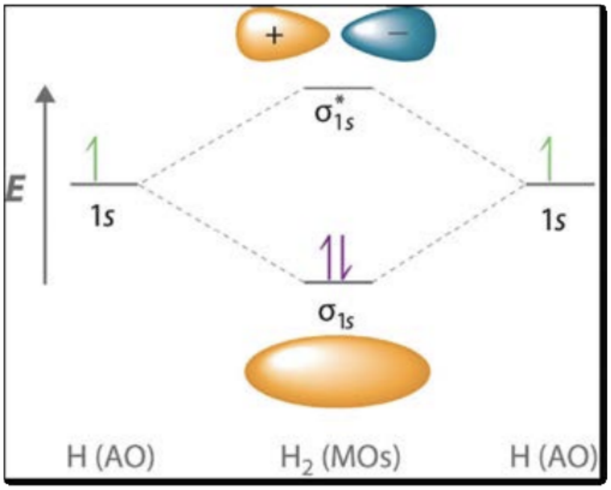
CCl_4: Difference in $C-Cl$ electronegativity: dipole moments; tetrahedral structure: cancel out, so nonpolar!



Lecture 11: Molecular Orbitals

Summary

Molecular orbital theory is a tool used to predict the shape and behavior of electrons that are shared between atoms. Two or more atomic orbitals are added together to make a linear combination of atomic orbitals—the LCAO method—allowing for quick characterization of the kinds of bonds formed between two atoms.



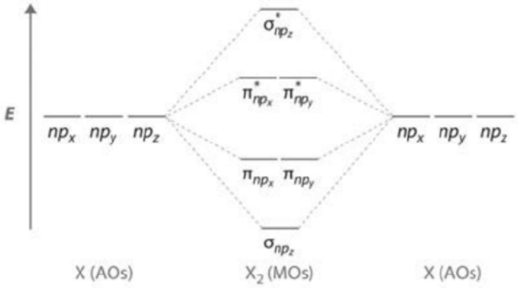
When atomic orbitals are added, they can either constructively interfere, forming a bond, or they can destructively interfere, forming an antibonding state. In a molecule, the bonding state is always lower in energy than the corresponding atomic orbital, while the antibonding state is always higher. Molecular orbital diagrams, or MO diagrams, are a convenient visualization tool to see how electrons are distributed between two atoms: hydrogen is shown to the right as an example.

The two hydrogen 1 s orbitals combine to form a σ_{1s} bond, which is lower in energy and therefore more stable. If we had started with helium instead, there would have been four electrons to distribute: two would form a σ_{1s} bond, but the other two would go in the $\sigma_{1s}*$ antibonding state, effectively cancelling out the bond.

After placing electrons in the MO diagram, bond order can be calculated:

$$BO=\frac{1}{2}\left(\text{ of e}' \text{ in bonding orbitals } - \text{e}' \text{ in anti-bonding orbitals}\right)$$

Stronger bonds have higher bond orders, and the bond order must be >0 for a bond to exist at all. For our example above, a hydrogen dimer has $\mathrm{BO}=1$, but a helium dimer has $\mathrm{BO}=0$. This explains why hydrogen gas exists as H_2, but helium gas consists of individual atoms!



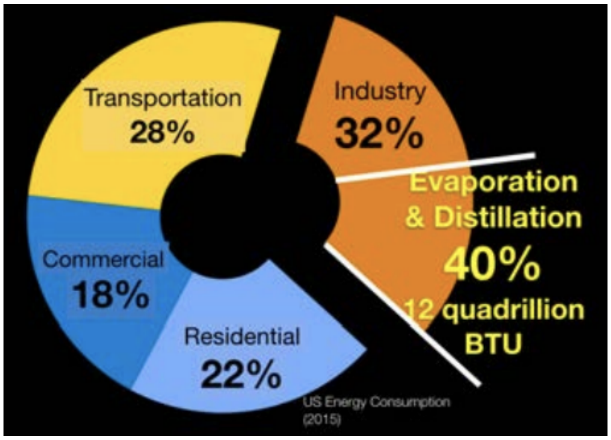
If an atom has p-orbitals as well as s-orbitals, additional bonds called bonds can form. The three p-orbital domains yield three kinds of bonds, one σ and two : σ_{npz}, π_{npx}, and π_{npy}, where n refers to the particular energy level being considered. Note that the σ bond forms for both s orbital overlap as well as one of the p orbital overlaps: the term σ bond means that the bond has cylindrical symmetry around the bond axis, something that is not the case for the bonds. Anti-bonding σ^* and π^* states also form from p-orbital MOs. A generic MO diagram for p-orbitals is shown to the left.

MOs can also be formed from heterogenous dimers: the same rules apply. Since each of the atoms has distinct energy levels associated with its s- and p-orbitals, the MO diagram formed using two different atoms is usually skewed, and the bonds that result are polar covalent bonds. The atom that is more electronegative is lower in energy. It can be helpful to count the number of electrons in the initial atomic orbitals and make sure that they are all used when filling up the MOs. Remember that if a dimer is positively charged, it has lost an electron, and if it is negatively charged, it has gained an electron: these have to be accounted for as well! If one of the atoms has more electrons than the other, like a bond between H and Cl, the excess electrons form nonbonding pairs - just like the lone pairs in the Lewis diagrams we drew before. If all of the electrons in the MO diagram are paired, then the dimer is diamagnetic, but if there are any electrons left unpaired, it is paramagnetic. For low molecular weight dimers, the 2 s and

2p atomic orbitals are very close in energy, and they can interact with each other. For dimers with lower MW than O_2, the $\pi_{2px,y}$ and σ_{2pz} orbitals switch, and the $\pi_{2px,y}$ states are filled up first.

Why this matters

There are two ways to separate pasta from the boiling water once it's cooked. One way is to pour the mixture through a colander, or a filter, to retain pasta on one side while letting the boiling water pass through. Another is to leave it on the stove and let all of the water boil off. Each of these separation techniques leads to the same outcome, but as you can imagine they are very different. I'm not talking about how the pasta would taste (let's ignore that part), but rather how much energy it takes to carry out this separation task. Pouring through a filter is easy, fast, and efficient, while leaving the pot on the stove would take longer and require a lot more energy.



Now shrink down from pasta to nano-pasta. In other words, the size scale of molecules. We separate molecules from one another all the time for a wide variety of industrial processes. In fact, if we look at the U.S. energy consumption, about 1/3 of it goes into what is vaguely labeled "Industry." But did you know that 40 percent of this energy for industry serves just one process, separating molecules? The reason that number is so large is that we only use the slow and inefficient thermal approach, not the much more efficient filter approach, to perform the separations. That's a whopping 12 percent of all energy used in the U.S. that goes into boiling one chemical off of another.

So why is it that we don't just pour these chemicals through a nano-filter, just like we do with pasta and colanders? If we did switch from thermal separation to a filter, we could save up to 90 percent of that energy! The reason we don't, is the filter itself. Current filters aren't yet up to standard. On the one hand, we've got filters made from polymers (materials we'll learn about later in the semester) that can separate the tiniest of molecules very well, but they're so delicate that they can't be used in the harsh chemical and thermal environments of most industrial processes. On the other hand, we've got filters made from ceramics (materials with strong ionic and/or covalent bonds) that are super resilient and can handle the conditions, but they can't get down to the sizes of the small molecules that need to be separated.

So it is that we come to our molecular orbitals, orbital filling, and the specific example of N_2 vs. O_2 covered in class. Because one of the big separations that we need to do on a massive scale involves exactly these two molecules. O_2 is plentiful in the air (unless you go into a closed room, light a candle, and wait 12 hours as we learned in lecture 2!), but for many applications we need O_2 in much higher concentrations than its naturally occurring 21 percent in air. Take combustion as an example: the 78 percent N_2 in the air has a negative impact on combustion processes since the nitrogen molecules get heated up during the reaction to very high temperatures, which is not only inefficient, but breaks down into toxic nitrogen oxide (NOx) gasses. Increasing the amount of oxygen and decreasing the amount of nitrogen leads to much higher combustion efficiencies, lower harmful emissions, and higher processing temperatures. Now, you may be thinking that I'm only talking about fossil fuel processing, and yes that is certainly a prime example of our use of combustion as a society, but getting purified $O2$ molecules reaches far beyond, to applications in the medical industry to sewage treatment to metal manufacturing, to name only a few.

The separation of O_2 from N_2 is in so much demand globally that it is performed at a quantity of 31 billion kilograms per year. Because the separation is done inefficiently using thermal processes, in this case going cryogenic, which is cooling instead of boiling but for the same purpose, 47 teraBtu (British thermal units, or the amount of thermal energy needed to raise one pound of water by one degree Fahrenheit) of energy are used per year just to do the separation! Just to be clear, that's

$47,000,000,000,000$Btu of energy, or if you prefer $13,774,340,298,094$Watt-hours. A typical household in the U.S. uses about 900,000 Watt-hours of energy per moth, just for reference.

How do we save up to 90 percent of the massive energy used to separate O_2 from N_2 by switching from thermal-based separation to a filter-based approach? The answer lies in those molecular orbitals! They tell us about the bonding of each molecule and the interactions of the molecules with yet-to-be-invented filter materials that could combine the best of both worlds from polymer to ceramic materials. The MOs of N_2 and O_2 also tell us that these molecules respond differently to externally applied magnetic fields, which may in turn be useful in boosting the separation efficiency. There is a tremendous opportunity for new filters that take these two most abundant molecules in the air and put them into separate compartments, but it all has to start with knowing how the electrons in the molecules behave. And that, of course, we get from molecular orbital theory.

Why this employs

The problem with fusion energy is that it’s uncontrolled. Way back in the 1950’s, Disney was making feel-good movies (grab some popcorn and check out, “Our Friend the Atom”), about how energy was very soon going to be, "too cheap to meter." 70 years later, why is this not the case? Fusion is so attractive on so many levels: unlike fission, which is the stuff of current nuclear reactors, fusion has no radioactive waste or byproducts, with the only outcome of a fusion reaction being ridiculous amounts of energy and helium. Fusion is the engine of the stars, so you know this energy is serious. Let's break it down: remember the battery vs. gasoline comparison I made in Lecture 8? Roughly, the best Li-ion batteries today can store about $1 MJ$ of energy per kg. Gasoline, on the other hand, can store $45 MJ$ per kg. But let's keep going. The explosive TNT stores around $4160 MJ/kg$. Uranium when used in nuclear fission stores a whopping $3,456,000 MJ/kg$! This incredible energy density is a strong argument for nuclear energy generation and is often invoked. But when we move to fusion, when we move to the stuff of the stars, all of these numbers feel tiny. The energy density of the fuel for fusion, which is a combination of tritium and deuterium, is an incredible $576,000,000 MJ/kg$. And that fuel is highly abundant and cheap. That's why the dream of fusion is still alive even after 70 years of trying, and in fact today there is a huge resurgence in fusion energy. For more information you don't need to go very far, check out the PSFC (Plasma Science and Fusion Center) right here at MIT. Or the new MIT spin-out called Commonwealth Fusion Systems.

If nuclear fusion is to become a reality (in just 10 years according to some, but we've also been hearing that since the Disney movie so we need to approach with careful optimism), one of the single most important ingredients to making it work will be magnets. Lots and lots of magnets and very powerful ones. That's because one of the most likely ways to get fusion to work is to contain the massive energy released (which, by the way, gets to temperatures up to 100 million degrees), is to confine the energy using magnetic fields. Now, in fusion reactor designs the magnetic fields are often generated with superconducting coils, so it's different from our unpaired electrons in the MO diagram of O_2. But the general idea that a material can be responsive to an external magnetic field comes from its electron filling, and the more electrons that are unpaired like in the O_2 molecule, the more responsive it can be.

So what are the jobs related to developing new magnets? You could go to work at a nuclear fusion start-up like Commonwealth Fusion, or to the large government-led fusion operations like the ITER program in France. But so many other industries need stronger, cheaper, lighter magnets that the job market extends far beyond just fusion. You could look for jobs in companies that manufacture magnets (there are many), or companies pursuing new ideas for recycling magnets (like Urban Mining Company), or as a scientist at a U.S. lab pushing the frontiers of magnets (like Florida's National High Magnetic Field Laboratory, or the one at Los Alamos), or at companies trying to make magnets that don't rely on rare-earth elements (like Toyota for example, among many).

Extra practice

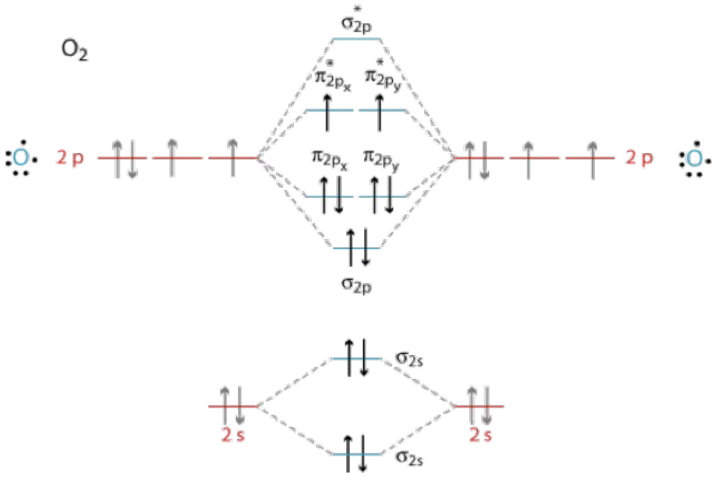
1. Consider $O_1 512$ and O_2^+

    a) Draw the MO diagram of each molecule.

    b) Find the bond order of each.

    c) Label each one as paramagnetic or diagnetic.

Answer

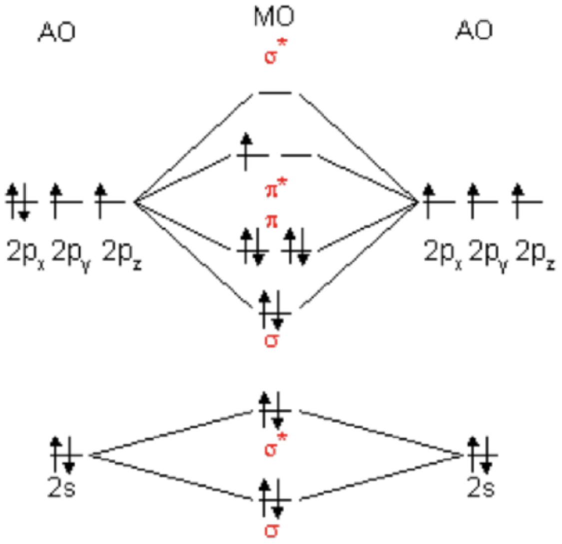


Electron Configuration: $(\sigma_{2s})^2\ (\sigma_{2s}{}^*)^2\ (\sigma_{2p})^2\ (\pi_{2p})^4\ (\pi_{2p}{}^*)^2$

Bond Order $= \frac{1}{2}(2 - 2 + 2 + 4 - 2) = 2$ Double Bond

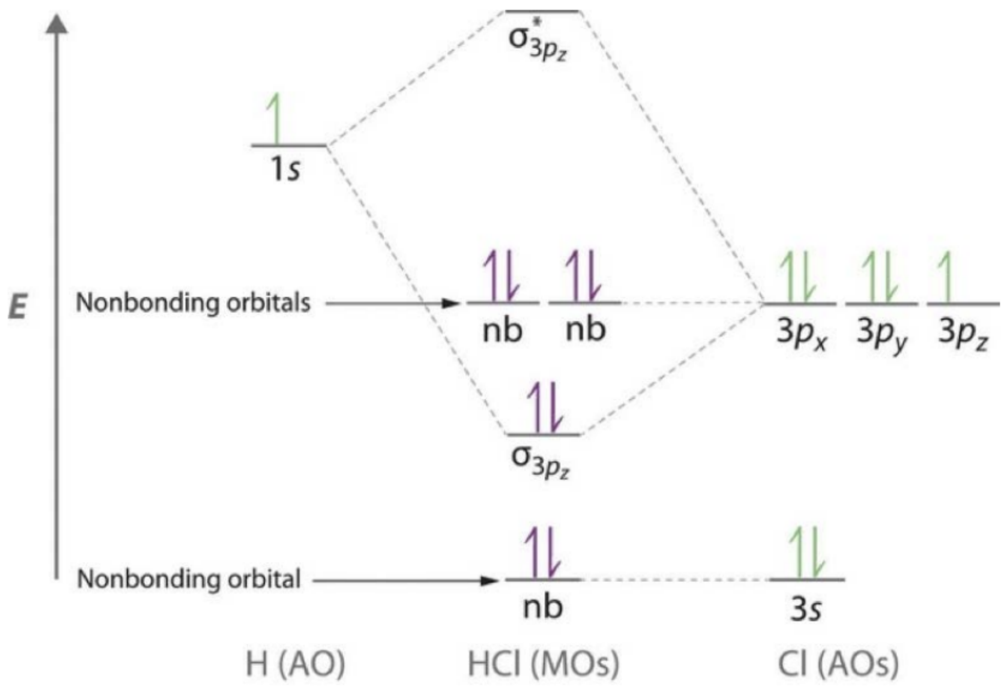
O_2 is paramagnetic because it has unpaired electrons.

O_2^+ is also paramagnetic, because it has an unpaired electron. Its bond order is 2.5



2. Draw the MO diagram of HCl.

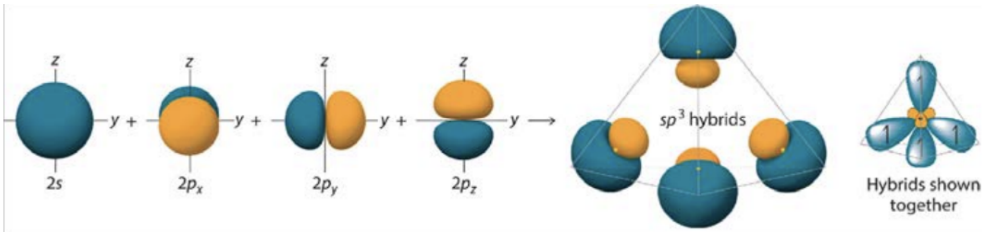
Answer



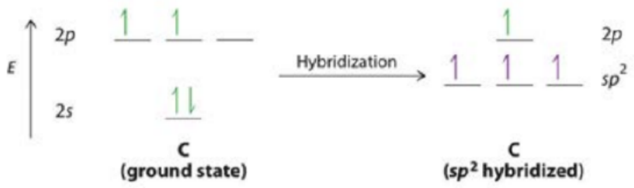
Lecture 12: Hybridization in Molecular Orbitals

Summary

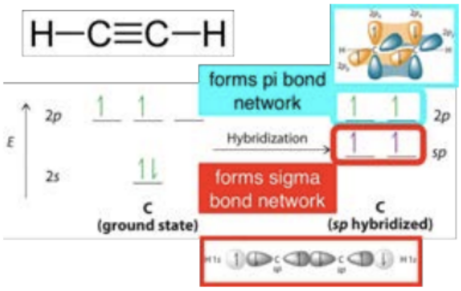
If multiple atomic orbitals within an atom have similar energy levels, they can **hybridize**, combining to form equal orbitals that have a lower average energy. Consider methane, $\mathrm{CH4}$, as an example: the carbon atom has two $2\mathrm{s}$ electrons and two $2\mathrm{p}$ electrons. The $2\mathrm{s}$ and $2\mathrm{p}$ states hybridize, yielding four equal-energy, unpaired electrons that are ready to bond with hydrogen atoms. As hybridization occurs, carbon's four electrons are redistributed so as to be maximally spaced apart, lowering the energy of the system and yielding the most stable state: a tetrahedral methane molecule. This kind of hybridization is called sp^3, because one s-orbital energy level combined with three p-orbital energy levels.



For the case of ethane, $\mathrm{C_2H_4}$, the hybridization process is slightly different, as shown here (this time as an energy level diagram). Each carbon forms only three bonds: two with hydrogen atoms, and one with the other carbon. The s-orbital energy level combines with two p-orbital energy levels to form three equal $mathrmsp^2$ bonds; the remaining $2\mathrm{p}$ electrons form a higher-energy π bond between the two carbon atoms and yield a double bond between the carbon atoms.

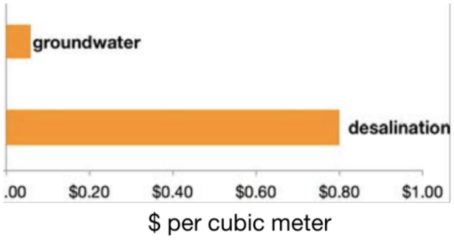


The next logical molecule logical molecule to consider is acetylene, $\mathrm{C_2H_2}$. In this case, each carbon is only bonded to one hydrogen, so only one $2\mathrm{p}$ energy level hybridizes with the $2\mathrm{s}$ energy level to form a sp hybridized bond. The remaining $2\mathrm{p}$ orbitals form two bonds, yielding a triple bond between the carbon atoms.



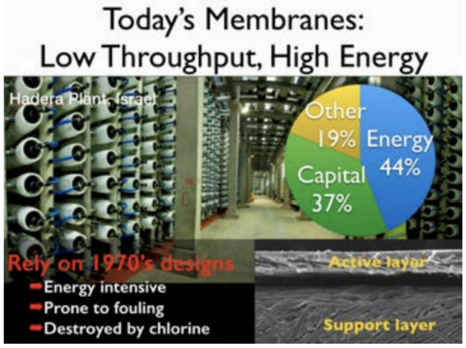
In summary, hybridization occurs to lower the overall energy of the system: atomic orbitals combine with each other to form mixed states with a lower average energy. Knowing the hybridization of the molecule is equivalent to knowing the molecular shape: VSEPR gives the geometric name corresponding to the specific combination of bond angles that minimize the overall energy of the system.

Why this matters



More than 3 billion people on this planet live in water-stressed regions. 1.8 billion people drink fecally contaminated water. 600 million people boil their water to clean it. In places where water scarcity is a serious issue, by some estimates 70% of all disease and 30% of all death can be attributed to the lack of water or water quality. Fresh water makes up just 2.5% of all water on earth, but more than 2/3 of that is tied up in glaciers. This means that only 1% of all water on the planet is drinkable, and the balance of this precious resource is way offscale.

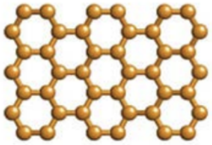
Given the level of global crisis that access to freshwater has become, it makes a lot of sense to turn our attention to the other 97% of water on the planet, saltwater in the oceans. The problem, of course, being that it's not drinkable (or useful in most agriculture), unless the salt is removed. The good news is that desalination is growing in terms of use and installed capacity, but the bad news is that it still costs far too much to become a ubiquitous substitute for groundwater.

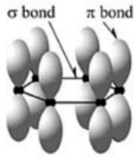

Today's Membranes:
Low Throughput, High Energy

Rely on 1970's designs
- Energy intensive
- Prone to fouling
- Destroyed by chlorine

How can we work on lowering the cost and increasing efficiency in desalination? First of all, we need to know what the current cost breakdown is, and as you can see in the pie chart in this image, the major cost of desalination is in the energy it takes to pump water through the system. By "system" I mean a pretreatment facility where seawater is run through sand to filter out large impurities (shells, rocks, seaweed, etc.), followed by the actual "desal" part of desalination, where the water is run through a set of membranes (40,000 of them in the plant shown in the picture) that remove the salt and allow freshwater to pass. Pumping the saltwater through these membranes requires by far the biggest part of the plant's energy consumption, so improving the membranes and making them more energy efficient is crucial. In fact, it's not just that the membranes used today are energy inefficient, but it's also that they get fouled up (bacteria and other organic matter grow on their pores) and are extremely delicate so can't be cleaned very well. This means for most of the time the plant is paying higher energy costs than it needs to (by a factor of 2 or 3 sometimes!) because it has to pump water through membranes that are filthy and blocked and can’t be cleaned. Now that’s what I call a materials design opportunity! Make a better membrane for the salt removal step of desalination, and make the process cheaper. That’s how we come to our Why This Matters and connection to today’s lecture.

We learned about the sigma and pi bonds that can form when the AOs of carbon atoms hybridize.





In the examples in class we had carbon bonded to hydrogen and sometimes also to itself. If we only have $sp2$ hybridization and we only have C atoms and no H atoms, then we arrive at a very, very cool material: graphene. It's bonded together in a honeycomb lattice sheet (a 2D sheet) with sp^2 bonds, and those extra p electrons form pi bonds across the plane to give it a huge stability boost. It's a very cool material and its isolation from graphite (which is just stacks of graphene) won the Nobel Prize in 2010. (The scientists who discovered graphene were able to separate it from a chunk of graphite using only run-of-the-mill tape! So remember, sometimes all you need for a Nobel Prize is pencil lead, tape, and determination). I can't possibly go into all the details for why graphene is cool, but if you search online you'll see right away. Another consequence of graphene is that it launched a whole field of " $2D$ materials" where researchers have realized that so many other materials can be made into these sheets that are only one or a few atoms thick. It's now even possible to make completely new stacks of 3D materials by mixing and matching $2D$ sheets (check out for example the paper by Geim and Grigorieva, "Van der Waals heterostructures," Nature volume 499, pages 419-425 (25 July 2013). By the way, Geim was one of the two scientists who won the Nobel prize for graphene's discovery. The other is Novoselov, but Geim is a bit special as he is the only person to ever have won both the Nobel and the IgNobel prizes, the latter for levitating frogs. But I digress.

The point is that graphene may just be the ultimate membrane. It’s only 1 atom thick, so in terms of viscous loss it’s hard to beat. Plus, it’s much more resilient than today’s polymer membranes so it can be cleaned easily. It’s no wonder graphene’s been considered as a potential for desalination since 2012, even by people you might already know, for example, “Water Desalination across Nanoporous Graphene,” by Cohen-Tanugi and Grossman, Nanoletters volume 12, pages 3602- 3608 (2012). Because of its massive potential in water desalination and also water treatement and purification in general, there are many research groups and even already a number of companies working towards commercializing graphene-based membranes (Via Separations, for example). This is all extremely exciting, but it’s also only possible because of the hybridization that occurs in carbon atoms, which combined with those pi bonds allows them to take the form of graphene.

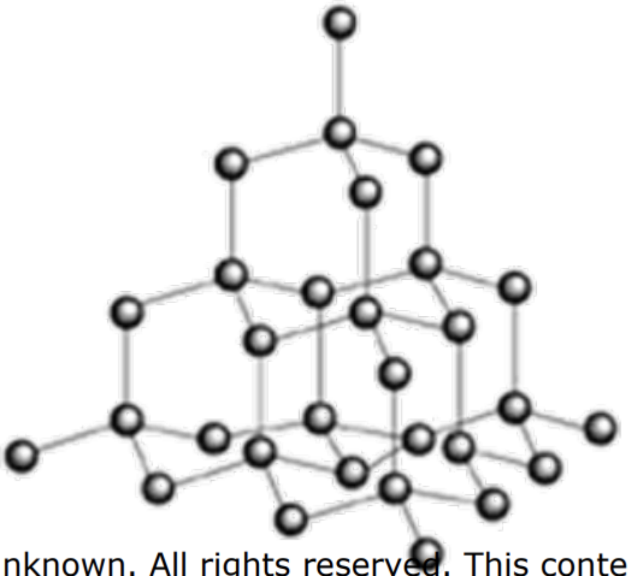
Why this employs

This is a tough one since hybridization in chemistry is what enables so many molecules to exist at all, and this impacts nearly all job sectors, not to mention life itself. But since we covered graphene in Why This Matters let’s stick to graphene here in the Employment category too. There are companies directly manufacturing graphene and investing a lot of $$ into making it cheap, at large scales, and at high quality (meaning very few defects if possible), or with tailored functional chemistries. There are also different versions of graphene, from pure graphene to graphene-oxide to reduced graphene oxide and so on. Graphene Supermarket, ACS Material, or Graphenea are all examples of companies making graphene products and all of them have job openings for students who know about hybridization.

But graphene production has been embraced in a big way by large companies, too. Toshiba has invested over $50M in manufacturing plants for new carbon materials, from graphene to other sp carbon nanostructures like carbon nanotubes and fullerenes. Other large chemical producers have joined the club, like Cemtrex, Mitsubishi Chemical, Cabot, or Aixtron, to name only a few examples. And these are all just companies thinking about making graphene, but then if we expand to ones that are using it to improve their technology, the list goes on and on. This is especially true in battery companies, both big and small, where the use of sp2 carbon nanostructures like graphene has tremendous potential. Applications involving catalysis and electronics are also fantastic candidates for the use of graphene.

Extra practice

1. Look at a single carbon in the portion of a diamond lattice below. Convince yourself that the structure could keep growing outwards infinitely in all directions.



a) What is the formal charge on any one carbon atom?

Answer

0, it’s forming 4 bonds

b) What is the hybridization of any one bond? How do you know?

Answer

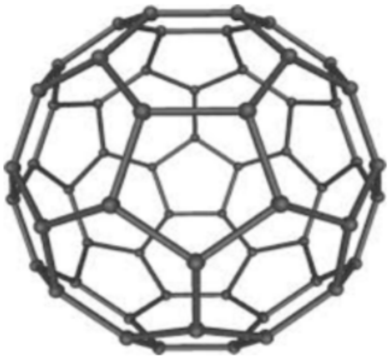
C is forming 4 sigma bonds, so it must have 4 equivalent hybridized orbitals: it must have used all three p-orbitals and its s-orbital: sp3

c) Is this a resonant structure? How do you know?

Answer

No - the electrons are all forming sigma bonds, so there’s no other configuration of electrons allowed

2. Look at a single carbon atom in the portion of a buckminsterfullerene molecule below (yes, it’s the logo for our class!)



a) The formal charge on any one C atom is 0. How many sigma and pi bonds must each carbon be forming?

Answer

There has to be a double bond associated with each carbon for it to be forming 4 bonds and have 0 formal charge, so each carbon is forming 3 sigma bonds and 1 pi bond

b) Is VSEPR satisfied? Is it almost satisfied?

Answer

Each sigma bond has to be $sp2$ hybridized, since three bonds are being formed total and they all lie in a plane

c) What is the hybridization of any one sigma bond? How do you know?

d) Is this a resonant structure? How do you know?

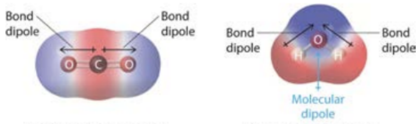
Answer to c and d

Yes - There are different configurations in which the pi-bonds can be made over the whole fullerene molecule, so there are resonances. Also, we infer that the p-orbitals forming the pi-bonds can either add or subtract giving delocalized electron molecular orbitals - pointing to resonance

Lecture 13: Intermolecular interactions

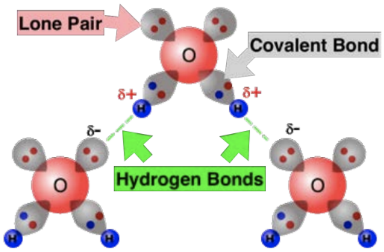
Summary

This lecture focused on **intermolecular forces (IMFs)**, which are interactions between molecules weaker than ionic or covalent bonds, but that on a larger scale take on an enormous role in giving materials their properties. First, we defined a **dipole**: a pair of charges, one positive and one negative, separated by a distance. We have already seen dipoles in this class—a covalent bond that involves a difference in electronegativities, for example if one atom is electropositive and the other electronegative, forms a dipole. The $\mathrm{H-Cl}$ molecule is a simple example shown here, where the arrow in the diagram points towards the more electronegative chlorine, and the δ^+/δ^- indicate an excess of positive/negative charge. The arrow is the direction of the dipole. It is possible for a molecule with polar covalent bonds to have no net dipole, as shown for $\mathrm{CO_2}$ below. This is because its two dipoles cancel. Water has a net dipole only in the y-direction.



(a) No net dipole moment (b) Net dipole moment

The presence of a net dipole means that the dipoles of the molecule will feel attraction to opposite charges. This other charge could be an ion, or another dipole. The former is called an **ion-dipole interaction**, and the latter a **dipole-dipole** interaction. These are attractions between molecules rather than bonds within them.



It is still possible for molecules with no net dipole to participate in intermolecular bonding, because even nonpolar molecules can experience temporary dipoles due to fluctuations in the electron cloud. These temporary dipoles can happen due to interactions with surrounding charges, in which case they are called **induced dipoles**. These can interact with ions or permanent dipoles or other induced dipoles. These fluctuations in the electron cloud can also be a result of temperature. When these temporary dipoles interact with each other, the attractive forces are called **London dispersion forces (LDF)**. It is easier to temporarily deform the electron clouds of some molecules compared to others. They have differences in **polarizability**. For example, larger atoms are more polarizable than smaller atoms due to their outer electrons being less affected by nuclear pull. The more polarizable a molecule is, the stronger its LDF. The LDF also depends on the surface area of the molecule, since greater surface area means more electron cloud that can be temporarily induced to shift, which in turn means higher LDF. Finally, we discussed **hydrogen bonds**, which occur when a hydrogen atom attached to a highly electronegative element in a molecule (such as nitrogen, oxygen, or fluorine) is attracted to a negatively charged region, like a lone pair of electrons.

Why this matters

https://www.americanscientist.org/article/how-gecko-toes-stick

Weak bonds aren't actually all that weak, especially when there are a lot of them. The gecko is a perfect example of this. It's a remarkable animal that can walk up and down walls and even across the ceiling without breaking a sweat! The reason is that its toes are padded with microscopic hairs (called "setae"), and each of these in turn has hundreds of nanoscale branches. One gecko toe can have as many as a billion little hairs! These hairs hold the key to its seemingly magical adhesive abilities and the reason there are so many of them is precisely because of what we learned in this lecture: weak interactions like van der Waals get stronger with more surface area. A billion little nano-strands on each toe gives the gecko's foot a whole lot of surface area, especially when those strands lie nearly flat against whatever surface the gecko is climbing or sticking to. When the strand runs parallel to a surface, it maximizes the amount of the strand that can engage in van der Waals attraction with that surface. When the strand is more perpendicular, the force is dramatically reduced.

https://www.smh.com.au/technology/stanford-university-students-create-gecko-gloves-that-allow-humans-to-scale-glass-walls-20141226-12dx31.html

Herein lies the secret of the Gecko, because it's not enough for it to have a super-adhesive toe, but it also needs to be able to alternate between super-adhesive and not adhesive at all. Otherwise, it would stick to the wall and not be able to move! So, the Gecko clearly knows all about the dependence of van der Waals attraction on surface area contact, and each time it takes a step it adjusts toe adhesion by changing the angle of its billions of toe hairs.

This matters not only because it's such a cool illustration of how amazing nature can be, but also because of how relevant improved reversible adhesives would be for a broad range of applications. Yes, this includes scaling buildings like Tom Cruise in Mission Impossible 4, but it also would impact areas ranging from advanced manufacturing to treating wounds. Just think about what it could mean to have a tape that's 1000 times stronger than current tape, and can be applied and removed thousands of times without loss of stickiness. Researchers and companies alike have been trying to mimic the Gecko's adhesive abilities for decades, and still we're not at a place where we can quite do it, although improved control over the chemistry and nanostructure of materials is getting us closer than ever. It all comes down to engineering the van der Waals attraction.

Why this employs

The last weak interaction we discussed in this chapter was that of the hydrogen bond. This bond is incredible in so many ways, not the least of which being the employment opportunities it provides. Hydrogen bonding is prevalent (and often dominant) in determining the way in which proteins fold and unfold, and in the way in which the helices of DNA hold together. It is the reason paper is possible, and the reason fish don't freeze in the winter in a pond, to name only a few examples. But the example I want to focus on for this Why This Employs is that of surface coatings. The way a surface interacts with water can be engineered by modifying either the way in which the water hydrogen-bonds to the surface, the way in which water hydrogen-bonds to itself, or both.

Coatings that repel water are needed all over the place, from keeping car windshields clear, to making clothes that stay dry in a rainstorm, to preventing condensation in power station turbines. The chemistry that goes into these coatings holds the key to controlling the hydrogen bonding, and there are a lot of companies interested in hiring people to work with such chemistry. This ranges from medium-sized materials companies like NEI Corporation, which makes a "superhydrophobic" coating called Nanomyte, or UltraTech, which makes spill-containment coatings, or Aculon, which states on their website, "Where there is a surface that has a problem, we like to think we can help solve that problem," to larger companies like DuPont that makes specialized coatings for the Oil and Gas industry, to small start-ups like DropWise, founded by our very own Course 2 Professor Kripa Varanasi. These are only a handful of examples of the many companies building products around controlling hydrogen bonds.

Extra practice

1. At $\mathrm{T}=25^{\circ}\mathrm{C}, \mathrm{F}_2$ and Cl_2 are gases, Br_2 is a liquid, and I_2 is a solid. This is because (choose one):

   A. London interactions increase with molecular size.
   B. Dipole-induced dipole interactions increase with molecular size.

C. Dipole-dipole interactions increase with molecular size.
D. Polarizability increases with molecular size.
E. London interactions increase with molecular size and polarizability increases with molecular size

Answer

E

2. Based on the following information:

CF_4, Molecular Weight 87.99, Normal Boiling Point $-182^\circ C$
CCl_4, Molecular Weight 153.8, Normal Boiling Point $-123^\circ C$

The intermolecular forces of attraction in the above substances are described by which of the following (choose one):

A. gravitational forces

B. London forces

C. ion-dipole forces

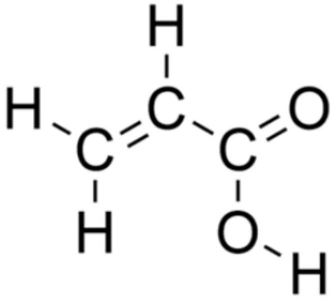
D. dipole-dipole forces (permanent dipoles)

E. repulsive forces

Answer

B

3. Acrylic acid is pictured below.



What is the dominant intermolecular force in a solution of acrylic acid? (also, what's the hybridization around every atom?)

Answer

H-bonding (all atoms are sp2 except for the $O-H$, which is sp3)

Lecture 14: Phases

Summary

Atmospheric pressure is the force per unit area exerted by the mass of the atmosphere onto everything it envelops, and other gasses, liquids, and solids can exert pressure in a similar fashion. In a closed system, an **equilibrium** develops as molecules convert from one phase to another (like liquid to gas), and vice versa (gas back to liquid). The pressure that one phase exerts on another depends strongly on what intermolecular forces are present in the system. Strong IMFs lead to low vapor pressures, while weak IMFs lead to high vapor pressures.

The vapor pressure of a material is different than the weight of a gas; rather, it's related to how likely a liquid or solid is to lose molecules to the gas phase. If the vapor pressure is higher than atmospheric pressure, the weight of the atmosphere isn't enough to trap the gas that is released, and the material begins to **boil**.

So far, boiling has been entirely described with respect to pressure, but temperature makes a difference too! The vapor pressure also depends strongly on temperature: as temperature rises, the vapor pressure increases exponentially. So as a material is heated up, its vapor pressure increases until it exceeds atmospheric pressure and it starts to boil. For example, if we start with water at $25 C$, its vapor pressure is about 0.02 atm. By the time it reaches $100^{\circ}\mathrm{C}$, the vapor pressure has increased 50 -fold to reach $1 \mathrm{~atm}$, at which point it begins to boil.

We learned previously that a higher temperature yields higher kinetic energy and more molecular movement. However, when a material is "at" a certain temperature, not every molecule moves around the same. The distribution of kinetic energies associated with a given temperature can be very broad, with long tails. So temperature is used to describe the average kinetic energy, but some molecules will have more and some will have less. The Clausius-Clapeyron equation gives the exponential relationship between vapor pressure and temperature:

$$\ln(P) = -\Delta H_{vap}/RT + C$$

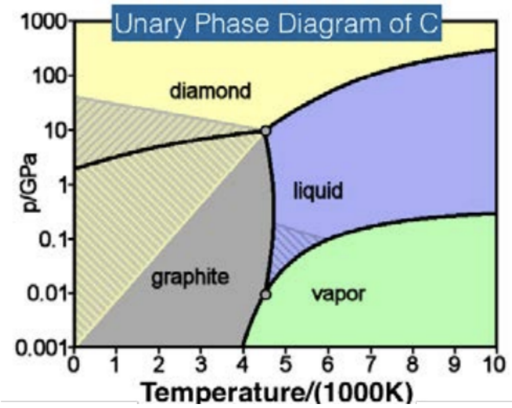
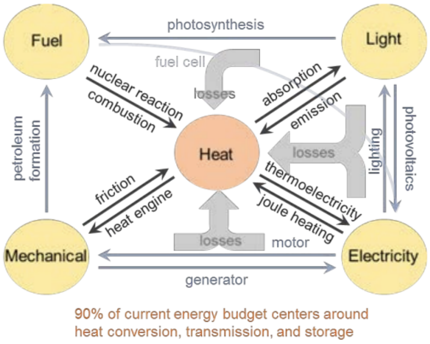


Diagram is in the public domain. Source: Wikimedia Commons.

where $\Delta H_{\text{vap is}}$ is the enthalpy of vaporization, or the energy per mole required to convert a liquid molecule into a gas molecule. There is a latent heat or enthalpy involved in every kind of phase change: ΔH_{vap} for vaporization, ΔH_{fus} for fusion, and $\Delta H_{\text{sub for}}$ sublimation. The enthalpy of sublimation is always larger than the enthalpy of fusion, because the solid-state atoms/molecules are more strongly bonded than liquid atoms/molecules. Hess' law tells us that any path from one state to another is a valid path, because the total energy required to change states will be the sum of energy differences along the path.

Phase diagrams are helpful to know what the equilibrium phase of a material is at a given temperature and pressure. Phase boundaries are called coexistence curves: at these points, two phases exist simultaneously. If a phase boundary is crossed, a phase change will occur. Phase diagrams are like “maps” of a material.

Why this matters

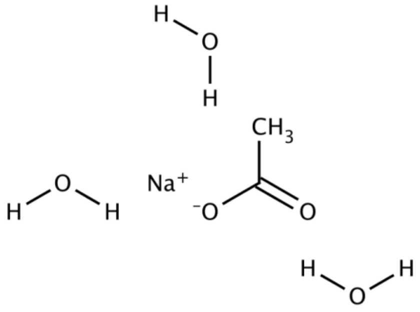


Heat is an essential form of energy transfer for human beings, not only for maintaining body temperature but also for a range of primary and advanced activities, from cooking and sterilizing, to operating engines and generating electricity. Control of thermal energy to benefit humanity dates back to pre-historic times and heat remains the single most valuable energy currency of our existence. As illustrated in this figure, nearly 90% of all energy consumed globally is either generated by or consumed as thermal energy at some point during the supply/demand cycle. It is therefore surprising, even striking, that to date we have no viable means for storing thermal energy. Unlike mechanical energy, where material can be simply pumped up a potential energy hill and held there until needed as in the case of pumped hydro, or electrical energy where electrons can be pushed up an electrochemical hill and held there as in a battery, for the case of phonons – the carriers of thermal energy – there is no such stability. Instead, thermal energy rolls back down the energy hill and cannot be stopped. Heat always dissipates. It leaks and we cannot contain it no matter how hard we work to insulate a thermal reservoir.

The slow leaking of thermal energy out of a material that's hotter than its surrounding is called "sensible heat." Eventually, enough energy will be transferred to the environment to make it the same temperature as the surroundings. In fact, if you take a thermodynamics class you'll learn that the very definition of temperature is, "that which is equal when heat ceases to flow between systems in thermal contact." So one way to store thermal energy is to heat something up, then that something will leak its heat out at some rate into some environment until its temperature is the same as that of the environment. The storage and release of sensible heat is used all the time, from a heating pack that you microwave and put on your sore neck to focusing sunlight on a concrete slab as in a solar thermal power plant, to the old idea of heating an entire mountain for long-term energy generation as it slowly cools down. (that last one hasn't been tried yet in case you're wondering. . . but it's a neat concept!). But whether a heat pack or a mountain, the problem with sensible heat is that you get what you get with almost no control. Apart from how much insulation you package your material with, there aren't many good ways to slow and no ways at all to stop the flow of heat. Because in this mode of thermal storage, we heat something up to some temperature and it starts cooling right away, there's also no control over the temperature you get out of the stored energy: it's constantly changing as it cools.

Ah, but there is in fact a way to "hold on" to thermal energy, and then release it back as heat when needed, much like electricity in batteries. And it gives you complete and total control over the release temperature. In fact, a simple bucket of wax is a thermal storage system. It works by taking advantage of its phase change: when wax melts it changes from solid to liquid, and the energy required to make this phase change happen is large (that would be the enthalpy of fusion, ΔH_{fus}, as discussed in the lecture). When the wax cools back down it becomes a solid again, and all that phase change energy is given back out upon solidification. Materials that are used like this, where the enthalpy of one of its phase changes is used as a way to store and release thermal energy, are called "phase change materials" (PCMs). It's a bit of an odd name since all materials are phase change materials, but the PCM label has stuck as a way to refer to ones where we try to do something useful technologically or scientifically with the energy stored/released by the phase change.

PCM's are used in many applications, including the simple heating pack (which I'll get to in a moment), but also in high temperature applications. Take the molten salts used in solar thermal power plants as an example. Sunlight is focused onto a salt or mixture of salts (like sodium and potassium nitrate for example), which melts the salt into a liquid during the day. When it cools down at night the now-solidifying salt maintains a precise temperature at its phase change for a long period of time (which is good for a power plant), until it freezes completely back into a solid. There are many other PCM materials and many other uses of PCM materials, and knowing the phase diagram so that one can dial in exactly the right temperature of sto red heat release is the first step to making it possible!



And let me conclude this Why This Matters with one more striking fact. I started by explaining that 90% of all energy is generated/consumed as thermal energy. But a massive 60% of the heat generated to power our world is wasted! We could capture and recycle much of that energy. There's a lot of interest and research in the development of new PCMs with higher storage densities (higher enthalpies of fusion), which means new chemistries. The ability to make a new PCM that possesses all of the key desirable metrics for a given application requires a deep understanding of the intermolecular interactions in the PCM which in turn lead to its phase diagram.

There's also exciting new work towards making PCMs "triggerable," so that it would stay stuck in the liquid state until some external trigger is applied. Then, when triggered, it would solidify and release all of its phase change energy, ready to be "charged" again as a solid. This already happens in some cases, and it takes advantage of the phenomenon of supercooling that we discussed in the lecture. In a pack of sodium acetate trihydrate (chemistry shown here), for example, it's fairly easy to supercool, so when the material heats up past its melting point of 58C it becomes a liquid but it can be cooled back down to room temperature without solidifying right away. It stays metastable in a supercooled state, until some trigger is applied like a little external mechanical force (or an ice cube would do it too). That trigger reminds the material that it actually wants to be a solid at this temperature, in other words it provides a nucleation site for the solid phase, and then since it's a good 30°C below the melting point it all ends up solidifying and giving off all its phase change (enthalpy of fusion) energy. There's a lot of interest and work towards developing new ways to keep PCMs supercooled, which in turn could make thermal energy storage look much more like electrical energy storage: triggerable and distributable energy on demand. That, in turn, would revolutionize the energy consumption landscape!

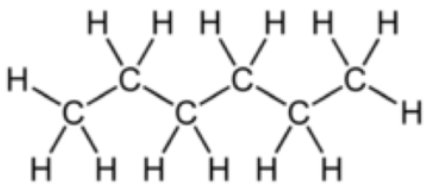
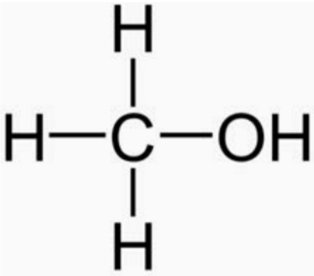
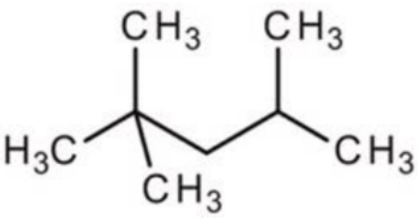
Why this employs

How can a phase diagram get you a job? It's easier than you might have thought! Many companies make and use materials (like, almost all), and in the use of materials many companies have needs. These could mean the development of completely new materials or it could mean the slight tweaking of existing materials properties. But either way, the starting place for any materials design is the phase diagram of the material. And one place where that starts is in knowing how to calculate phase diagrams. There are companies you could work at that directly make and sell sophisticated software to compute phase diagrams (check out thermo-calc or factsage for example), and then there are the thousands of companies that post jobs where knowledge of how to use such software is required.

Want to design new rocket engines? Lockheed has openings where deep knowledge of thermodynamics is required. Or how about the "thermodynamics engineer" posting at United Launch Alliance (which makes rocket engines too). Or if you want to make buildings more energy efficient you could join PassiveLogic, which is working on, "developing the next generation control technology for the future of smart cities," and is currently seeking a, "thermodynamics and simulation intern." Or you could join one of MIT Course 3's spin-outs, Boston Metal, which is working on greener metal production and has a current opening that requests applicants have a, "strong understanding of thermodynamics/phase equilibrium." Of course, this list goes into the thousands because ultimately any form of engineering uses materials, and the form of materials used is based on its phase diagram.

Extra practice

1. Rank the following molecules in ascending vapor pressure order:

i) Hexane	ii) Methanol	iii) Isooctane
		

Answer

Methanol has the least vapor pressure because its OH group allows it to hydrogen bond to other methanol molecules. Next is hexane because, though it does not have hydrogen bonding capabilities, it is more linear than isooctane so can experience greater London dispersion forces. Isooctane has the highest vapor pressure because it has no hydrogen bonding capability and is less stackable than hexane so it has less London dispersion forces present.

2. Three ice cubes are used to chill a soda at $20C$. The soda has a mass of 0.25 kg. The ice is at $0C$ and each ice cube has mass 6.0 g. Find the temperature when all ice has melted.

Answer

The ice cubes are at the melting temperature of $0C$. Heat transfers from the soda to the ice. Melting of the ice occurs in two steps: first the phase change occurs and solid ice transforms into liquid water at the melting temperature, then the temperature of this water rises. Melting yields water at $0C$, so more heat is transferred from the soda to the water until the water plus soda system reaches thermal equilibrium.

$$Q_{\text{ice}} = -Q_{\text{soda}}$$

The heat transferred to the ice is:

$$Q_{ice} = m_{ice} \times L_f + m_{ice} \times c_W \times (T_f - 20C)$$

Bringing all terms involving T_f on the left-hand-side and all other terms on the right hand side, solve for the unknown quantity T_f:

$$T_f = \frac{m_{\text{soda}} \times c_W \times 20C - m_{ice} \times L_f}{(m_{\text{soda}} + m_{ice}) \times c_W}$$

The resulting value is $13C$.

3. Imagine a substance with the following points on the phase diagram: a triple point at $.5$ atm and -5°C; a normal melting point at 20°C; a normal boiling point at 150°C; and a critical point at $5\ \text{atm}$ and 1000°C. The solid liquid line is "normal" (meaning positive sloping).

a) Roughly sketch the phase diagram, using units of atmosphere and Kelvin.

Answer

1-solid, 2-liquid, 3-gas, 4-supercritical fluid, point O-triple point, C-critical point -78.5°C(The phase of dry ice changes from solid to gas at -78.5°C)

b) Describe what one would see at pressures and temperatures above 5 atm and 1000°C.

Answer

One would see a super-critical fluid, when approaching the point, one would see the meniscus between the liquid and gas disappear.

c) Describe what will happen to the substance when it begins in a vaccum at -15°C and is slowly pressurized.

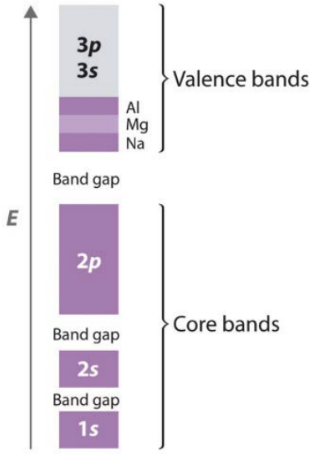
Answer

The substance would begin as a gas and as the pressure increases, it would compress and eventually solidify without liquefying as the temperature is below the triple point temperature.

Lecture 15: Electronic bands in solids

Summary

When two atoms come together, their atomic orbitals combine to form a set of bonding and antibonding molecular orbitals (MOs). When 10^{24} atoms come together to form a solid, their atomic orbitals combine to form a **continuous band of electronic states**. The bands are filled up with electrons: how full they get depends on how many electrons each constituent contributes and how closely spaced in energy the bands are.



For example, here is the band energy diagram for Na, Mg, and Al. All of these elements have full $1\mathrm{s}$, $2\mathrm{s}$, and $2\mathrm{p}$ bands: these "core bands" are therefore completely filled with electrons. Na has one additional $3\ \mathrm{s}^1$ valence electron, which fills up $1/8$ of the combined $3\ \mathrm{s}/3\mathrm{p}$ band. Similarly, Mg has valence electron occupation of $3\ \mathrm{s}^2$ and Al has $3\ \mathrm{s}^2 3\mathrm{p}^1$, which fill up the $3\ \mathrm{s}/3\mathrm{p}$ band even more.

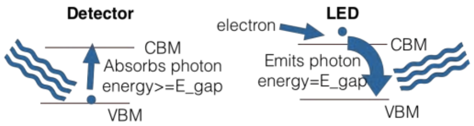
Here, the $3\ \mathrm{s}$ and $3\mathrm{p}$ bands are shown as one combined band: when bands are very close in energy, they can overlap, and essentially combine to form one continuous set of states. When there is an energy gap between the most energetic electrons that live in one band and the least energetic electrons that live in the next band, a band gap forms, like those shown here between $1\mathrm{s}$ and $2\mathrm{s}$, $2\mathrm{s}$ and $2\mathrm{p}$, and $2\mathrm{p}$ and $3\ \mathrm{s}/3\mathrm{p}$ bands. Note that the term band gap is reserved to describe only one of these band gaps, as discussed below.

Knowing the band filling tells us a lot about the properties of the solid. If the highest energy band is partially filled, the material is a metal. If the highest filled band is completely full of electrons, then there is a gap between it and the next-highest band: this is the band gap of the material, and these solids are called semiconductors. In semiconductors, the highest energy band that is completely filled with electrons is called the **valence band**, and the next highest unoccupied band is called the **conduction band**. If the band gap is very large, say > 4 or $5\mathrm{eV}$, then the material is electrically insulating.

The band gap has a property similar to that in the antibonding MO or nodes in higher-energy AOs: namely, all of the energies within the band gap are forbidden, so all of the electrons must be in a band, not in-between. Within a band, electrons can move around: if there is no gap and the material is a metal, it is easy for electrons to freely move around, and conductivity is high. It's harder for electrons to move around in a semiconductor, but it's possible for an electron to get an energy boost and transition from one band to another; often, these boosts come from light or heat. Of course, it takes less energy to cross a small gap between two states than a large one: it is much more likely for thermal energy (about $0.025\mathrm{eV}$/atom at room temperature, $300\mathrm{K}$) to excite an electron into the conduction band of a semiconductor like Si than an insulator like diamond (C).

Electrons can also be excited into the conduction band via light: semiconductors with energy in the range from about $1.5-3\mathrm{eV}$ can be excited by visible light (about $400-800\ \mathrm{nm}$). If a photon's wavelength corresponds to just the right energy to match the bandgap, that electron can jump across the forbidden energy region. In this case, it jumps to the conduction band and becomes free to move around! With this in mind, it is possible to control the flow of electrons across the gap-and the conductivity of the semiconductor-with light. If the band gap is larger than the lowest wavelength visible light, the material can't absorb higher-energy photons, and the material is transparent in the visible light range.

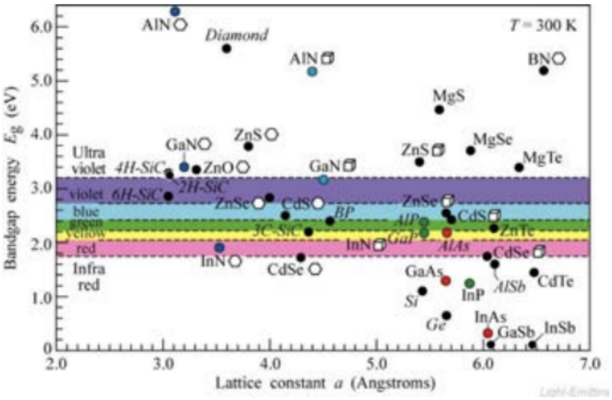
Why this matters



The world we live in uses a lot of light. And in case you haven't noticed, more and more of that light comes from LEDs, or light emitting diodes. Whether it's your phone or laptop or television or car or fridge or house or office or street, odds are the way it lights up is with LEDs. And those work because they are semiconductors. As discussed in lecture, a semiconductor forms when the bonding in a material together with its structural arrangement leads to the formation of a band gap of just the right size (a few eV). From this we immediately have two well-known devices. First, electrons in the valence band maximum (VBM) can be excited by light into the conduction band minimum (CBM) where they conduct, a device otherwise known as a photo-detector. Second, we can have the opposite: put electrons into the CBM and as they cascade down to the VBM, photons are emitted, a device otherwise known as an LED.

In lecture 3, I used television as the topic of Why This Matters and mentioned that the reason color TV took so long to develop was that stable, inexpensive, red phosphors were a challenge. For LEDs it turns out it was also a particular color that delayed their ubiquity, but in this case it was blue, on the higher end of the gap. For phosphors it was chemistry that held the key to inventing new molecules that could absorb electrons and shine red. Once again, 50 years later, it was chemistry that held the key to unlocking a new material, in this case a semiconductor that could take a current of electrons and convert them into blue light. The trick comes in being able to engineer the band gap of the solid.

Check out this plot of band gap vs. the lattice constant, which is a measure of the spacing between atoms in a periodically repeating crystal. We'll be digging into crystals in a few weeks, but for now you can consider the x-axis to be simply any structural feature of the solid. The point is that there is a strong dependence, and once this dependence was known and understood, then new alloys could be developed with just the right chemistry and therefore structure, to give just the right bandgap and therefore color.



Take a look at GaN on the plot and notice that its bandgap is just a tad too high if we want blue to be emitted as electrons cascade from its CBM to VBM. On the other hand, other materials like InN have bandgaps that are far lower in energy than what is needed to emit blue. It turns out that alloying different materials together is one of the most effective ways to "tune the bandgap," and that's exactly how scientists got to blue. They already had red and green, so once they got blue they were able to combine them all together to get white LEDs, which have completely taken over the market since.

The idea of purposefully modifying the bandgap of a material is called bandgap engineering, and it is the centerpiece of the semiconductor revolution. It reaches far beyond LEDs, as the bandgap is a crucial property in lasers, transistors, detectors, and so much more of our electronic world.

Why this employs

How can knowledge of the band structure of a solid lead to a job? This may, in fact, be the easiest Why This Employs section to write of the whole semester! Semiconductors are so ubiquitous in our world that it's nearly impossible to move without interacting with them. They're in almost any and every electronic device. They're so important some would call this the age of the semiconductor. Moore's law depends on making tinier devices out of them each year. They make electricity from the sun. They provide light from electricity. They communicate for us. They compute for us. I could go on.

The semiconductor industry is massive and there are many jobs in many companies, and many MIT students go on to work in this industry. There are so many jobs in the semiconductor industry that there's a website called semiconductorjobs.com. And many other similar websites. Even more interestingly, the industry is no longer just about making faster chips or specialized chips like for wireless communication. It's gotten so much bigger because of all of the various needs for these materials and devices, from consumer electronics to smart cars to Hollywood to space exploration to artificial intelligence. There are jobs related to all of these areas, both in the traditional semiconductor industry (think, Intel, AMD, Semtech, TI, and dozens more), but also in the companies working on these applications (think, Bosch, Toyota, Dreamworks, Microsoft, Google, and hundreds, maybe thousands more), as well as companies doing both, like Samsung.

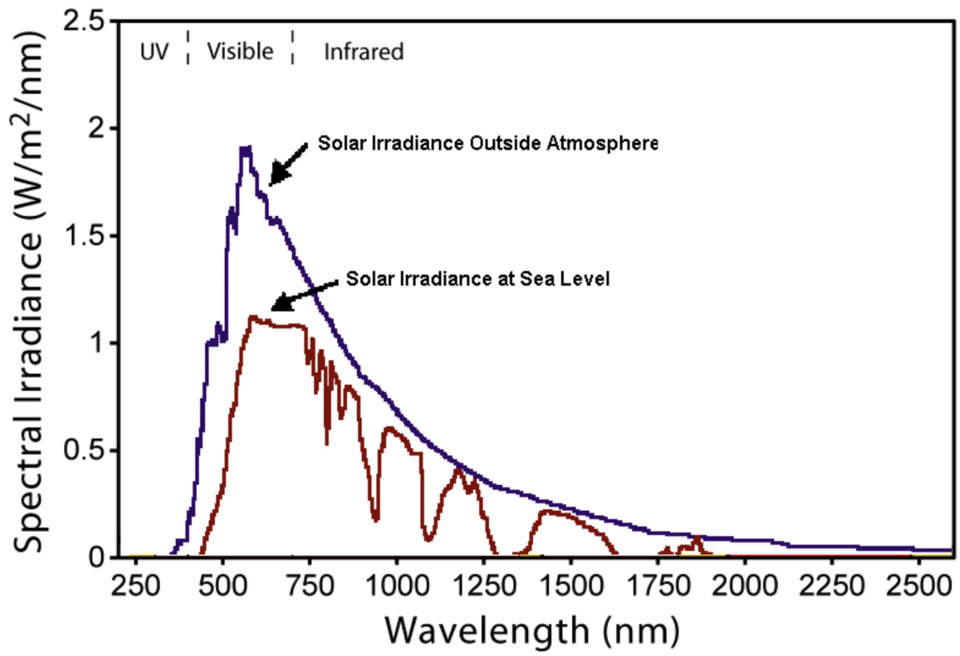
Example Problems

1. Suppose your LED is made of silicon and you want to make it absorb higher wavelength light. Should you alloy it with germanium or carbon? Explain your answer.

Answer

Absorb higher wavelength = smaller bandgap. Thus alloy with Ge since larger atom = smaller bandgap.

2. Below is a plot of sunlight intensity at Earth's surface as a function of wavelength.



Calculate the band gap wavelength of each of these well-known semiconductors, and mark the range of wavelengths of light that each semiconductor could absorb. Which do you think would make the **worst** solar cell? Choose one:

Answer

Use the good old energy to wavelength conversion trick:

$$E(eV) = \frac{1240}{\lambda(nm)}$$

A. Si $\text{(band gap 1.14eV)} = 1088 \text{ nm} = 1.088\text{microns}$

B. Ge $\text{(band gap 0.67eV)} = 1851 \text{ nm} = 1.851\text{microns}$

C. GaAs $\text{(band gap 1.39eV)} = 892 \text{ nm} = 0.892\text{microns}$

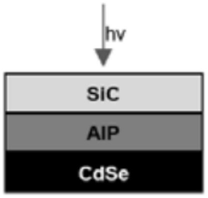
D. InSb $\text{(band gap 0.16eV)} = 7750 \text{ nm} = 7.750\text{microns}$

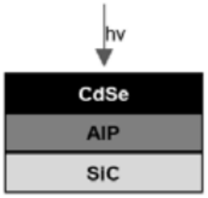
Each material will absorb light with wavelengths shorter than this band gap wavelength (so everything to the left of that wavelength on the graph).

The InSb absorption spectrum will extend well off the side of the graph (it absorbs EVERYTHING) - but because the bandgap of InSb is so small, the electrons it excites don't carry very much energy (they lose the excess to heat) so it would be a horrible solar cell.

A. Si (band gap 1.14eV)
B. Ge (band gap 0.67eV)
C. GaAs (band gap 1.39eV)
D. InSb (band gap 0.16eV)

3. You have three different materials: AlP (band gap 2.45eV), SiC (band gap 3.0eV), and CdSe (band gap 1.74eV). Which of the following three geometric arrangements is likely to be the most efficient at converting sunlight to electricity? Explain your answer.





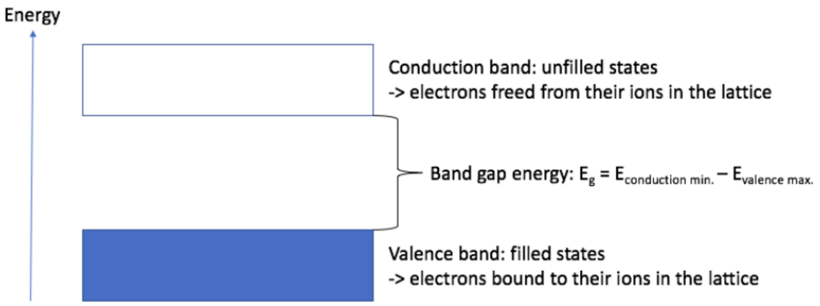
Answer

Top left: all wavelengths absorbed and least thermal energy released.

Lecture 16: Semiconductors and Doping

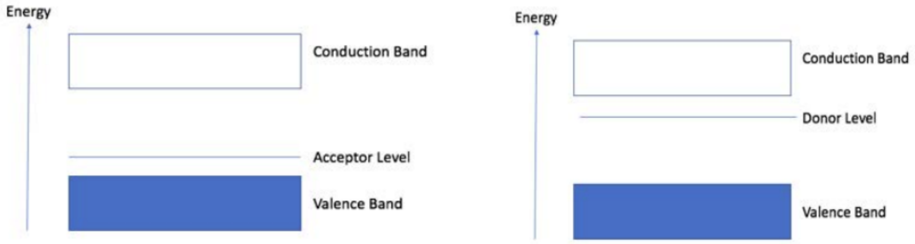
Summary

Semiconductors have this name because their conductivity of electrons lie somewhere between those of insulators and metals. The **band gap** of a semiconductor, meaning the space between its **conduction band** and **valence band**, is larger than that of a metal but smaller than that of an insulator. Initially, the electrons are bound to the **lattice** (the arrangement of atoms in the solid) and cannot conduct. Their energy states are within the valence band. In order for electrons to conduct, they must obtain enough energy to leave the valence band and enter the conduction band, which involves passing the band gap (forbidden energy states).



LEDs are semiconductor devices that emit light with wavelength corresponding to their band gap energy as an electron falls from the minimum of the conduction band to the maximum of the valence band.
If an electron is promoted to the conduction band with an excess of the band gap energy, this excess energy will be dissipated as heat.

Two ways in which these initially bound electrons can achieve conduction are via a thermal energy transfer and through **doping**, which involves introducing **impurities** (a relatively small number of foreign atoms compared to the number of atoms in the lattice) to increase the density of **charge carriers** (electrons or **holes**, the absence of an electron which essentially acts as a positive charge). (Note: there’s a third way we discussed in the last lecture, by kicking electrons above the gap using photons). There are two types of doping, p-type and n-type. P-type doping involves adding impurities with fewer electrons than the atoms in the undoped lattice (i.e. aluminum doped into silicon). P-type doping creates holes. The presence of these holes enables conduction in the lattice and the creation of an acceptor energy level.

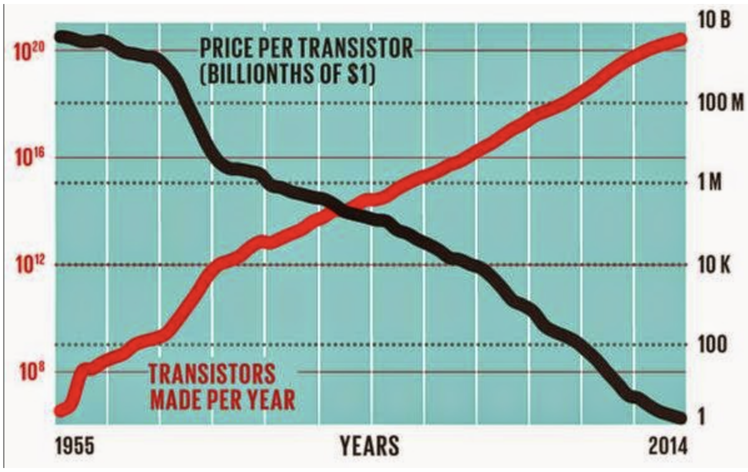


N-type doping involves adding impurities with more electrons than the atoms in the undoped lattice (i.e. phosphorus doped into silicon). N-type doping introduces additional electrons (negative charge carriers). These electrons have an energy corresponding to the donor level, and are able to conduct with a much smaller addition in energy compared to the electrons in the valence band.

Why this matters

The entire semiconductor industry is built on ways to dope Si, Ge, GaAs, and other semiconductors with precise amounts of desired impurities, to make n-type and p-type semiconductors which then get put in the billions into a single chip in extremely complicated arrangements. This is how the very first transistor was made, by putting an n-type and p-type semiconductor in contact with one another. You can learn all about the very first transistor in so many great resources (like this short video explanation for example, https://www.youtube.com/watch?v=JBtEckh3L9Q). Here's a picture of that very first transistor, which doesn't look like what you'd see on a computer chip today–but it's the first p-n junction and it opened the door to a revolution.

Just to get a little perspective: In 2014 250 billion billion transistors were made, which amounts to a pace of 8 trillion transistors per second. Here's a chart of what we call Moore's law, which isn't a law at all but rather simply what happens when a lot of incredibly smart scientists and engineers work on something for 60 years.



Speaking of smart, how do we, as humans, do our natural computing? How do the computers we make stack up to the brains we use to make them? You see, Moore's law looks, and is, impressive, but it's a measure of computing power, not power consumption. Data centers alone currently account for 3% of global CO_2 emissions and estimates are that within 10 years over 20% of all electricity will be consumed by IT. Most of this energy goes into sending current through trillions and trillions of p-type and n-type semiconductors.

Just for fun, let's compare the power consumed by a computer that has the equivalent number of processors as the human brain. A typical adult human brain has about 10^{11} neurons, or nerve cells, each one connected to about $10,000$ other neurons via connectors called synapses, which are the superhighways of information processing in the brain. A brain has a total of around 10^{14} synapses.

With 1 transistor being equivalent to about 10 synapses, we can build a computer as powerful as the brain, or at least with as much computing capacity, with 10^6 computer chips (each chip packing 10 billion transistors). This would require around $10\mathrm{MW}$ to power. That's $10,000,000$ Watts of power needed to run the artificial brain. In comparison, the human brain runs on about 20 Watts!

The reason I'm making this comparison in our Why This Matters is that the $\mathrm{p-n}$ junction and the transistor brought forth an amazing revolution spanning many orders of magnitude. But we're still short another 6 zeros on power consumption reduction, if we ever want to try to match the brain, for which another revolution is clearly needed.

Why this employs

Since I brought up the human brain and compared it to computer chips, let's focus this section on the brain-machine interface. This has been, of course, the subject of many science fiction movies (yes, The Matrix), but it's also been the focus of many research labs and government programs for at least the past 30 years. This is because of the massive potential in enabling the human-brain interface to help patients with a wide range of neurodegenerative disease. And all of this work has brought us to quite an exciting time in efforts to merge the brain with machines, one in which many new commercial entities are forming.

Elon Musk, for example, launched Neuralink a few years ago. This is a pretty exciting company not only because of its initial concept, but also because they have brought in highly talented and interdisciplinary teams of scientists, doctors, and engineers. Many of the people involved in such an effort will need to know about semiconductors and doping, and in this case the serious challenge of creating electronics that are "brain friendly" (take a look at the work of Professor John Rogers, as an example). A number of companies have invested in this area, like Boston Scientific, Abbot, Blackrock Microsystems, CorTec, or NeuroNexus, to name only a few. And government programs are also growing efforts, for example through DARPA or the NIH BRAIN Initiative.

Example problems

1. Doping levels in semiconductors typically range from $10^{13}/\mathrm{cm}^3$ to $10^{18}/\mathrm{cm}^3$, depending on the application. In some devices (like transistors) you need several n- and p-type materials with different doping concentrations.

Si has a density of $2.328\ \mathrm{g/cm^3}$. What is the ratio of Si atoms to dopant atoms in $10^{13}/\mathrm{cm}^3$ doping and $10^{18}/\mathrm{cm}^3$ doping?

Answer

To find the ratio between Si atoms and dopant atoms, we need to find the number of Si atoms per cubic cm. This is a straightforward stoichiometry problem:

$$\frac{2.328\mathrm{gSi}}{1\ \mathrm{cm}^3\mathrm{Si}} \times \frac{1\mathrm{molSi}}{28\mathrm{gSi}} \times \frac{6.022\times10^{23}\ \mathrm{atomsSi}}{1\mathrm{molSi}} = \frac{5\times10^{22}\ \mathrm{atomsSi}}{\mathrm{cm}^3}$$

Now we take the ratio of Si atoms to dopant atoms, obtaining:

a) $5\times10^{22} : 10^{13} = 5,000,000,000 : 1$

b) $5\times10^{22} : 10^{18} = 50,000 : 1$

a) $10^{13}/\mathrm{cm}^3$

b) $10^{18}/\mathrm{cm}^3$

2. You dope Ge with $2.43\mathrm{mgMg}$.

a. What kind of doping is this? What charge carriers are introduced?

Answer

p-type doping; holes are introduced

b. How many carriers does each substitution yield?

Answer

each substitution yields 2 carriers

c. Calculate the number of charge carriers created by the addition of 2.43mgMg.

Answer

$$2.43\text{mg} \times 10^{-3}\frac{\text{g}}{\text{mg}} \times \frac{1\text{ mol}}{24.3\text{ g}} = 10^{-4}\text{ mol}$$
$$\text{2 carriers per substitution: } 2 \times 10^{-4}\text{ mol holes}$$
$$2 \times 10^{-4} \times 6.602 \times 10^{23} = 1.32 \times 10^{20}\text{ holes}$$

d. How much Ge should you start with if you want a charge carrier density of $1016/\text{cm}3$?

Answer

$$10^{16}\text{carriers/cm}^3 = 1.32 \times \frac{10^{20}}{x}$$
$$x = 1.32 \times 10^4\text{ cm}^3\text{Ge}$$

3. For 13 cm3 of Si, calculate the number of milligrams of B atoms needed in order to have 3.091*10 17 carriers/cm^3. Assume that the dopant only substitutionally incorporates into the Si.

Answer

p-type: carriers are holes

$$13\text{ cm}^3 \times \frac{3.091 \times 10^{17\text{ carriers}}}{1\text{ cm}^3} \times \frac{1\text{ atom}}{1\text{ carrier}} \times \frac{1\text{ mol}}{6.022 \times 10^{23}\text{ atoms}} \times \frac{10.81\text{ g}}{1\text{ mol}} \times \frac{1000\text{mg}}{1\text{ g}} = 0.0721\text{mg}$$

Lecture 17: Metallic Bonds and Properties of Metals

Summary

Metals are formed from atoms that have partially-filled electronic bands: the valence electrons are loosely bound, forming a **sea of electrons** throughout the solid. The liberated valence electrons are free to move around the fixed cations: they are shared by all of the atoms in the solid, rather than fixed to one specific atom. The bonds that form between metal atoms are called metallic bonds. Unlike ionic or covalent bonds, where the electrons involved in the bond are closely bound up with the ions, metallic bonds don’t belong to one ion or another.

Metals are characterized by their **high electrical conductivity, high thermal conductivity, high heat capacity, ductility**, and **luster**. Each of these properties can be correlated to the electronic structure and the sea of electrons picture.

Because the electronic bands in metals overlap—there is no band gap—electrons can move freely through the closely-spaced energy states. If an electron at the surface is perturbed, it is easy for the energy to transfer across the solid: the Drude model for conduction relates electron drift to applied field, yielding **conductivity**. The free electrons can also vibrate, so solid metals can efficiently transfer thermal energy, or **heat**. The thermal conductivity of metals is directly proportional to the electrical conductivity through the Wiedemann-Franz law. The properties of metals can also be controlled via alloying. For example, bronze is a metal alloy with Cu and Sn in a 4:1 ratio. Though the presence of Sn lowers the overall conductivity to 10% of pure copper, bronze is much more resistant to corrosion. Brass is a metal alloy with Cu and Zn in a 2:1 ratio. Though the conductivity is 28% of pure copper, the brass is much more malleable than pure copper.

Two mechanical properties are shared by most metals: malleability and ductility. Both are a measure of how much a material can deform without breaking. **Malleable** materials can be compressed a lot without breaking, while **ductile** metals can be stretched a lot without breaking. High malleability and ductility allow metallic solids to be drawn into wires, or hammered into complex shapes. For example, a platinum rod 1cm in diameter and 10cm long can be drawn into $\equiv 2777\text{km}$ of wire just by pulling. Surprisingly, these mechanical properties can be directly correlated to the electronic structure. As the solid is deformed and ions move around, the sea of electrons can easily move around, allowing atoms to rearrange without breaking enough bonds to lead to fracture.

Periodic trends in metallic bond strength are directly related to electronic structure. Metallic bonds are typically weakest for elements with nearly empty (Cs) or nearly full (Hg) valence subshells, and strongest for elements with half-filled valence shells (W). When the valence band is half-filled with electrons, the ratio of bonding orbitals: antibonding orbitals is maximized. In

MO theory, atomic orbitals combined to form bonding and antibonding states. In the band picture, the bottom of the valence band represents 100% bonding character and the top of the band represents 100% antibonding character. Therefore, **half-filled valence bonds** yield the strongest metallic bonds. For transition metals, the atomic orbitals are so close in energy that they often overlap, creating wide energy bands with shared characteristics. Metals in groups 6-9 are most likely to have $\approx$ half-filled valence bands, so the metallic bonds they form are strongest.

Why this matters

Corrosion of metals is the worst. The global cost of corrosion is estimated to be $2.5 trillion. Yes, trillion! This is equivalent to 3.4% of the global GDP in 2013. We don't think much about corrosion in our day-to-day lives. We think about it as the rusting of the spokes of a bike wheel or some old-looking gears. But if a pipe corrodes enough, it can crack. If a boat corrodes enough, it can sink. These are extremely serious problems that involve not only a dramatic loss of money, but also a serious safety risk and potential loss of life. If you dig into the topic of corrosion, you'll find that many industries have adopted what they call, "corrosion management systems." What this really means is that they are aware it's a big problem, and they're going to try to do something about it. But what can they do? The answer to that question is, of course, chemistry. And because of chemistry, $500 billion annually is saved by preventing, or at least dramatically slowing, corrosion. Much more work needs to be done.

The automotive industry is an excellent example of an industry that has moved from minimal corrosion control in the 1970's when the life of a car was typically set by the corrosion of the body and frame, to state-of-the-art corrosion control through advanced painting/coating technology and the use of corrosion-resistant materials. In this chapter I mentioned the use of alloying as a way to make metals more resilient, with the example of bronze which is copper with a dash of tin. This is exactly how anti-corrosion coatings are developed and they can come in the form of paints or additional metal alloy layers or treatment of existing metal surfaces. Large structural metals like those used in bridges or wind turbines are often treated with zinc and aluminum-based coatings to provide long-term corrosion prevention, while many steel and iron fasteners are coated with a thin layer of cadmium to block hydrogen absorption, which can lead to stress cracking. Nickel-chromium and cobalt-chromium alloys are often used as corrosion prevention coatings because they have very low levels of porosity which makes them extremely resistant to moisture, which in turn inhibits rusting. Oxide ceramics like alumina (which remember we've already discussed when we talked about ionic bonds!) can make excellent and strong coatings.

The chemistry of corrosion is a highly active and extremely important area of research, and deeper understanding of the chemistry of how it happens, as well as how chemistry can be used to prevent it, represents a continued massive challenge and enormous opportunity.

Why this employs

How can metal make a job? Let's go with an example that's a big part of our future, and is actually really cool: 3D printing. Of metals. In a few short years, 3D printing of metals has gone from concept to fringe to near-mainstream. Many companies can now 3D print metal parts and many innovations are still happening at these companies. What kind of people do these companies hire? Those who know about the electron sea, of course!

There are many companies in this space, including one of our very own, an MIT-based spin-out called Desktop Metal that formed in 2017. One of the exciting aspects of 3D metal printing is that there's no one standard, at least not yet. So many different companies are working on pushing the frontiers of different technologies, from Desktop Metal which uses something they call Bound Metal Deposition, to Concept Laser which sinters metals with a laser and is now owned by GE, to Arcam (also now owned by GE) which uses an electron beam to melt the metal, to Xact Metal which uses something called Powder Bed Fusion, to ExOne which uses something called binder jetting, to Vader Systems which utilizes magnetic fields, to Cytosurge which claims nanometer resolution, to many more companies and many more approaches to the printing process. All of these approaches require continued development of new chemistries ("inks") and new ways to manipulate those into tailored, complex, and high-resolution shapes.

Example Problems

1. Metals vs. semiconductors

a) Why are metals better electrical sonductors than semiconductors?

Answer

Metals do not have a band gap, so their electrons can freely conduct, giving rise to the "sea of electrons" effect

b) How often do doped semiconductors reach the electrical conductivity levels of metals?

Answer

Doping in semiconductors is never enough to reach the conductivity levels of metals. This is because the concentration of dopants (the impurities that contribute electrons or holes to the bulk material) is extremely small and is not enough to alter the material's band structure.

2. Why is silver (Ag) more electrically conductive than platinum (Pt)?

Answer

Ag is more electrically conductive than Pt because of atomic radius–increased atom size leads to increased atomic spacing, which increases electron movement.

3. Rank the following metals in order of increasing metallic bond strength, and explain your reasoning:

A. Co

B. Cd

C. W

D. Ni

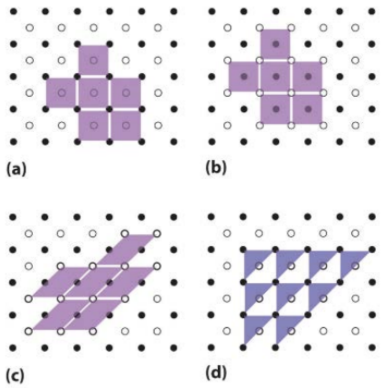
Answer

Metallic bonds tend to be weakest for elements that have nearly empty or nearly full valence shells. They are strongest for those with half-filled valence shells. Therefore,

weakest: $\mathrm{Cd}, \mathrm{Ni}, \mathrm{Co},$ strongest: W

Lecture 18: The Perfect Solid: Crystals

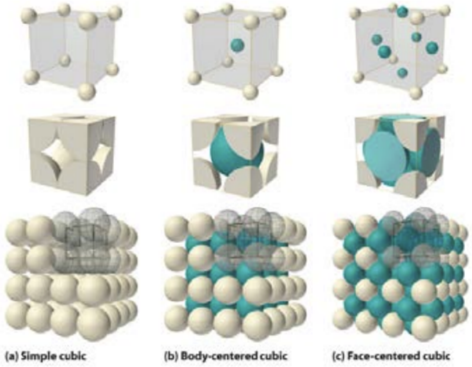
Summary



Crystalline solids possess long-range order: the arrangement of the bonds plays an important role in determining the properties of crystals. Each crystal has a unit cell, a repeating unit like a stamp that can be tiled into a pattern. Often, there are many unit cells that could be chosen for a given crystal; it's conventional to select the smallest unit cell that contains all of the necessary information. In the figure, (a), (b), and (c) all show valid unit cells and how they tile, but (d) isn't valid because when tiled, it doesn't cover all the space: there are gaps. In 3D space, unit cells comprised of various atomic arrangements give information about crystalline solids. The unit cell also gives information about how atoms pack together. The packing fraction is a measure of how much of the 2D area of the unit cell is filled up by atoms:

Packing fraction = (area occupied by atoms)/(total area available)

In 3D space, there are only 7 distinct unit cells that can fill all of space with no voids. Bravais figured out how to arrange atoms into unit cells; it turns out there are only 14 unique Bravais lattices. In 3.091, we'll focus on cubic unit cells, which have all sides the same length and all angles = 90 degrees. There are three distinct cubic unit cells.

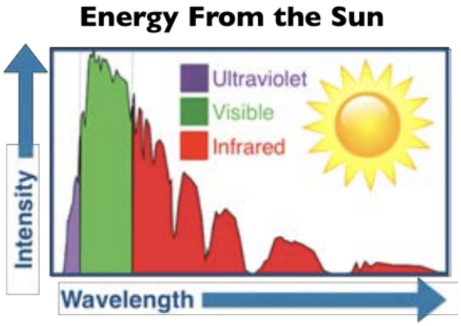


The top row indicates the position of atom centers for each of the cubic lattices. Next, the atoms are shown as filling up the maximum amount of volume: this helps to visualize how many atoms are in each unit cell. Finally, each of the unit cells are shown in the context of a bigger section of a crystal. Several key metrics help determine the macroscopic properties of a crystal, including the atomic packing fraction (APF) and the coordination number. The atomic packing fraction is calculated in 3D space:

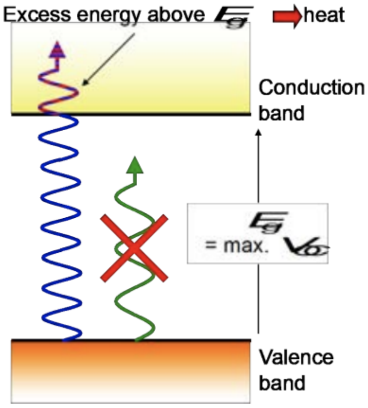
APF=(atoms in unit cell)*(volume of atom)/(volume of unit cell)

The volume of an atom can be approximated as the volume of a hard sphere: $V = 4/3 * \pi * r^3$. For each of the cubic lattices, the radius of the appropriate hard sphere can be related to the lattice constant (width of the unit cell). Finally, the coordination number, or the number of nearest neighbors, gives information about how many atoms are available to form bonds. The number of atoms in the unit cell is the sum of the parts of atoms shared between neighboring unit cells. For example, the body-centered cubic (BCC) unit cell has a full atom at the center and also an atom at each corner that is shared equally between 8 cells. Therefore, the total number of atoms in a BCC unit cell is 8*1/8+1=2 atoms/unit cell.

Why this matters



Let's go back to an application of semiconductors that I mentioned a few lectures ago but didn't delve into. It's about using light energy to excite electrons above the bandgap, and the fact that this means you can harness light as a form of electricity with the right materials. That's called a solar cell, or a photovoltaic device. Here's the energy we receive on planet earth from the sun. We saw this plot when we gave the example of the ozone molecule as a key reason we don't receive much UV on the planet (since ozone absorbs it high up in the atmosphere). This time, I'm using the plot to show that not only does the intensity strongly depend on the wavelength of light, but much of the energy we receive comes either in the visible or the infrared parts of the spectrum. Naively, you may think the best solar cell would simply absorb everything; in the language of our bandgap and semiconductor lectures, that means it would have a very small bandgap, since the smaller the gap, the lower the energy of the photon can be to excite an electron above the gap. In a solar cell, once an electron is excited above the gap, that negative charge then gets extracted out of the device from the conduction band, while the positive hole gets extracted from the valence band. Those extracted charges can then do work (like charge your phone).



Ah, but were it only so easy! The challenge is that once the electron is excited it very quickly "thermalizes" down all the way to the bottom of the conduction band. It's a process that happens so quickly that there's very little we can do about it (although there is an active area of research to extract "hot electrons" out of materials, before they can thermalize, but no working devices at this point). This thermalization means that the amount of energy the electron can have when it is ready to do work, no matter how high in energy the photon was that excited it, is equal to the energy of the band gap. That's shown here in this energy diagram as the blue squiggly line. A photon of this blue energy would be absorbed by the material, and the excited electron wouldn't lose any energy since it didn't go higher than the bandgap. But if a higher frequency light is absorbed, like that purple squiggle, then the photon still creates an excited electron in the material, although any excess energy above the bandgap is lost, since the electron quickly drops down to the conduction band minimum before it can be extracted.

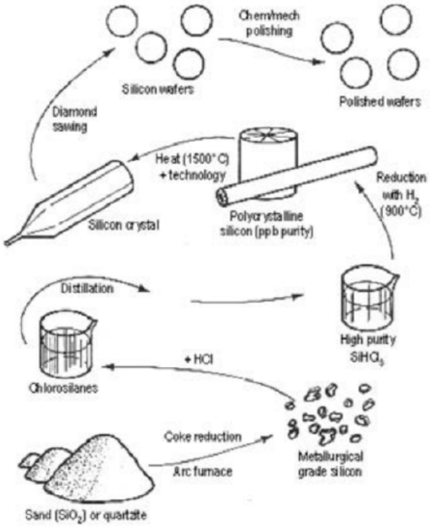
On the other hand, if the photon that comes in has an energy lower than the bandgap, say that green squiggle in the diagram, then it won't be absorbed at all (no states are present to be excited into). And here is why understanding the chemistry of solar cells is so important, for we have competing drivers: the lower the gap, the more of that spectrum can be absorbed, but the less energy the electron has to do work and the more energy lost to thermalization, while the higher the gap the more energy the electron has in that CBM, but fewer photons can be absorbed. This is because, as we learned, the semiconductor can only absorb light equal or greater in energy to its band gap. This trade-off means there's an optimal bandgap for a solar cell made from one single material, and that optimal gap is right around 1.3 eV. That's quite close to the bandgap of silicon, which is 1.1eV.

Yes, but that is only if we have a perfect crystal! In fact, silicon could have a much lower bandgap, depending on how good of a crystal it is. If it has defects (these are interruptions in the lattice and stay tuned, that topic is coming soon!), then the bandgap can go way down, with the limit being that silicon could even become metallic if the crystallinity is messed up too much. This explains part of the reason why silicon has been expensive and also has to go onto glass as opposed to plastic substrates: namely, because a silicon solar cell has to be made very thick (100's of microns).

The truth of the matter is that silicon is a terrible light absorber. That's right, the solar cell material that dominates the world market at $>85\%$ is horrible at doing one of the most important things it needs to do: absorb sunlight. Silicon is still is capable of absorbing, of course, but it's just inefficient so it just has to be made very thick in order to capture all of the light. Compare that to other materials that can absorb light efficiently like a dye molecule, which could absorb all the sun's energy in 1000x thinner layers. The thickness of silicon is a double-whammy: first, it means the solar cell is brittle, cannot bend, and must go on glass which makes the whole device heavy, and 2) it means the excited charges have a much further distance to travel in the material before they can reach an electrode and be extracted for work. And that means high cost, since it's a lot of material that needs to be made as perfectly crystalline as possible. It can be (almost) done, but it's difficult, expensive, and requires huge fabrication plants. But getting that quality, that crystallinity over large distances (yes, microns are very large distances for an electron or an atom!), is worth it because crystallinity holds the key to the semiconductor properties. In this case, it's the electron transport we're talking about, and the more ordered and crystalline the lattice is, the better for the charges to move around.

Why this employs

Since this lecture is all about crystallinity, let's take a look at the employment opportunities in making crystals. It is true that you can dig up rocks from the ground and they may already have crystalline order in them, like the inside of this rock shown here. But most of the time these crystals are useless for technology since they contain all sorts of orientations all jumbled up together, they often have a lot of defects in them, and also they're usually not pure elements but rather minerals containing the element of interest along with impurities (like oxygen). So the question is: how does one make as pure of a crystal as possible out of a single element? Let's take silicon as an example.



Here's a figure of all the steps that it takes to turn sand into crystalline silicon. As you can see, there are a lot of them, and many involve high temperatures or chemical mixing. A lot of companies operate at different stages of this chart. For example, getting from sand to "metallurgical grade silicon" is something a lot of smaller companies do, like Mississippi Silicon, Elkem, or Silicon Materials, Inc., to name only a few. These are often companies with a few hundred employees so they may not have a large number of job postings, but there are many companies so if you do a deep dive into the full landscape of silicon producers you'll likely find some good opportunities.

Once a company has made high enough purity silicon, they can then mold it into an ingot. This also requires further purification and also again high temperatures. Most of the companies that make high-purity ingots are currently based in China, although there are others scattered around the world including in places like Japan, Germany, and Korea. And once there's an ingot, it can be sliced into wafers that can then be made into devices. Here we have a lot of large companies specializing in this process, like Applied Materials or Lam Research, among many others.

Example problems

1. Calculate the atomic packing fraction (APF) of a simple cubic unit cell.

Answer

Volume of unit cell $=a^3=8r^3$ (because lattice constant, $\mathrm{a}=2\mathrm{r}$)

Volume of one atom $=r^3$

of atoms in simple cubic unit cell $=1$

Lattice constant, $\mathrm{a}=2\mathrm{r}$

$\mathrm{APF}=($ volume of one atom $) /($ volume of the unit cell $) \mathrm{x}$ (number of atoms in a cell)

$$\frac{\frac{4}{3}\pi r^3}{8r^3}\times 1=\frac{\pi}{6}=52.4\%$$

2. Which of the three cubic structures do you think is more likely to form at high pressure? Why?

Answer

FCC is more likely than BCC which is more likely than SC. Higher packing fraction means atoms are closer together

3. CsCl forms an interpenetrating SC lattice, which looks like a BCC lattice but with 2 different types of atoms. For this problem, we'll use a BCC lattice and assume that the $\mathrm{Cl}-$ ions are at the corners.

a) How many of each type of atom are in the unit cell?

Answer

$1 \mathrm{Cl}-$ ion and $1 \mathrm{Cs}+$ ion

b) What is the lattice constant, a (the length of one side of the unit cell), in terms of the atomic radii r_{Cs} and r_{Cl}? What is the value of a in Å?

Answer

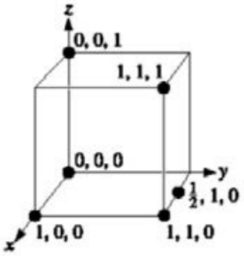
Close packed direction = body diagonal

$$\sqrt{3}a=2r_{Cs}+2r_{Cl}$$
$$\sqrt{3}a=2(2.38A)+2(1.00A)=3.90A$$

Lecture 19: Slicing a Crystal: the Miller Planes

Summary

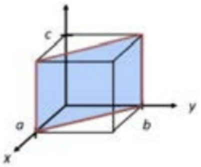
A **crystal lattice** is a map that indicates how identical points are arranged in space. In the last lecture, we placed a single atom at each lattice site, and from there we could calculate atomic packing fraction. However, anything could be placed at the lattice sites, as long as the same thing is put at every lattice site. The lattice is “how” to repeat; “what” to repeat is called the **basis**. The unit cell serves as a way to think about where we are in the crystal.



For **points** in the lattice, Cartesian coordinates $(\mathrm{h}, \mathrm{k}, \mathrm{l})$ are used: conventionally, they're scaled by the lattice constant. A **direction** within the crystal is described by a vector: these vectors always start at the origin, so directions are completely described by the end point of the vector, which lies on a face of the unit cell. The notation is slightly different for crystallographic vectors: the end points are scaled to all be integers, and they're enclosed by brackets with no spaces, [hkl]. For example, the vector from $(0,0,0)$ to $(1/2,1,0)$ in the diagram is the crystallographic direction [120]. This notation is called **Miller Indices**. A negative direction is indicated with an overbar: the vector from $(0,0,0)$ to $(-1,0,0)$ is written as $[\bar{1}00]$. In a cubic system, all directions with the same set of Miller Indices are equivalent, regardless of order: these can be grouped into **families** of directions: these are indicated with angle brackets, $\langle hkl \rangle$.

Miller indices can also be used to describe crystallographic planes, which can be determined by following 4 steps:

1. Read off the points at which the plane intercepts the axes in terms of fraction of the unit cell length
2. Take reciprocals of the intercepts
3. Divide by the greatest common factor to yield integer values
4. Enclose in parentheses, with no commas (hkl)



For example, this plane intercepts the x-axis at $x = 1$, the y-axis at $y = 1$ and it never crosses the z-axis, so the z intercept is $z = \infty$. The reciprocals of these values are 1,1, and 0, so thus is the (110) plane.

A **family** of planes in the cubic system contains all of the planes with the same set of Miller Indices but in any order. Families of planes are indicated by curly brackets, $\{hkl\}$.

The packing density in a given plane is calculated as

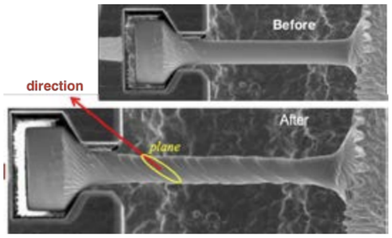
Planar packing density = (atoms in the plane)/(area of the plane) [atoms/area]

Note that the planar packing density is not the same as the planar packing fraction, which is unitless! Finally, the distance between planes described by the same set of Miller indices, d, can be determined in terms of the lattice constant, a:

$$d = \frac{a}{\sqrt{(h^2 + k^2 + l^2)}}$$

Why this matters

One of the key properties that depends on the density in a plane is the energy to cleave a crystal. This turns out to be extremely important since cleaving is just what it sounds like: cutting, or in other words, breaking. If a crystal can be cleaved in a certain crystallographic direction more easily than another, then that is the direction in which the crystal will break most easily. In fact, this is why crystals are so often “faceted,” even when they’re just dug right out of the ground. The Why This Matters for today isn’t about how a crystal looks, but rather how it breaks. That planar packing density can tell us which plane gives in to a strain put on a crystal, and therefore how the crystal winds up deforming under strain.



Take a look at the crystal being pulled here in this picture, before a tensile strain is applied and afterwards. Notice that when it’s stretched, it has those tilted disclike shapes. That’s because it breaks along the Miller planes that have the lowest packing density since those are most weakly bonded. Not only does this inform us as to when a crystalline material will break, but it gives us the atomic-scale picture of how it breaks and what shape it takes as it breaks. Now, a lot of solids may not have large differences in the energy required to break different Miller planes, so this type of phenomenon may not occur when it’s under tensile strain. For many metals the bonds are not so directional and the material can simply deform easily because of that sea of electrons accommodating the stretch (remember that wire drawing example from Lecture 16?). Then there’s the other end of the spectrum, where a material is so anisotropic that in one direction the planar density and bonding type are completely different than in the other directions. Graphite (pictured here) is a beautiful example of this.

Thin long wires can be made out of graphite, too. In fact, carbon fibers, as they’re called, make up a $1.7B market today, and it’s a market that’s growing strong. If we could just get the cost down by about a factor of 10 or so, then carbon fibers would be able to compete with materials like steel on cost while being stronger, lighter, and more resilient. Just for comparison, today’s carbon fibers are 10x stronger than steel while being 5x lighter! If the cost of carbon fibers could be lowered, then we’d replace everything we could with them because they’re just that good. Carbon fibers are not graphite but they are like graphite, in the sense that they have large sp^2-bonded planes of carbon that are aligned together. But in order to give it added strength either the planes are kind of crumpled, or they’re bonded to one other through covalent links. Either way, it’s the ability to engineer the chemistry of the Miller planes that makes all the difference.

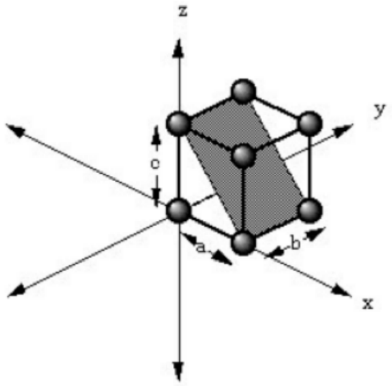
Why this employs

Let’s keep going with the carbon fibers concept from the Why This Matter section above. As I mentioned, carbon fibers could completely revolutionize structural materials and make so many aspects of our lives lighter, stronger, and more efficient. But a lot of work is yet to be done on the fibers themselves to lower their cost, as well as to integrate them into other products, from fabrics to plastics to concrete to metal. A lot of companies are doing extremely interesting work related to these problems. And yes, it all starts from a solid understanding of those Miller planes and crystallographic directions.

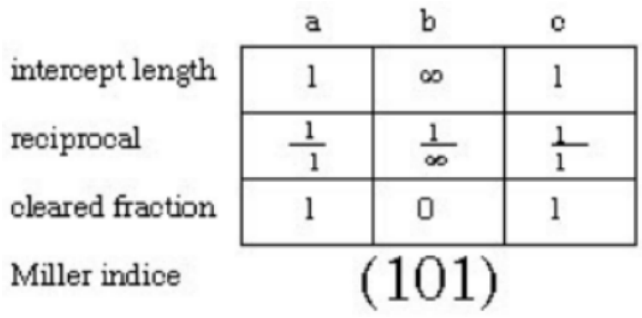
Hexcel has annual revenue over $2B and their flagship product is carbon fiber and composites. Note that both their name as well as logo are all about those hexagons in graphite! Hexcel is also cool because on their website they directly list student internship opportunities. Another company in this space is Solvay which makes thousands of products, many of which involve crystal planes of graphite. There’s Toray, with its origins in race cars, which lists carbon fibers as one of their 5 core businesses, and there’s Nippon Steel which has a whole subsidiary devoted to Granoc, a light-weight fabric or yarn made from carbon fibers. Its proprietary carbon fiber chemistry, they promise, is, “spinning the future.”

Example Problems

1. Give the Miller indices of the shaded plane:



Answer

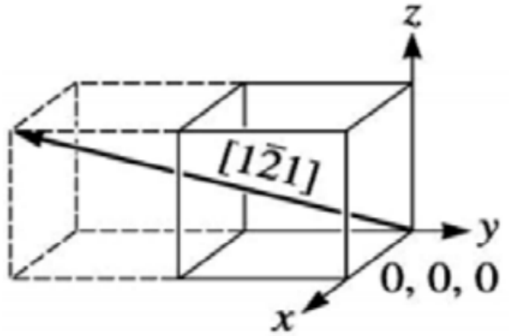


	a	b	c
intercept length	1	∞	1
reciprocal	$\frac{1}{1}$	$\frac{1}{\infty}$	$\frac{1}{1}$
cleared fraction	1	0	1
Miller indice	(101)		

2. Draw the following in a cubic unit cell:

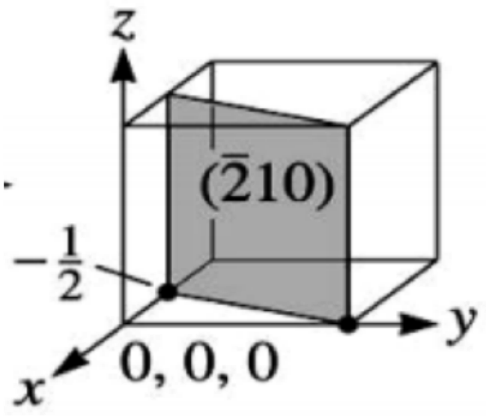
a) ($\bar{2}$10)

Answer



b)[1$\bar{2}$1]

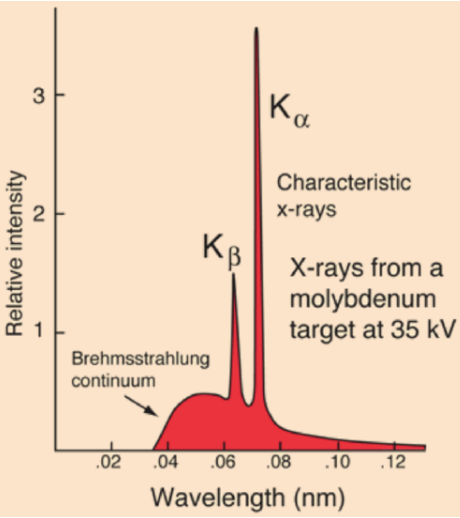
Answer



Lecture 20: X-ray Generation

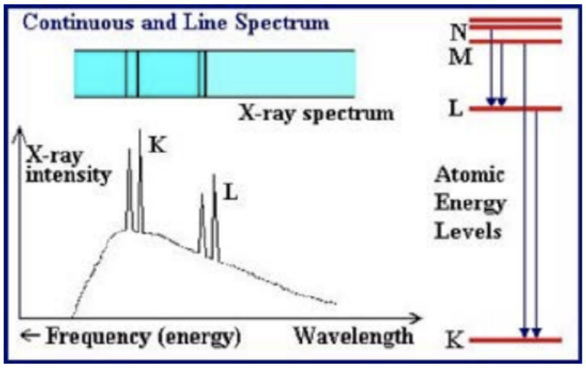
Summary

Atoms are too small to see with visible light, but x-rays have just the right range of wavelengths to image at the atomic scale. Wilhelm Rontgen first discovered x-rays by observing electrons striking a metal target in a cathode ray tube. Electrons were emitted from a heated filament and directed by an electric field inside the tube to very high velocities. When the high-speed electrons strike metal atoms, two kinds of xrays are generated. Continuous x-ray radiation is caused by the deflection of an incoming electron as it interacts with a metal target atom: as the name suggests, the allowed wavelengths for the Bremsstrahlung (which translates to ”braking radiation”) are a continuous spectrum above a lower bound. The lower bound on wavelength (upper bound on energy) is set by the energy of the incoming electron, because the energy of the emitted x-ray cannot be greater.



The second type of x-ray that can be generated is a product of the electronic structure of the metal target atoms. When a high-energy electron is incident on a metal atom, it can knock out an electron in the inner core of the target atom, allowing a higher energy core electron to cascade down. If the electron cascades down from the $n = 2$ to the $n = 1$ energy level, the photon that’s emitted is called an alpha photon. These x-rays are discrete: they occur at a single wavelength that corresponds to the difference in energy levels.

Crystallographers use a slightly different notation for the energy levels within an atom: the ground state $(n = 1)$ is called the K shell, $n = 2$ is the L shell, and $n = 3$ is the M shell. Using this notation, a photon that is emitted via the process of an electron falling from $n = 2$ to $n = 1$ is called a K-alpha photon. The energy difference between inner-shell electrons is huge- that’s why the photons that are emitted are x-rays.



Heavier elements have bigger differences between the energy levels, so the K-alpha wavelength is smaller. It is therefore possible to determine which kind of atom the x-ray was emitted from, just by knowing the wavelength: these x-rays are called characteristic xrays.

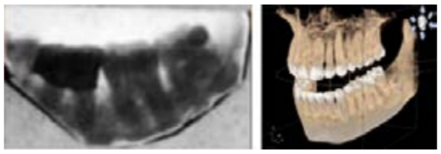
In this plot, the Brehmsstrahlung and the characteristic x-rays are shown together, as they'd be measured. The first two peaks are the K-beta (M to K) and K-alpha (L to K) lines, since those correspond to the biggest energy transitions within the atom. Then come the L-beta (N to L) and L-alpha (M to L) lines, which are much smaller energy gaps. The intensity can be changed by changing the number of electrons that are incident on the target. The lower-bound Brehmsstrahlung wavelength can be changed by adjusting the kinetic energy of the incident electrons, though this wouldn't change the location of the characteristic x-ray peaks at all. The only way to shift the characteristic x-rays is to change the target metal used to generate the x-rays. If the energy of the incident x-rays is too low, though, no characteristic x-rays would appear: the incident electrons must have enough energy to knock out a core electron to kick off the cascade.

Why this matters

The discovery of x-rays, and the subsequent ability to fully control what wavelength of x-ray is generated, has had so much impact on modern life that it's really tough to choose only one example for Why This Matters. But I guess since I have to pick, I may as well go back to the roots of Rontgen himself and one of the very first ways he used his new rays. That would be to take a picture of his wife! More precisely, her hand - it's the first x-ray picture ever taken and it started a revolution (The black circle on the second finger from the left is her ring, by the way).

The key thing about x-rays, which Rontgen noticed right away, is that they are able to pass through soft body tissue like skin and flesh, but they get absorbed by the denser material like bone. This means that if you shine x-rays on a body part, the bones inside cast shadows, which can be captured with a photographic plate. This was an incredible advance for medicine because for the first time a doctor could see inside a living patient without having to cut the patient open. Some of the earliest users of x-rays in medicine were military doctors, who could use them to optimize removal of bullets from a wounded soldier. As doctors saw how useful they could be, x-rays became central to diagnosis and by the 1930s they had led to the specialized field of radiology.

Not only are x-rays currently utilized routinely in many aspects of medicine, but the technology of x-ray imaging continues to improve dramatically. Beyond improved contrast in the images, one very recent breakthrough applies techniques originally developed for the Large Hadron Collider in Geneva, which is still the world's largest particle accelerator at 27 km long. With a combination of advanced shutters, cameras, and software, a completely new type of x-ray imaging is possible, with 3D and color images. Take a look at this very first x-ray picture of teeth, taken in 1896 with a 9-minute exposure time (!). Now look at a modern-day x-ray picture of teeth next to it. That's an incredible improvement, and even more so when you realize that the picture on the right is fully 3D and a dentist can spin it around to see all angles.



Why this employs

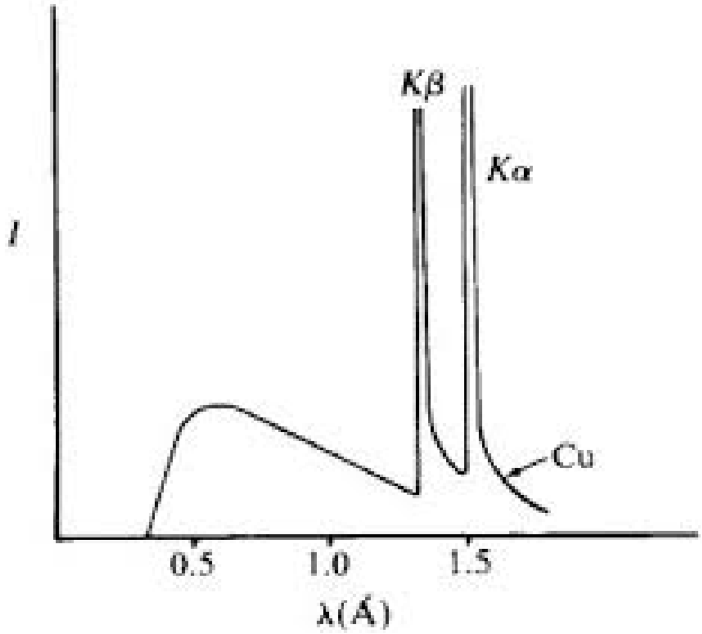
There's a whole lot of X-ray generation that goes on in the world, and the medical imaging example I gave above in Why This Matters is only one part of it. For example, X-rays are also used as scanners at airports, or as ways to do quality control for many industrial parts, or to analyze the degradation of valuable paintings, or in the field now called "X-ray astronomy," to name only a few examples. X-rays are also used not only to see an illness like cancer, but also to treat it ("radiation therapy"). Just the medical market for X-rays alone is set to surpass $16.5B globally by 2025. And all these uses for X-rays spells jobs.

There are many companies out there that make X-ray equipment. Siemens for example sells 6 different types of "digital X-ray equipment," but that's just one category – they've also got a robotic X-ray machine, as well as two types of CT scanners (yes those also use X-rays), and a fluoroscopy machine which uses X-rays to examine movement. And that's just one company! Siemens is a very large company, with the subsidiary "Siemens Healthineers" making this type of equipment. 41% of their US workforce of 13K people is in RD, engineering, IT, or tech support. And there are many others: Philips, GE Healthcare, Hitachi Healthcare America, Medtronic, Samsung Medical Devices, Eizo, Xoran Technologies, and United Imaging, Canon Medical Systems, and I'm still just getting started. All of these companies are selling wide ranges of X-ray equipment and they're all competing with one another for customers, which means they're constantly trying to improve their technology and differentiate what they're selling from their competitors. And beyond these large companies, there are many small-scale companies looking to innovate the field. For example the company MARS Bioimaging, based in New Zealand, is commercializing the 3D color X-ray technology that came out of the Hadron Collider.

And that's just the equipment side. There are also all the companies working on new software to analyze the images produced by all this X-ray equipment. For example, there are many start-ups applying AI to analyze the X-ray image data and in some cases AI has been shown to perform better than human doctors!

Example problems

1. Look at the x-ray spectrum below. You can see that $\lambda_{\kappa\beta}$ is lower than $\lambda_{\kappa\alpha}$. What about $\lambda_{\Lambda\alpha}$? Draw this peak on the spectrum.



Answer

$$\begin{aligned} E_{\kappa\alpha} &= 13.3(6-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right)=255\text{eV} \\ L_\alpha &: n_i=3; n_f=3+1=4 \\ L_\alpha &: n_i=3; n_f=3+1=4 \\ E_{L\alpha} &= 13.6(6-7.4)^2\left(\frac{1}{2^2}-\frac{1}{3^2}\right)=3.7\text{eV} \\ E_{\kappa\alpha} &> E_{L\alpha} \\ \lambda_{\kappa\alpha} &< \lambda_{L\alpha} \end{aligned}$$

2. What is the wavelength of κ_αx-rays produced by a copper source?

Answer

$$\begin{gathered} E=\frac{hc}{\lambda}=-13.6(Z-1)^2\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right) \\ Z=29, n_f=1, n_i=2\lambda=1.54A \end{gathered}$$

Further Reading

Lecture 10: Shapes of Molecules

- Additional VSEPR reading and practice:

  https://chem.libretexts.org/Bookshelves/General_ Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/09._Molecular_Geometry_ and_Bonding_Theories/9.2%3A_The_VSEPR_Model

- More on molecular shapes and medicines (not tested):

  https://www.pearsonhighered.com/ blbmw13einfo/assets/pdf/blbmw-ch09.pdf

Lecture 11: Molecular Orbitals

- Video breaking down Molecular Orbital Theory:

  https://www.youtube.com/watch?v=P21OjJ9lDcs

- Cool tool for visualizing molecular orbitals of water:

  http://www.bcbp.gu.se/~orjan/qc/h2o/ index.html

Lecture 12: Hybridization in Molecular Orbitals

- More detailed reading on hybridization:

  https://opentextbc.ca/chemistry/chapter/8-2-hybrid-atomic-orbital

Lecture 13: Intermolecular interactions

- Reviewing intra- vs. inter-molecular interactions:

  https://www.khanacademy.org/test-prep/ mcat/chemical-processes/covalent-bonds/a/intramolecular-and-intermolecular-forces

- Hydrogen bonds–essential for life:

  https://www.cbsnews.com/news/nature-up-close-water-and-life-as-we-know

- How Geckos Stick to Der Waals:

  https://www.sciencemag.org/news/2002/08/how-geckos-stick-der-waals

Lecture 14: Phase diagrams

- Tracing a phase diagram:

  http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch14/ phase.php

- More on phase changes, including interactive boiling point example:

  https://courses.lumenlearning. com/boundless-chemistry/chapter/phase-changes/

- On the thermodynamics of tempering chocolate:

  https://acselementsofchocolate.typepad. com/elements_of_chocolate/TEMPERINGCHOCOLATE.html

Lecture 15: Electronic bands in solids

- More on band theory:

  http://hyperphysics.phy-astr.gsu.edu/hbase/Solids/band.html

- More on semiconductor materials:

  https://www.pveducation.org/pvcdrom/pn-junctions/semiconductor-materia

- Britney Spears' Guide to Semiconductor Physics (one of the all-time best websites on the Internet):

  http://britneyspears.ac/lasers.htm

Lecture 16: Semiconductors and doping

- Review of doping:

  https://phys.libretexts.org/Bookshelves/University_Physics/Book%3A_University_Physics_(OpenStax)/Map%3A_University_Physics_III_-_Optics_and_Modern_Physics_(OpenStax)/9%3A_Condensed_Matter_Physics/9.6%3A_Semiconductors_and_Doping

- Beyond 3.091– P-N Junctions:

  https://www.pveducation.org/pvcdrom/welcome-to-pvcdrom/ pn-junctions

- How LEDs work:

  https://electronics.howstuffworks.com/led.htm

Lecture 17: Metallic bonds and properties of metals

- Review of metallic properties:

  https://courses.lumenlearning.com/introchem/chapter/bonding-in-metals-the

- Dive deeper into metallic bonding:

  https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Chemical_Bonding/Fundamentals_of_Chemical_Bonding/Metallic_Bonding

- How metals are extracted from the earth:

  https://www.bbc.co.uk/bitesize/guides/z3v9msg/ revision/1

Lecture 18: The perfect solid: crystals

- Review of SC, BCC, and FCC crystals:

  https://www.youtube.com/watch?v=_h-Xv9nsJLc

- More on unit cells and packing lattices:

  https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_A_Molecular_Approach_(Tro)/12%3A_Solids_and_Modern_Materials/12.3%3A_Unit_Cells_and_Basic_Structures

Lecture 19: Slicing a crystal: the Miller Planes

- Step-by-step Miller:

  https://www.youtube.com/watch?v=9-us_oENGoM

- Beyond 3.091–crystallography and reciprocal space:

  https://www.youtube.com/watch?v=DFFU39A3fPY

Lecture 20: X-ray generation

- More details on x-ray generation:

  http://xrayweb.chem.ou.edu/notes/xray.html

- X-rays in medical imaging:

  https://www.hopkinsmedicine.org/health/treatment-tests-and-therapies/ xrays

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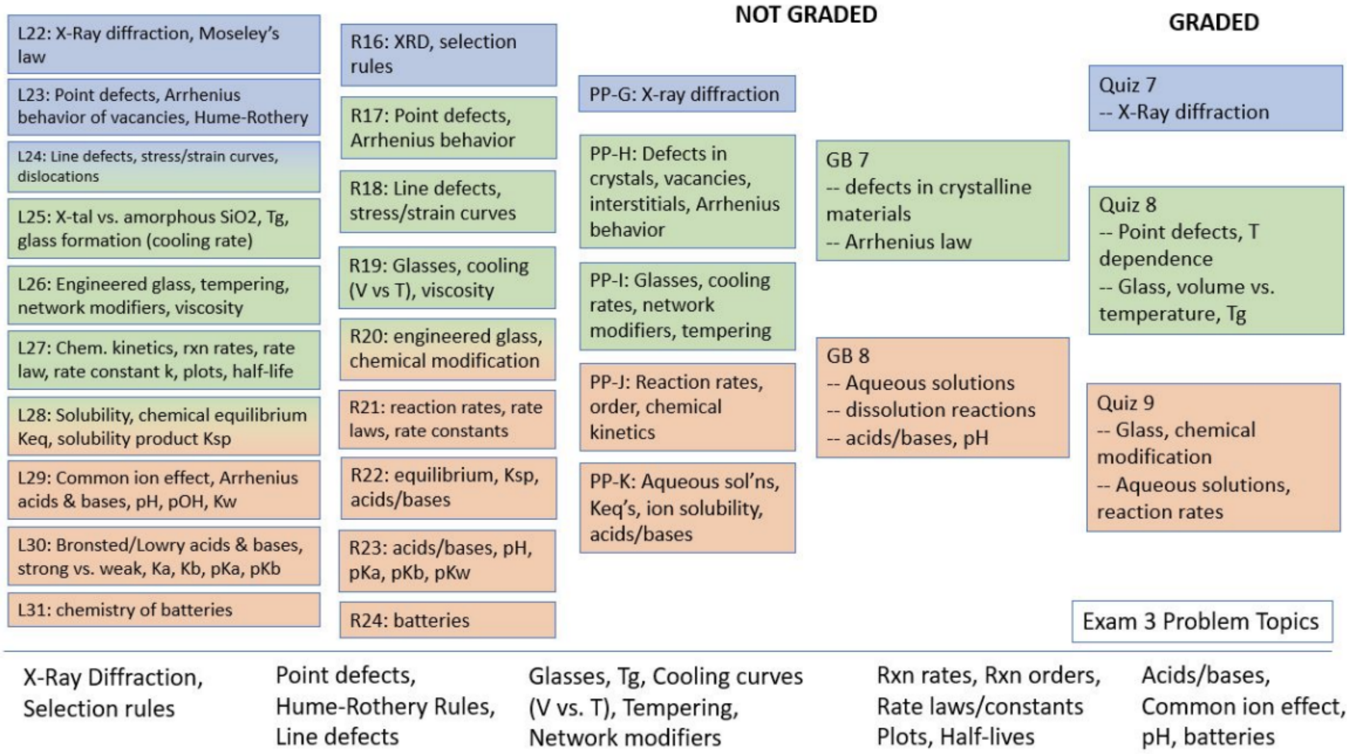
5.3: CHEM ATLAS_3

How This Connects: Unit 3, Lectures 21-30

The purpose of this document is to serve as a guide and resource that gives you a quick overview of each lecture. For each lecture, there is a summary of the main topics covered, the Why This Matters moment, and the new Why This Employs section, plus a few example problems. So why did we make this? We hope it's useful to get a good snapshot of any given lecture. Whether you couldn't make it to a lecture or you couldn't stop thinking about a lecture, this is a way to quickly get a sense of the content. It also gives me a chance to provide additional details that I may not have time for in the Why This Matters example, and also it lets me try out the Why This Employs section, which I certainly will not have time to discuss much in the lecture. Hopefully you find it useful!

One point about these lecture summaries. Please note that the lecture summaries are not meant to be a substitute for lecture notes. If you were to only read these summaries and not go to lecture, yes you'd get a good sense of the lecture from a very high level view, but no, you wouldn't get enough out of it for it to be your only resource to learn the material!

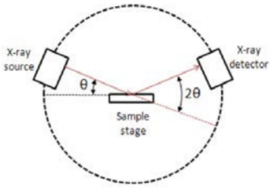
Below is an image of the Exam 3 Concept Map. This demonstrates how each of the aspects of the course fit together: you have lots of resources! The Practice Problems, Recitations, Goodie Bags, and Lectures are ungraded resources to help you prepare for the quizzes and exams. All of the material listed on this concept map is fair game for Exam 3.



Lecture 21: Bragg's Law and x-ray Diffraction

Summary

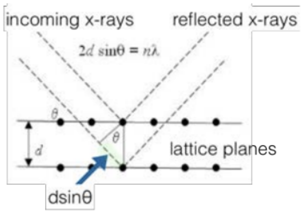
X-ray diffraction (XRD) is a method used for characterizing solids. It relies on the diffraction of x-rays upon striking crystal planes (the Miller planes we've learned about!) By assuming that each plane of atoms is continuous, and that they reflect the incoming x-rays such that the incident angle and the reflected angle are equal, the Braggs derived the equation that bears their name and relates the distance between repeating planes (d) and the x-ray angle of incidence (θ) to the x-ray wavelength:



Two x-rays striking equivalent Miller planes with the same angle of incidence will constructively interfere if the additional distance that one of the travels is equal to the wavelength of the x-ray. Quantitatively, if $\lambda = 2d\sin\theta$, the intensity of the outgoing x-rays with wavelength λ are enhanced. the constructive interference will occur whenever the path length distance is an integer multiple of the wavelength: $2d\sin\theta = n\lambda$ for integer n. For 3.091, we'll assume $n = 1$. When constructive interference occurs, a signal will reach the detector in the XRD machine and a peak will be observed in a plot of the x-ray intensity. For destructive interference, no peak will be observed. Knowing the angle that gives rise to a peak as well as the wavelength of the incident x-rays allows us to obtain the distance between the planes that produced the reflection. This is known as the **Bragg condition**:

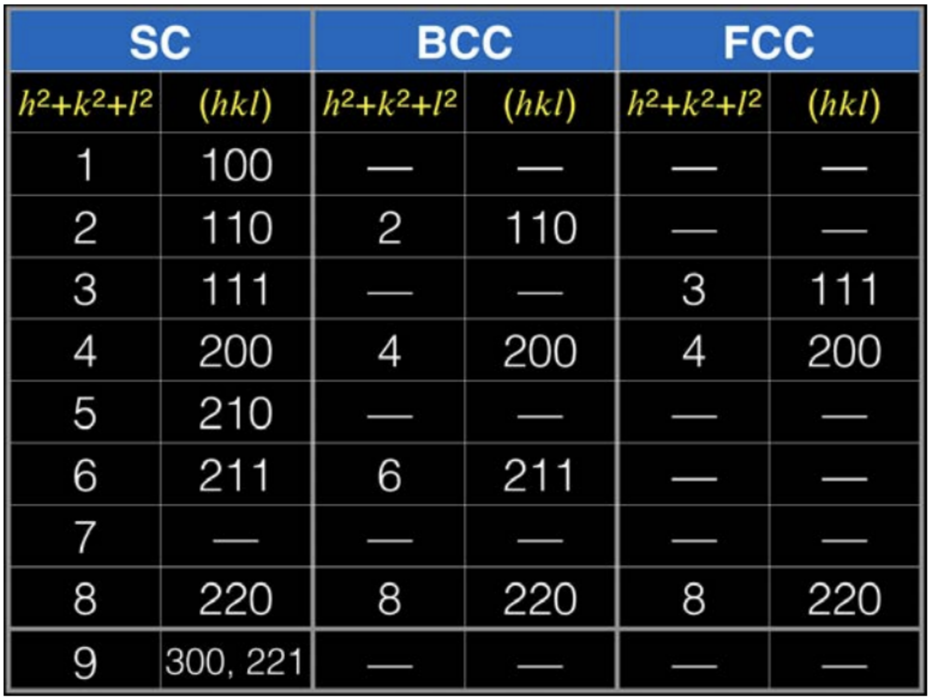
$$2d_{hkl}\sin\theta_{hkl} = \lambda$$

For a given Miller plane, denoted by (hkl), the Bragg condition is satisfied by a pair (d,θ) of inter-planar spacing and incident angle.



For each of the crystal structures (SC, BCC, or FCC), there are reflections that even when the Bragg Condition is met lead to destructive interference, due to crystal symmetry. The pattern of peak absences was used to derive a set of rules called **selection rules**, which allow us to know, or at least narrow down the possibilities of, the crystal structure of a material based on its XRD peaks. For the case of SC, there are no rules and any plane is fine. There are no forbidden reflections.

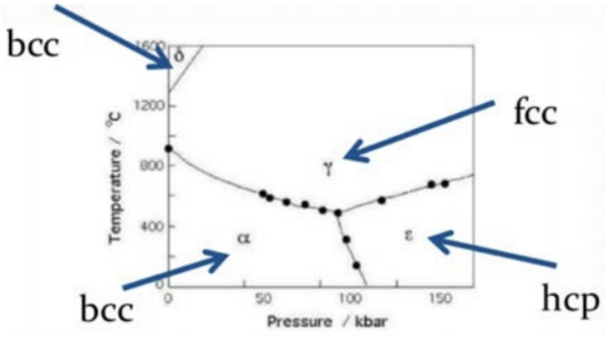
For the case of BCC, allowed reflections are those where $\mathrm{h+k+l}$ is an even number. Forbidden reflection are those for which $\mathrm{h+k+l}$ is an odd number. For the case of FCC, allowed reflections are those where $\mathrm{h,k,l}$ are all odd or $\mathrm{h,k,l}$ are all even. Forbidden reflections of FCC are those where h,k,l is mixed odd/even.



SC		BCC		FCC	
$h^2+k^2+l^2$	(hkl)	$h^2+k^2+l^2$	(hkl)	$h^2+k^2+l^2$	(hkl)
1	100	—	—	—	—
2	110	2	110	—	—
3	111	—	—	3	111
4	200	4	200	4	200
5	210	—	—	—	—
6	211	6	211	—	—
7	—	—	—	—	—
8	220	8	220	8	220
9	300, 221	—	—	—	—

Why this matters

For solids, structure can be as important as the chemistry itself, and they are deeply connected. When I look up the crystal structure of a element in the Periodic Table I see what it is for the ground or lowest energy state of that element. This is the overall “happy place,” energetically speaking, of the material. But materials can take on other, metastable structures and be very happy there, too. And Why This Matters is because the properties can be completely different depending on which crystal structure the material takes, and XRD is the single most important characterization method we have to determine crystal structure. We’ve already seen the difference between graphite and diamond, which contains the same exact element (carbon) but just arranged in a different structure. The same is true for, well, pretty much everything. Take another element, iron, as an example.



Here’s a phase diagram for iron. As you may remember from Lecture 14, a phase diagram is a plot of the different phases of a material as a function of some variables, in this case pressure and temperature. Notice that at normal, or “ambient,” temperature ($\approx 300\mathrm{K}$) and pressure ($\approx 1\mathrm{bar}$) conditions, iron is a BCC crystal. This is also what you’ll find if you look up its crystal structure in the PT. But notice from reading the phase diagram that if we raise the temperature it becomes FCC, and if we raise the pressure it goes into the HCP (it’s not cubic so we haven’t covered it) phase. Fun fact: if you keep raising the temperature eventually it will go back to being BCC.

The reason all of this matters is that the structure changes the properties. In the case of iron, the element’s magnetic properties are affected. If it’s FCC then it will be ’antiferromagnetic’ as opposed to the BCC ’ferromagnetic’ behavior. I recommend taking a magnetics course in the future to learn more about these terms! This has huge implications in magnetic technologies. And I know you’re probably thinking: sure, but we don’t build too many iron-based technologies that operate at $1000\mathrm{K}$! You’re right, but the trick is that often times we can coax these materials to get stuck in one of those metastable phases and then use it for technologies while it's in that phase. Again, diamond is a great example: it's not the ground state of carbon so it is metastable as diamond instead of graphite, but we know that it stays stuck there for a long time so for most technologies that use diamond (say, a piece of jewelry), we don't worry about it changing out of its metastable phase.

Coming back to the topic of the lecture, when we make something, whether that something is as old as elemental iron or as new as a nanostructured perovskite, the simplest and most common way we have to tell its crystal structure is by XRD. In some cases, the use of XRD can unravel the structural mystery of a material, as in the case of the double-helix for DNA or the many proteins since. In other cases, it's used to not unlock the secret to a completely new structure, but rather to classify a material into one or the other well-known structures. Sometimes the reason is to understand a material, sometimes it's to engineer the material properties, and often times it's both. But whatever the motivation, this incredibly powerful characterization tool has revolutionized what we know about solids.

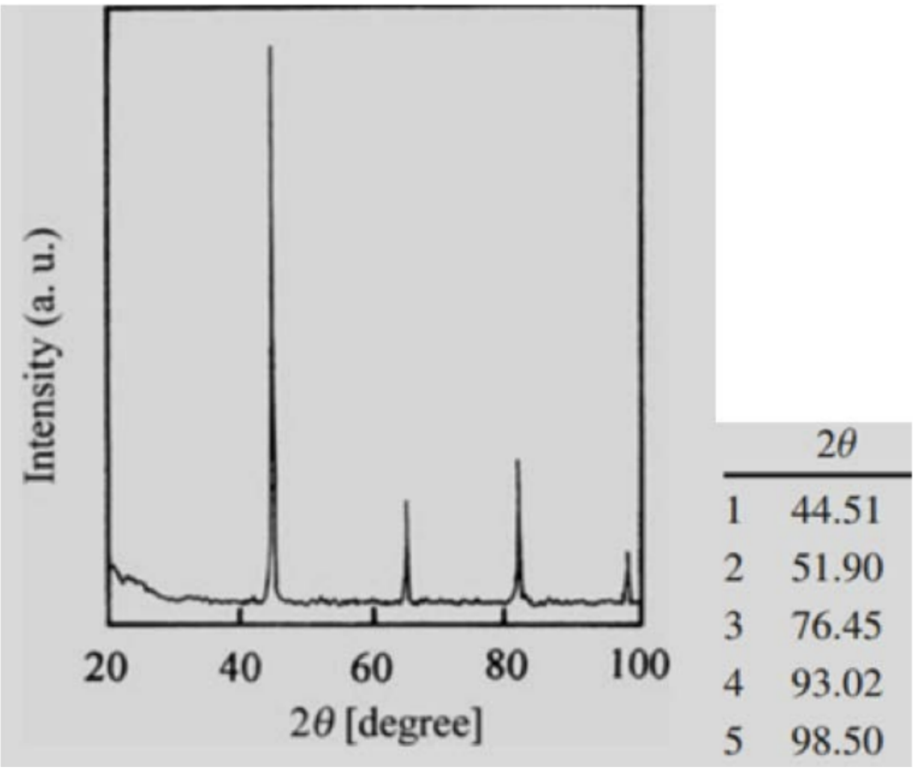
Why this employs

We've been referencing these crystallographers (who are very picky about notation!) for several lectures now. But who are these people? And more to the point: who hires them? A whole lot of X-ray crystallographer jobs are out there in the biotech industry, in companies of all sizes. Blueprint Medicines, which looks like a Harvard spin-out and is just down the street, has an opening now with the title, "Senior Scientist/Principal Scientist, X-Ray Crystallography," with the first job function description being, "Provide x-ray crystallographic and protein structure-function support, including structure-based drug design, to on-going drug discovery projects and new target discovery initiatives." And the larger pharmaceutical and biotech companies have even more jobs. Take Novartis, which also has a big headquarters near MIT, just down Mass Ave. They're hiring people to perform "crystallography experiments including crystallization screening using automated liquid handling. GlaxoSmithKline has an opening for someone to "enable higher throughput x-ray crystallography." Johnson and Johnson is hiring people with X-ray crystallography expertise to do, "automated chemistry." And I have to mention one last example because of the title of their current opening, Bristol-Myers-Squibb is looking for a, "Research Investigator, Solid-State Chemistry." Gotta love it! They want, "an entry level scientist with background in X-ray crystallography, X-ray diffraction, and solid-state characterization." That's now you!

And it's not all about pharma. Hospitals are hiring X-ray crystallographers too (these are not the same position as a radiologist), to work on research projects for example with openings at Mass General and Dana Farber. And many research positions in X-ray diffraction are out there too, from positions at the Howard Hughs Medical Institute to university labs and centers all across the country.

Example Problems

1. Determine the structure (simple cubic, body centered cubic, or face centered cubic) to which this XRD pattern most likely corresponds (copper κ_{α} x-rays were used).



	2θ
1	44.51
2	51.90
3	76.45
4	93.02
5	98.50

Answer

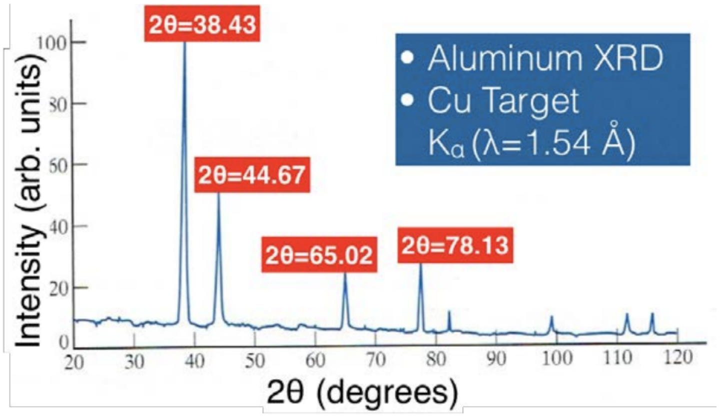
2θ	**θ**	**$\sin^2\theta$**	**normalized**	**integers**	**plane**
44.51	22.25	0.1434	1	3	(111): all odd
51.90	25.95	0.1915	1.33	4	(200):all even
76.45	38.23	0.3829	2.66	8	(220):all even
93.02	46.51	0.5263	3.66	11	(311):all odd
98.50	49.25	0.5739	4	12	(222):all even

Given that the indices of each plane are either all odd or all even, using the selection rules we are able to determine that this structure is FCC.

Lecture 22: From x-ray Diffraction to Crystal Structure

Summary

This lecture we finished analyzing the XRD spectrum of an Al sample, shown below.



The plot was obtained by shining K-alpha x-rays from a Cu target onto our Al sample. What we want to do is figure out the crystal structure and the lattice constant of Al. To answer these questions, we need our handy Miller plane separating distance equation (where ' d ' is the distance between two repeating Miller planes with indices hkl in a cubic system, and ' a ' is the lattice constant):

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+{}^2}}$$

and the Bragg condition:

$$2d_{hkl}\sin\theta_{hkl} = \lambda$$

Notice that both of these equations include d_{hkl}. We can use this to our advantage and substitute one equation for d_{hkl} into another to obtain the following:

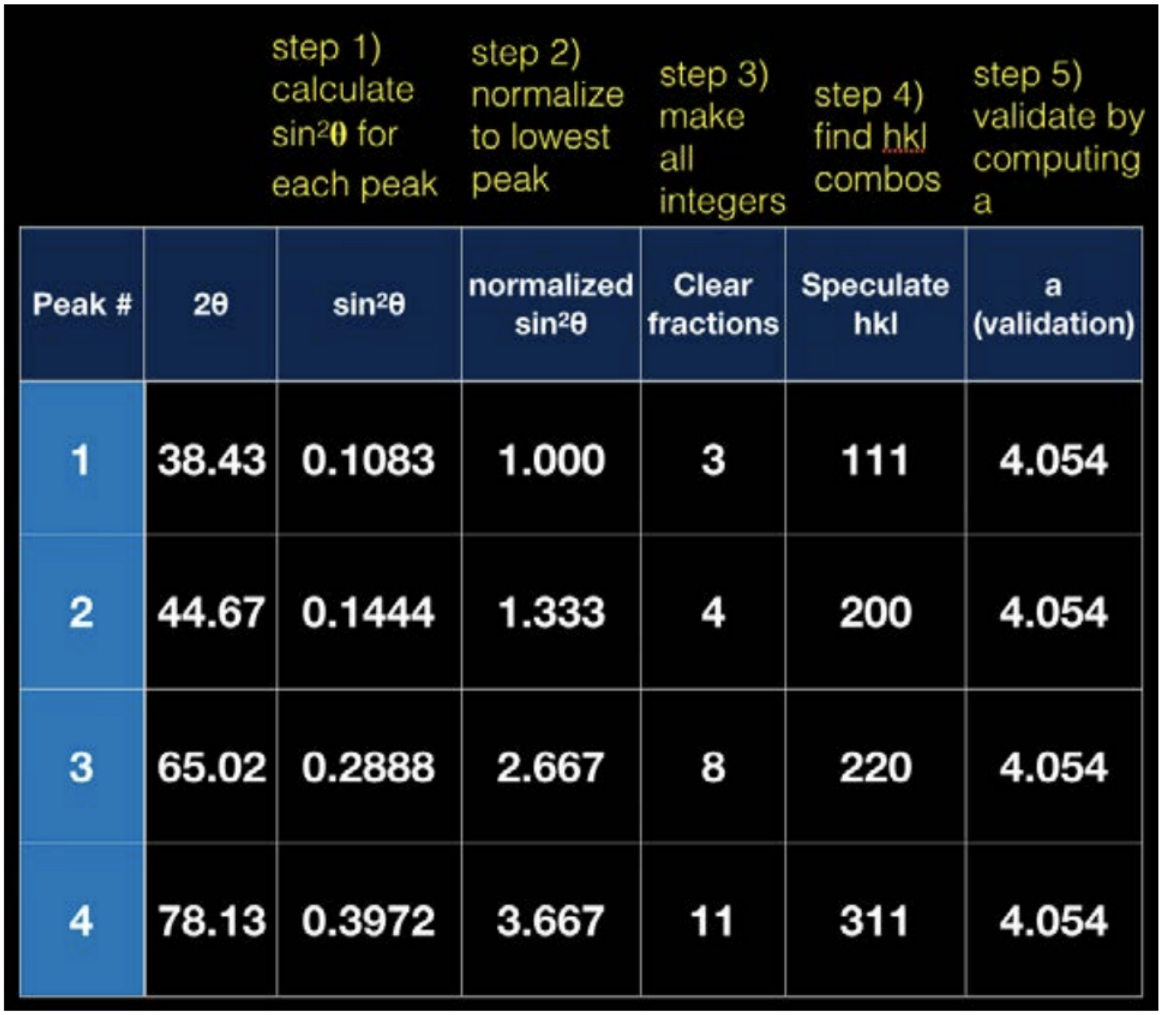
$$\left(\frac{\lambda}{2a}\right)^2 = \frac{(\sin\theta_{hkl})^2}{h^2+k^2+l^2}$$

We know the value of the wavelength, because it is fixed by the K_a x-rays from the copper source. These x-rays have a wavelength of 1.54Å. So the expression for our example becomes:

$$\left(\frac{1.54\text{Å}}{2a}\right)^2 = \frac{(\sin\theta_{hkl})^2}{h^2+k^2+l^2}$$

Now we have constants on both sides of the equal sign, because the lattice parameter does not change. We can make an educated guess of the hkl value by following the procedures outlined in the chart on the following page.

From the selection rules we know that Al is an FCC metal, since the (hkl) combinations are always either all even or all odd. We can also take a value of θ and a value of h, k, and l and plug these into the equation above to find the lattice parameter, given in the rightmost column of the chart.



step 1) calculate $\sin^2\theta$ for each peak

step 2) normalize to lowest peak

step 3) make all integers

step 4) find hkl combos

step 5) validate by computing a

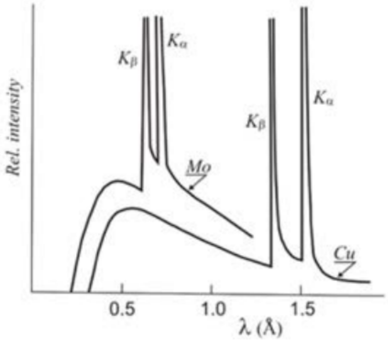
Peak #	2θ	$\sin^2\theta$	normalized $\sin^2\theta$	Clear fractions	Speculate hkl	a (validation)
1	38.43	0.1083	1.000	3	111	4.054
2	44.67	0.1444	1.333	4	200	4.054
3	65.02	0.2888	2.667	8	220	4.054
4	78.13	0.3972	3.667	11	311	4.054

Why this matters

Photo of Henry Moseley is in the public domain.

This is Henry Moseley (image, Royal Society of Chemistry). He's pictured there in his lab, holding in his hands, of course, a modified cathode ray tube. He was experimenting with X-rays. But Moseley's interests were less about the crystal structures and Bragg conditions and more about the X-ray lines themselves and what they meant. He carried out a systematic study of the metals used to generate the Xrays, comparing the X-ray emission from 38 different chemical elements.

Some work had already been done that led to our understanding of the characteristic and continuous parts of the X-ray generation spectrum, as we discussed a few lectures ago. But a full systematic study had not been carried out until Moseley's work. Take a look at the difference between the two X-ray spectra generated with two different targets: Mo and Cu. Note the K_α and K_β lines for each one, and that they're shifted to lower wavelength for Mo compared to Cu. As we know, this is because of difference in energy between the shells of $n=1$ and $n=2$ (for K_α) or $n=1$ and $n=3$ (for K_β), and it makes sense this energy difference is greater (corresponding to lower wavelength) for Mo since it’s heavier than Cu. But what exactly is the dependence, and why is it present? Let’s look at the data for a sequence of targets, directly from a subset of Moseley’s data.



These are characteristic X-ray lines for Ca up through Zn, so going across the d-block elements of the fourth row in the PT. Note that it’s not actually Zn but rather brass, which we’ve already learned is a mixture of Zn with Cu – that’s because Zn would melt under the high energy electron bombardment before it could give off any characteristic X-rays, so Moseley gave it the extra strength it needed by making brass, and then subtracted out the emission from Cu. Nice trick!

What Moseley found was that if the characteristic emission lines were plotted as the square of their energy vs. atomic number, that you'd get a straight line. He fit the data by considering the lines to come from a core excitation, so a difference in energy levels from Bohr's model:

$$E_{x-ray} = 13.6[eV](Z-1)^2\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = \frac{3}{4}(13.6[\mathrm{eV}])(Z-1)^2$$

This is now called Moseley's law. Can you see why it's $\mathrm{Z}-1$ instead of Z as in the Bohr model? It's because the electron cascading down to generate the X-ray is "seeing" a 1-electron screening of the nucleus. That's because one of those core 1s electrons was knocked out, but there's one left there that screens out a positive charge, hence the $\mathrm{Z}-1$. So what did this trend in the data mean? Here's what Moseley said in his 1913 paper, "We have here a proof that there is in the atom a fundamental quantity, which increases by regular steps as one passes from one element to the next. This quantity can only be the charge on the central positive nucleus, of the existence of which we already have definite proof."

The reason this is such a big deal, and why I'm making it the Why This Matters for this chapter, is that even through the Mendeleev periodic table had been around and more elements were being discovered and added, there was a major flaw in the periodic table: the position predicted by an element's atomic weight did not always match the position predicted by its chemical properties. Remember that the positioning by Mendeleev was based on weight and properties and when the periodicity called for it, he chose to order the elements based on their properties, rather than their atomic weight. But was there something more fundamental than atomic weight?

Moseley's data only made sense if the positive charge in nucleus increased by exactly one unit as you go from one element to the next in the PT. In other words, he discovered that an element's atomic number is identical to how many protons it has! I know this seems kind of obvious to us now, but back then "atomic number" was simply a number with no meaning, other than the element's place in the periodic table. The atomic number was not thought to be associated with any measurable physical quantity. For Mendeleev, periodicity was by atomic mass and chemical properties; for Moseley, it was by atomic number. This led to a much deeper understanding of the periodic table and his insights immediately helped to understand some key mysteries, for example where to place the lanthanides in the PT $(\mathrm{La}=\#57, \mathrm{Lu}=\#71)$, or why Co comes before Ni. And the gaps that Mendeleev brilliantly left open in his PT to create periodicity now made sense by missing atomic numbers in a sequence, for example elements $43, 61, 72$ and 75 were now understood to contain that many protons (they were discovered later by other scientists: technetium, promethium, hafnium and rhenium).

Moseley died tragically in 1915 at age 27 in a battle in WW1. In 1916 no Nobel Prizes were awarded in physics or chemistry, which is thought to have been done to honor Moseley, who surely deserved one.

Why this employs

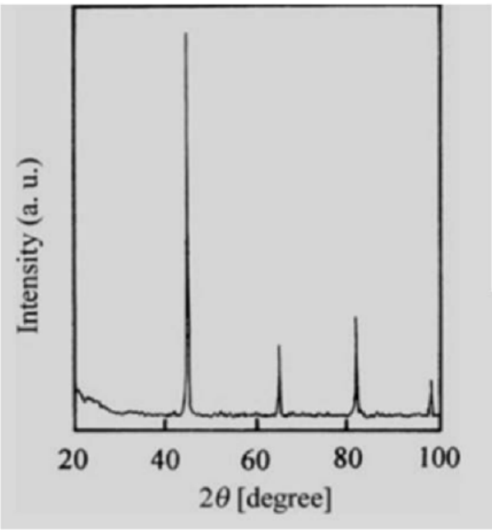
We've covered X-ray generation and machine manufacturers two chapters ago, and in the last chapter we looked at jobs related to X-ray crystallography. For this last Why This Employs related to Xrays, it's time to go big or go home. And when I say big, I mean really big. When electrons or for that matter any charged particles are accelerated to near light speeds, then the acceleration they experience simply to stay in a loop produces massively energetic radiation. The wavelength can vary dramatically, but very often these enormous accelerators are used to make super-high-energy X-rays. The intensity of these rays is dazzlingly bright, millions of times brighter than sunlight and thousands of times more intense than X-rays produced in other ways. This level of brightness makes them useful for pretty much any and all areas of research and fields of science. Some types of measurements are only possible when synchrotron light is used, and for other types one can get better quality information in less time than with traditional light sources. They've been shown to be useful in so many areas it's impossible to list them all, but certainly in biology, chemistry, physics, materials, medicine, drug discovery, and geology, to name only a few fields, synchrotrons have made a dramatic impact. They're in such demand that often one needs to book time on them many months in advance. A typical synchrotron can have as many as 50 "beam lines" that grab the high energy X-rays out of the loop and focus them in a beam where experiments are done. These lines are usually booked and put to use 24 hours per day, 7 days per week, all year round. Here’s a photo of one of them, the Advanced Photon Source at Argonne National Laboratory in Illinois. Their tagline overview statement reads, “The Advanced Photon Source (APS) at the U.S. Department of Energy’s Argonne National Laboratory provides ultra-bright, high-energy storage ring-generated x-ray beams for research in almost all scientific disciplines.”

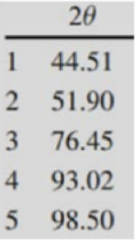
The Employment part of this is pretty cool. These facilities, which are called “synchrotrons,” are all over the world, and they require thousands of people to build and then run. The international nature of them is astounding: just do a image search for synchrotron and you’ll find pictures of them all over the planet. And that means jobs in many different locations. Some are old, like the one at Berkeley National Lab (but it’s still kicking!), some are medium-sized like that APS pictured above, and some are huge like the Hadron Collider I referenced in the last lecture as a place where 3D X-ray imaging was invented. Colliders are also synchrotron light sources, since they’re built to accelerate particles at very high speeds. Even though colliders may be used to smash particles together at these speeds, they’re also often used simply as a way to generate high intensity light.

I don’t have a specific job title in mind, but if you look at a list like this one: https://en.wikipedia.org/wiki/List_of_synchrotron_radiation_facilities you’ll see where these synchrotrons are, and for each one of them there’s an “employment” link you can click on to explore possible jobs.

Extra practice

1. Determine the element that made up the sample from Lecture 21 Extra Practice Problem 1. The XRD pattern is reproduced below (copper k_a x-rays were used).

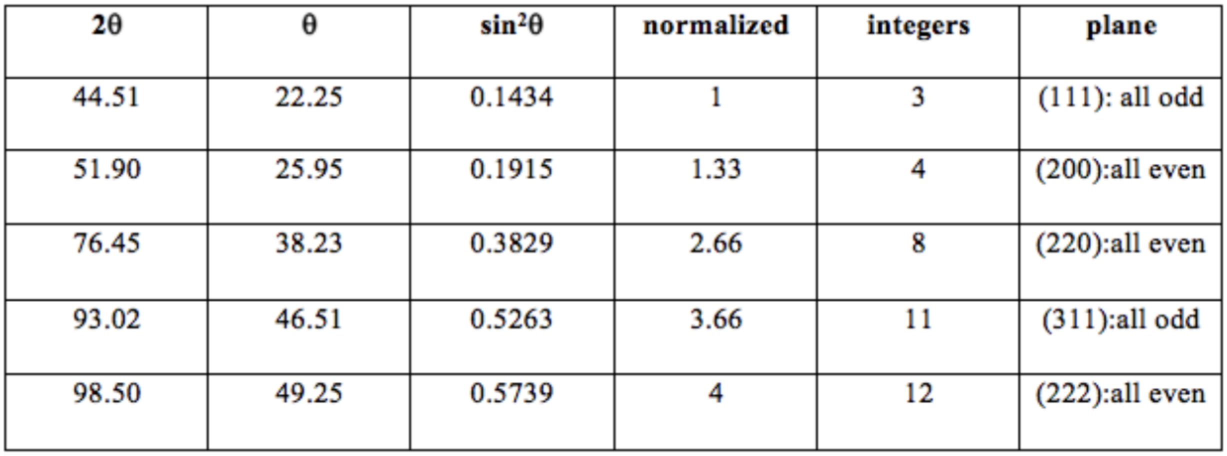




	2θ
1	44.51
2	51.90
3	76.45
4	93.02
5	98.50

Answer

To know which element was used as the sample, find the lattice parameter (a) using the equation for interplanar spacing (d_{hkl}), Bragg's law, and Moseley's law. For $\mathrm{h, k, l}$ and θ_{hkl}, pick a plane and a corresponding angle from the chart we developed last chapter, shown below:



2θ	θ	sin²θ	normalized	integers	plane
44.51	22.25	0.1434	1	3	(111): all odd
51.90	25.95	0.1915	1.33	4	(200):all even
76.45	38.23	0.3829	2.66	8	(220):all even
93.02	46.51	0.5263	3.66	11	(311):all odd
98.50	49.25	0.5739	4	12	(222):all even

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$
$$\lambda = 2d_{hkl}\sin(\theta_{hkl})$$

The energy corresponds to $\mathrm{Cu(Z=29)}k_\alpha$ radiation:

$$E = \frac{hc}{\lambda} = 13.6[eV](Z-1)^2\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)$$
$$\lambda = \frac{hc}{-13.6(Z-1)^2\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)}$$
$$d_{hkl} = \frac{hc}{-13.6(Z-1)^2\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)2\sin\theta_{hkl}}$$
$$a = \frac{hc\sqrt{h^2+k^2+l^2}}{-13.6(Z-1)^2\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)2\sin\theta_{hkl}} = 3.53A$$

This lattice parameter corresponds to Ni.

2. You would like to perform an XRD experiment, but you don't know what target is used in the diffractometer in your lab. You put in a calibration sample of iron, which is BCC and has a lattice parameter of 2.856 angstroms. If you observe the following XRD pattern, what material is the target? You are pretty sure that there is a filter that prevents anything with lower energy than k_a radiation from hitting your sample.

The peaks observed are as follows:

counts	10	1000	20	2200	8	5	1200	2500
2θ	17.38	20.87	24.67	29.62	30.30	35.15	36.45	42.37

a) What kind(s) of x-rays are hitting the sample?

Answer

k_α AND k_β

b) How many planes are represented by the data? Which planes are they?

Answer

4 planes are represented: (110), (200), (211), and (220)

c) What are the interplanar spacings associated with these planes?

Answer

$$\frac{2.856}{\sqrt{h^2+k^2+l^2}}$$

Plugging in each (hkl), the spacings are 2.02, 1.43, 1.17, and 1.01 A

d) Which element was used as the target?

Answer

$$\begin{aligned}\lambda &= 2d_{hkl}\sin(\theta_{hkl})\\ \lambda_{k_\alpha} &= 0.73A\\ \lambda_{k_\beta} &= 0.61A\end{aligned}$$

Answer

$$E=\frac{hc}{\lambda}=13.6(Z-1)^2\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)$$

For $k_\alpha, n_i=2$ and $n_f=1$. For $k_\beta, n_i=3$ and $n_f=1$.

$$\begin{aligned}&h=4.135\times10^{-15}\mathrm{eV.s}\\ &c=3x10^8\ \mathrm{m/s}\\ &\mathrm{Z}=42\end{aligned}$$

Lecture 23: Point Defects

Summary

A point defect is a localized disruption in the regularity of the crystal lattice. There are four types of point defects: vacancies, interstitial impurities, self-interstitials, and substitutional impurities.

Arrhenius determined a law for the temperature dependence of the rate at which processes occur:

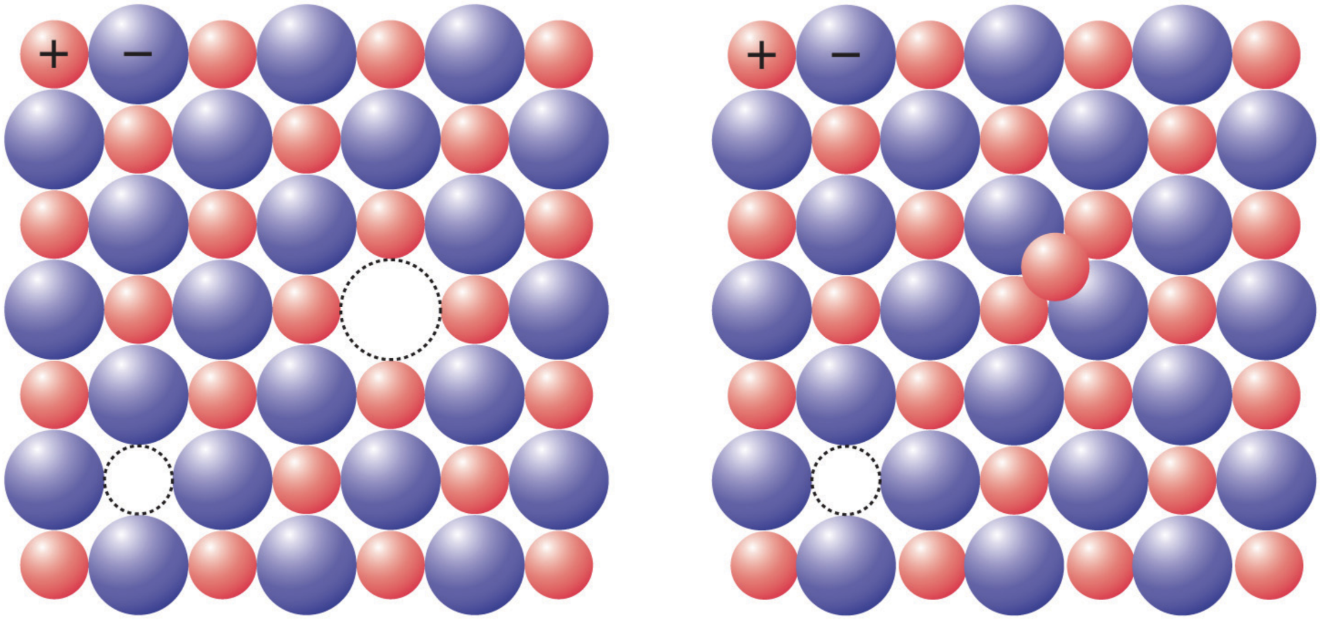
$$k=Ae^{-E_a/RT}=Ae^{-E_a/k_BT}$$

where R is the gas constant (or k_B is the Boltzmann constant) and E_a is the activation energy. The term in the exponent should be unitless: therefore, if the activation energy is given in $\mathrm{J/mol}$, use the version with R, but if the activation energy is given in J, use the K_B version. Recall that the gas constant is just $R=K_B*N_A$. The units are determined by the prefactor A, which can be thought of as an average kinetic energy of the system.

Vacancies are always present in every solid because they're a result of thermally-activated processes. We can consider the rate of formation of a vacancy and the rate of removal of that same vacancy as two thermally-activated processes, each with their own rate. At any given temperature, when the rate of forming the vacancy is the same as the rate of "de-forming" the vacancy then the vacancy concentration in the crystal will be in equilibrium. Since each rate is thermally activated we can use an Arrhenius equation to describe both the forward and back process, and setting them equal for equilibrium one arrives at a formula describing how the vacancy concentration depends on temperature:

$$N_v=Ne^{-E_a/k_BT}$$

where N_v/N is the fractional concentration of vacancies and E_a is the activation energy $[\mathrm{J}]$ required to remove one atom. If the vacancy occurs in an ionic solid, charge neutrality must be maintained. Therefore, the defect either forms as a Schottky defect, where a pair of charges (one cation and one anion) is removed, or as a Frenkel defect, where the vacant atom sits elsewhere in the lattice on an interstitial site. For a Schottky defect in an ionic solid like $\mathrm{CaCl_2}$, two anions $\left(\mathrm{Cl^-}\right)$ must be removed for each cation $\left(\mathrm{Ca_2^+}\right)$ vacancy to maintain charge neutrality. Frenkel and a smaller cation, like AgCl, AgBr, and AgI, for example.

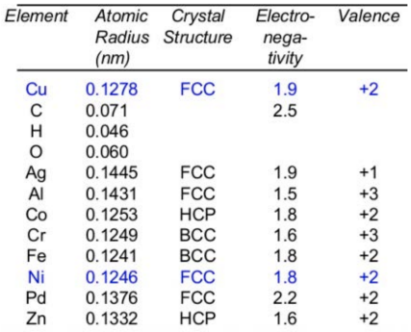


(a) Schottky defect

(b) Frenkel defect

Interstitial defects can occur in covalent solids as well: in this case, an extra atom occupies a site that is not part of the lattice, but the charge neutrality requirement doesn't necessitate the creation of a vacancy provided the interstitial atoms have the same charge as the lattice atoms. For example, a C interstitial in Fe is charge neutral. If the interstitial atom is the same type of atom as the lattice, like a Si atom in a Si lattice but not on a lattice site, the defect is called a self-interstitial. The energy required to form a self-interstitial $(2-5\mathrm{eV})$ is much higher than for a vacancy $(0.5-1\mathrm{eV})$, so these defects are much less common: this can be rationalized by thinking about how hard it would be to squeeze an atom between similarly-sized atoms arranged in a closely-packed lattice.

Atoms which take the place of another atom in a lattice are called substitutional defects. Generally, the Hume-Rothery rules provide guidelines to which atoms can be a substitutional defect: the atomic size must be within $+/-15\%$, the crystal structure must be the same, the electronegativity must be similar, and the valence must be the same or higher.

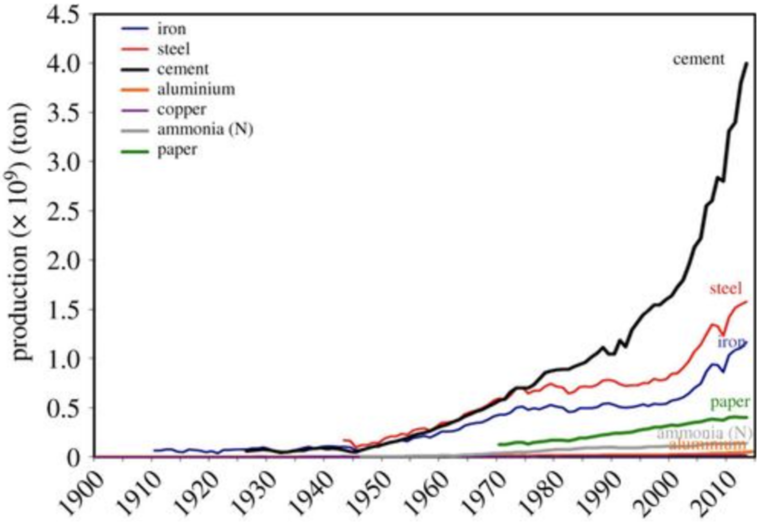


Element	*Atomic Radius (nm)*	*Crystal Structure*	*Electro-nega-tivity*	*Valence*
Cu	0.1278	FCC	1.9	+2
C	0.071		2.5	
H	0.046			
O	0.060			
Ag	0.1445	FCC	1.9	+1
Al	0.1431	FCC	1.5	+3
Co	0.1253	HCP	1.8	+2
Cr	0.1249	BCC	1.6	+3
Fe	0.1241	BCC	1.8	+2
Ni	0.1246	FCC	1.8	+2
Pd	0.1376	FCC	2.2	+2
Zn	0.1332	HCP	1.6	+2

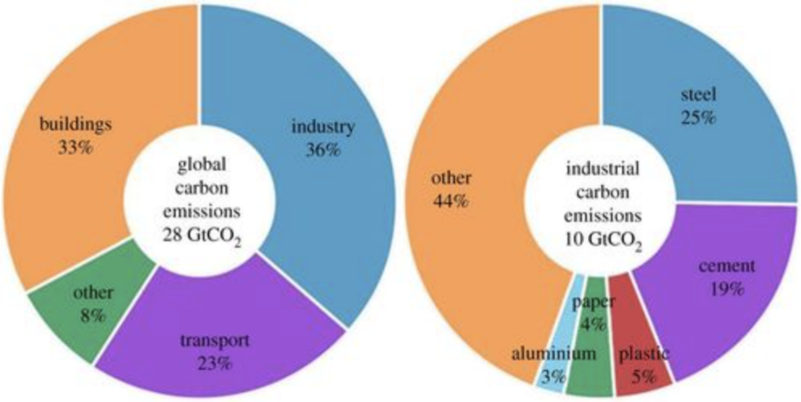
Why this matters

Let's pick up on the interstitial defect of carbon in iron, otherwise known as steel. This particular defect is one that has positive benefits if it's controlled carefully and the right amount of carbon (not much, it turns out) is placed in the right positions within the iron lattice (the tetrahedral holes, for example, in bcc Fe). In fact, the change in iron's properties are absolutely tremendous and represent a spectacular example of how defects can be used beneficially. If you Production vs. time figure removed due to take a piece of pure iron and ap- copyright restrictions. ply sideways strain on it, then its resolved shear stress is quite low, around 10

MPa. That means that if you push sideways on a piece of pure iron it will deform under 10 MPa of pressure. But with just 1% C on interstial sites, the C-doped iron can have a resolved shear stress as high as 2000 MPa, 200 times larger than the undoped case!



Now, this phenomenon has been known and practiced for over 2500 years, when people first observed the mechanical strength imparted on iron when it was heated by a charcoal fire (the charcoal was the carbon source). But that's just it: 2500 years ago, or 1000 years ago, or even just 100 years ago, not a whole lot of steel was being made each year. This is now changing, and it's changing dramatically, and it's Why This Matters.



Industrial Carbon Emission Chart

Take a look at the chart above (from US Geological Survey, UN, FAO, World Aluminium Association) of the production amount for some of the materials humans make on a scale massive enough to require enormous chunks of the world's energy consumption. Cement and steel are the top two, and estimates put them at 10-15% combined of annual global $\mathrm{CO_2}$ emissions. If we look at just $\mathrm{CO_2}$ emissions from industrial processes, steel has the biggest share at 25% of the total. But even more important are those slopes in the production trends: note that the use of these products is growing and will continue to grow dramatically into the future. Back 2500 years ago it didn't matter how steel was made. They also had no idea why the charcoal gave iron those properties. Today, not only do we need to find new ways to make steel more efficiently, but we also know what's happening in the material at the atomic and bonding scale. In other words, we understand its solid state chemistry.

How can we make steel in a more energy efficient manner? Answering that question relies on knowledge of the point defects in the material, and specifically on the energy it takes to get carbon into the interstitial lattice. And it's not always obvious. For example, if we compare the atomic size of C with the sizes of the available interstitial volumes in Fe, it's clear that it doesn't quite fit, and some type of lattice distortion will have to take place in order to accommodate the interstitial defect, even as small as a C atom. But that means it's not as simple as occupying the defect site with the most room, since we need to know how atoms get strained in response to the defect being there. Take the example of -iron: in that phase you would think a C atom occupies the larger tetrahedral hole, but in fact it prefers to go to the octahedral interstitial site. The reason for this preference is that when the C-atom goes into the interstitial, strain gets relieved for the octahedral site by two nearest neighbor iron atoms moving a little bit, while for tetrahedral site, four iron atoms are nearest-neighbor and the displacement of all of these requires more strain energy. This is just one phase of iron and two different sites. There may be ways to move C atoms into other phases more easily, that would take less energy, and give the same strength. Or perhaps there are other ways beyond fire (which is why steel-making takes so much energy) to get the defect chemistry just right. This is a hard problem, but it's a critical one: take a look at this chart from a recent paper published in Science that breaks down which sectors will be hardest to make "green." Note the prominence of steel and cement! To solve such hard problems, we will need advances in defect chemistry.

Why this employs

This is an easy one: there's actually a job position called "Defect Engineer"! At Global Foundries, they care about defects for the basic manufacture of semiconductor materials while at Intel, there are openings for Defect Engineers to work on 3D XPoint which is a new non-volatile memory technology. Intel also has an opening for a "Defect Reduction Engineer." These and so many more similar openings are for industries where devices are made in clean rooms, often very clean cleanrooms. A "Class 1" cleanroom, for example, means that if you take a meter cubed of air at any given place in the room, you would count less than 10 particles of size 100 nanometers, less than 2 particles size less than 200 nanometers, and zero particles larger than that. The reason fabrication facilities need such a high level of air purity is that they're making features on the order of 10's of nanometers and so any small defect can be a big problem.

Now, then again, these are not necessarily point defects (although certainly 100 nm particles that hit a layer of silicon while its being processed can cause point defects). How about technologies where the point defect is the key part of the technology itself? In that case you may be talking about a solid oxide fuel cell (SOFC). These are typically metal-oxides and they work by conducting oxygen ions through the material. But the only way an oxygen ion can move is if there are oxygen vacancies present, and in enough density at reasonable temperatures. Many companies work on developing efficient, low-cost, and low temperature solid oxide fuel cells. Every single car manufacturer for example, has an interest in this as a possible future way to power transportation (Nissan has a cool demo car). Other companies like Precision Combustion, Elcogen, or Bloom Energy all work to build SOFCs, with that last one stating, "better electrons" *on their homepage. Nice. (although I thought all electrons were identical. . . but anyway). The point is that there's a growing interest in SOFC and an already strong market set to reach $1B by 2024. With greater control over those oxygen vacancies, the ability to make the materials cheaper, and the ability to control defects at lower temperatures, the use of SOFC could increase even much more than that!

Extra practice

1. Sketch the following defects:

    a) Schottky

    b) Frenkel

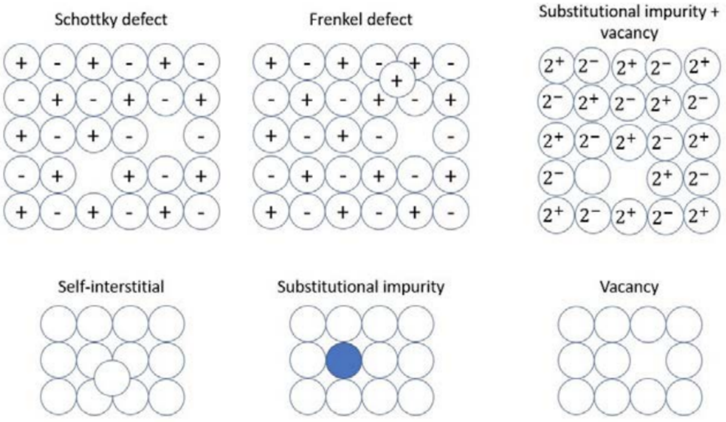
    c) Substitutional impurity+vacancy

    d) Self-interstitial

    e) Substitutional impurity

    f) Vacancy

Answer



2. Solid oxide fuel cells rely on the reaction of fuel with oxygen to form water. A ceramic oxide can be doped to introduce oxygen vacancies that allow charge to conduct through the solid electrolyte. Zirconia $(\mathrm{ZrO2})$ can be doped by adding $\mathrm{Sc2O3}$. If 0.5 g of $\mathrm{Sc2O3}$ can be incorporated into 10 g of $\mathrm{ZrO2}$ while maintaining the zirconia structure, how many oxygen vacancies are generated?

Answer

We are doping $\mathrm{ZrO_2}$ with $\mathrm{SC_2O_3}$. The Zr^{4+} ions are replaced by the Sc^{3+} ions, creating a charge imbalance of -1 with each substitution. This means that for every 2 such replacements, or every $2Sc^{3+}$ ions added, there will be a -2 imbalance, and an oxygen vacancy $\left(V_O''\right)$ will be created to compensate and achieve charge neutrality.

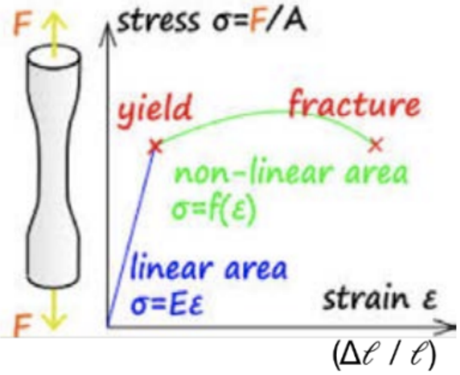
$$0.5g\mathrm{Sc_2O_3}\left(\frac{1\mathrm{molSc_2O_3}}{137.9g}\right)=0.0036\mathrm{molSc_2}$$

$0.0072\ \mathrm{molSc}c^{3+}\mathrm{added}=0.0036\ \mathrm{mol}V_O$ ”
Total number of oxygen vacancies $=2.18\times10^{21}$

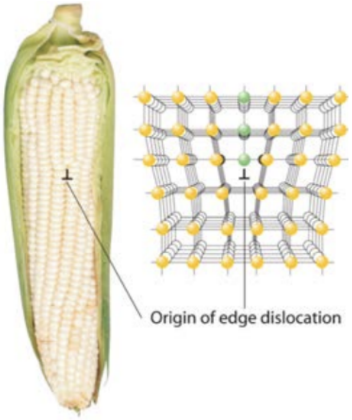
Lecture 24: Line Defects and Stress-Strain Curves

Summary

Line defects are 1-dimensional defects in a crystal that affect many macroscopic materials properties, including deformation. In 3.091, we'll focus on two types of deformation: elastic deformation, which is reversible (strain only occurs when there is a stress applied, and it goes back once the stress is removed), and plastic deformation, which is permanent.



Elastic deformation can be likened to connecting all of the atoms with springs: Hooke's law, F=-kx, tells us that there is a restoring force that returns the material to its initial state. This corresponds to the initial linear region in a stress-strain curve. If a material is brittle, it will likely break in the linear regime. However, if the material is ductile, it can undergo plastic deformation: the material no longer responds linearly to the applied stress. One deformation mechanism that occurs during plastic deformation is called slip: individual planes of atoms slide past each other due to the presence of a line defect. A dislocation is a type of line defect that forms when atoms are slightly misaligned: an extra plane of atoms exists in the crystal.



Dislocations can move through a crystal when a force is applied. Atoms slip over another to relieve the internal stress caused by applying a force. How can we tell what the slip planes are? In order for the material to slip, two adjacent planes of atoms must slide past each other. As this happens, the bonds between the planes must break and re-form. Therefore, slip planes must be planes that have the lowest inter-planar bond density. You can verify that this means that the most densely packed planes will be slip planes, because they have the highest intra-planar bond density. This means that slip occurs parallel to the closely packed planes: together, the slip planes and slip direction form a crystal's slip system. Many materials can undergo dislocation-mediated slip, but metals in particular are known for this mechanism of deformation. The sea of electrons we learned about in metals allow bonds to move around (break and re-form in a new spot) with ease compared to ionic and covalent solids, which have much more rigid electronic structures.

When stress is first applied to an elastic material, dislocations form initially as planes of atoms pull apart. If two dislocations run into each other as they're moving around, the defects can become pinned, so they can no longer move through the crystal. As more and more dislocations are pinned, they become tangled and slip doesn't occur: the material would continue to deform elastically but it would require much more force to deform it. In other words, dislocation pinning makes materials harder. This mechanism of material strengthening is called work hardening. Work hardening causes the yield strength to increase, but at the expense of ductility.

Why this matters

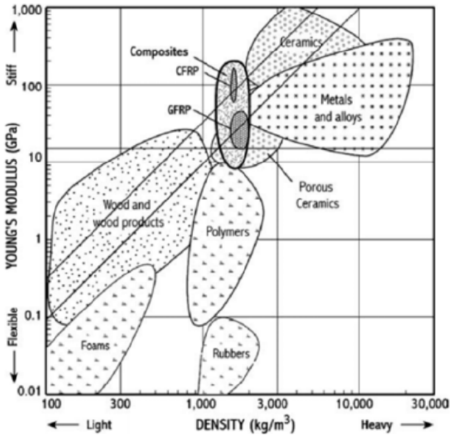
Let's talk about wind energy. Wind has the same intermittency challenges that solar has (so in other words it can only really be useful on a large scale if we can store the energy cheaply and efficiently). But wind also has many advantages and is a very appealing way to generate electricity. That's why the installed wind capacity has seen tremendous growth globally over the last 20 years. In the U.S., more than 5% of our total electricity is now generated by the wind.

Global Cumulative Installed Wind Capacity 2001-2016 (pg. 3) chart

A wind turbine is actually based on fairly simple technology, which is one of the reasons it's so appealing. Basically, the wind turns the blades, which provides the force to run an electric motor in reverse to generate electricity. The challenge is that the most consistent, high energy winds occur at high altitudes, so the blades are more efficient the larger and higher up one can make them go. This means that the blades have to support tremendous mechanical loads from the high wind power. And to make matters more difficult, the blades have to be able to go back and forth between high, low or no wind depending on the time of day. (as an aside, I love to look at maps and if you're interested in seeing how the wind speed varies around the globe, there are a lot of cool maps that show this to you).

So in other words, we need blades that are strong enough that they don't break apart under the extreme stress of the wind force, but flexible enough that they can bend without irreversible deformation. And what is it that we need to understand and engineer in order to make better blades? The line defects of course!!

Take a look at this plot of materials.



Here we're looking at the density of the material on the x-axis and the Young's modulus on the y-axis. The Young's modulus is simply a measure of the elastic stiffness of the material, so if we go back up to our stress/strain curve at the beginning of this chapter, it's related to the slope of the linear elastic regime. For a wind turbine blade, we'd like it to be lightweight and strong, but also flexible. As we learned in this lecture, the line defects are related to the plasticity, which is related to the yield stress, which is related to how much a material can be elastically strained.

From the chart, we can compare the different classes of materials (like metals vs. ceramics vs. polymers, etc) for two of these properties: density and stiffness. What's interesting about this is that there are enormous parts of the chart that are currently empty. In other words, there's a lot of work to be done to find and prepare materials that are both heavy and flexible, or light and strong. And you know what this means: new chemistry combined with control over line defects!

Why this employs

Let's go big. This boat, for example, is called the SS Schenectady, and it has a bit of a problem. Mostly that it's cracked in half. A lot of ships built during World War II were made from low-grade steel, which was too easy to fracture at the temperatures of the sea. In fact, they did test the strength of their steel but only in the dry dock, so the test temperature was higher than the operational temperature. Once the ship was in the colder water, the steel became much more brittle and it became much easier for defects to form, and once they formed it was easy for them to grow under applied stress. One certainly doesn't want plastic deformation of a ship's metal, but one does not want this type of brittleness either. Getting the right strength for the right application under the right conditions requires a lot of knowledge of the materials and their defect properties. And there are a lot of jobs in this space too. Think about it: pretty much everything we build today has to have some sort of operating conditions where the mechanical properties can be counted on to work as expected. Otherwise, ships crack in half, bridges collapse, and roads buckle.

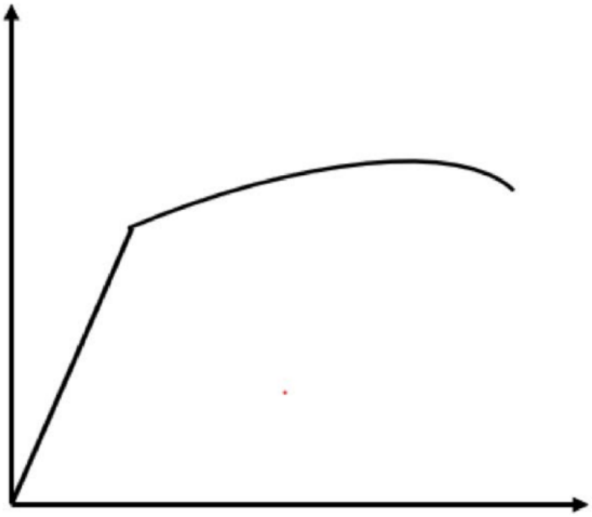
Since I just gave the example of the ship, how about this one: the U.S. Department of the Navy has an opening for a "Materials Engineer" where they explicitly ask for experience in, "strength of materials (stress-strain relationships)." Corning's Manufacturing, Technology and Engineering division is hiring a "Scientist/Engineer" to do modeling of the strength of materials, presumably mostly glasses. There's an opening for a "Research Engineer – Materials Behavior," at GE to design mechanical properties of new structural materials and coatings being for aircraft propulsion. There are so many jobs in this space I couldn't possibly even categorize them all: pretty much any company that makes or deals with materials has jobs available related to their mechanical strength and failure. From ships, to buildings, medical devices to clothing, spacecraft to furniture, defects hold the key.

Extra practice

1. You obtain the following stress-strain curve for an aluminum sample (FCC).

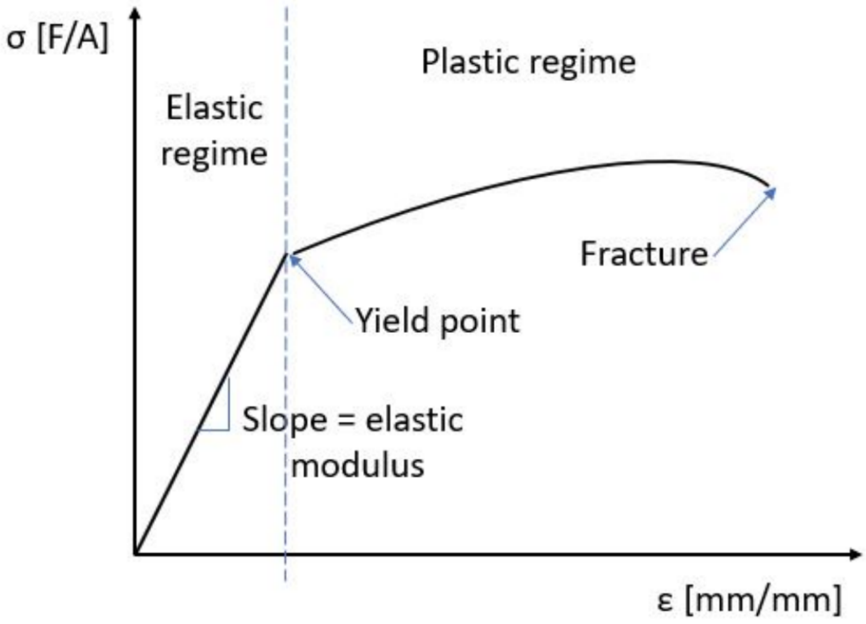
a) Label the following regions on the plot (and the axes!):

Elastic regime   Plastic regime   Yield point   Fracture point   Elastic modulus



Answer

Axes: stress, σ on the y-axis, has units of force/area. Strain, ϵ on the x-axis, is unitless, but often represented as length/length



b) What is the slip system in aluminum?

Answer

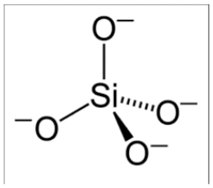
The slip system for FCC is the close-packed direction and close-packed plane: $\langle 110\rangle$ and $\{111\}$Recall that the angle brackets are used to denote families of directions, and the curly braces are used to denote families of planes!

Lecture 25: Amorphous Materials: Glassy Solids

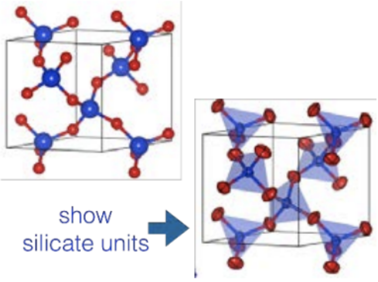
Summary

Glasses are “amorphous materials:” all of the atoms are randomly arranged in a non-repeating structure. In 3.091, we'll focus on one type of glass: silica, or SiO_2. Each silicon atom has four valence electrons, so it is happy to form 4 single bonds. If an oxygen bonds to each of these valence electrons, each of the oxygens is left with an extra electron, forming a $(SiO_4)^{4-}$ molecule.

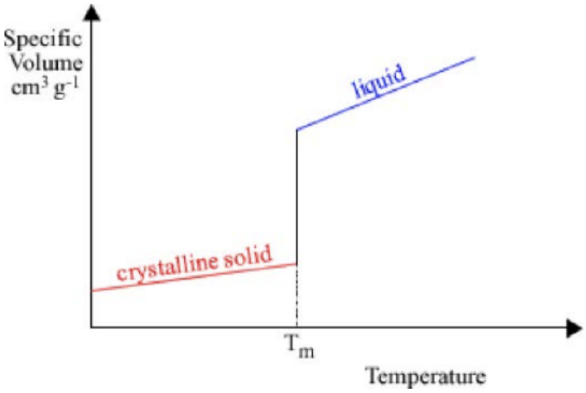
However, when a solid is formed from these silicate molecules, the O can be shared between neighboring silicates, forming a bridge.



The individual tetrahedral silicate molecules stay intact, but they can freely rotate relative to the other silicate molecules in the solid. When they don't arrange in an ordered fashion, silica glass is formed. Whether the solid that forms is crystalline or glassy depends strongly on the processing conditions the silica undergoes.



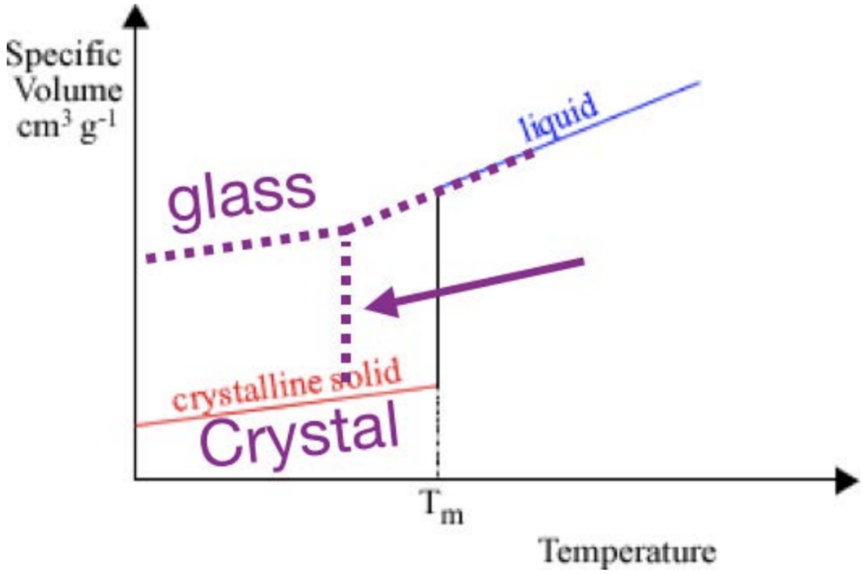
One metric to quantify the processing conditions is by looking at how the molar volume changes as a function of temperature. For a crystal, the plot looks like this. There's a sloped line that corresponds to the solid material, then a jump, then a different sloped line that corresponds to the liquid phase. The jump occurs at the melting temperature T_m: when the material melts or freezes, it undergoes a huge change in volume. The slope of each line is defined as the coefficient of thermal expansion. However, sometimes when a material is cooled, it can remain in the liquid phase below T_m: this is called supercooling. When a liquid is supercooled, continues to act like a liquid until one of two things happens:



1. It crystallizes, characterized by a big jump down to the crystalline solid line and then solid behavior
2. It suddenly becomes a solid, "freezing" in its disordered state and becoming a glass. This transition is characterized by a change in slope at T_g, the point at which solid forms (called the glass transition temperature), but no discontinuity in the freezing curve.

How can we know which path a material will take? It depends on materials properties: if the liquid has a high mobility (low viscosity), the molecules can move around easily and arrange into the energetically-preferential crystalline structure. Highly viscous or low mobility liquids are much more likely to get stuck in a glass. Further, if the crystalline structure is very complicated, or if the liquid is cooled very quickly, it's hard for the atoms to find crystalline sites before the solid forms: these cases are also more likely to lead to glass formation.

The volume per mole is a good measure of the disorder in the material: the further the molar

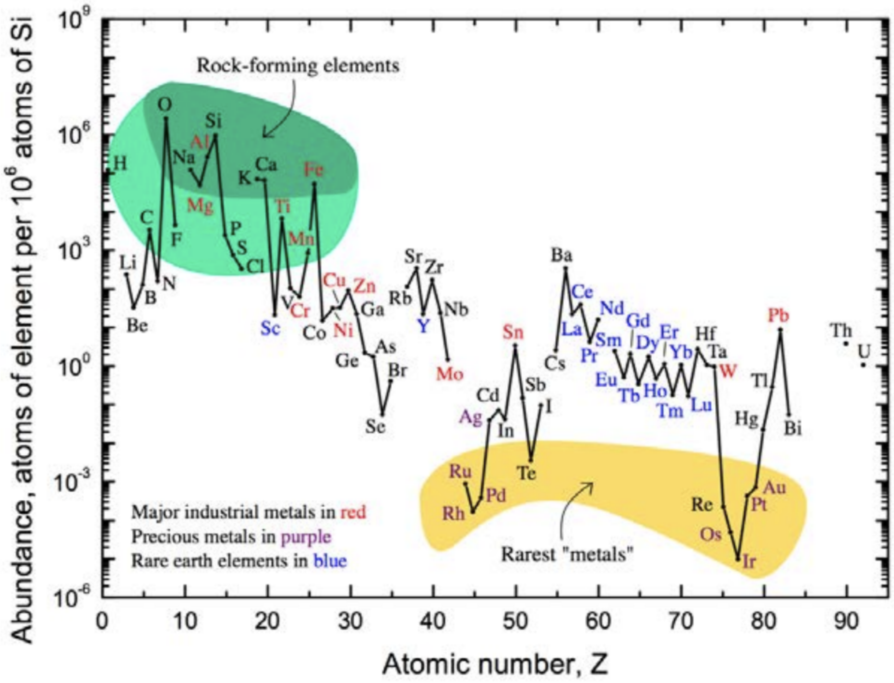


volume is from the crystalline case, the more glassy the material is. Although a material only has one melting point, it can have multiple glass transitions depending on how it is processed. XRD is one tool that can be used to determine whether a material is a crystal or a glass: as the material gets more and more disordered, the sharp peaks observed in the XRD pattern disappear into a broad amorphous halo.

Why This Matters

SiO_2 glass is made from sand and there's a whole lot of it on the planet. SiO_2 stands out as a base material that has really awesome properties. That's partly because of its tremendous abundance. Check out this plot of the abundance of atoms in the earth's crust. Note that of all of the elements in the periodic table, oxygen and silicon are #1 and #2. This means that silica is cheap, and we're not going to run out, unlike other elements. In fact, there are many "critical elements" like Li Co, Ga, Te, and Nd to name a few, labeled as such by the Department of Energy because there is concern that there will not be enough of them in the future to meet global demand. But Si and O are the opposite of critical: they are dramatically abundant. And this presents tremendous opportunity to use SiO_2 as a base material for wide-ranging applications.

And this is why the chemistry that we learned in this lecture matters: because we learned that



the key properties of glass, and the way that it's processed, all come from the chemistry. The ways in which we continue to use glass on this planet can increase as human population and technological needs/use continue to increase, but how can we do utilize glass more sustainably given that the base material is so abundant? Or what other applications can glass be useful where it's currently not used today? Can glass be made "greener"? One cool example for how this could work is in the work of Markus Keyser, who invented the "Solar Sinter." This is a self-sufficient 3D printer of glass objects that you can drive out into the dessert, feed the sand and sunlight that are both plentiful, and print glass objects. The sunlight is used both to power the electric motor of the printer but also the create enough thermal energy to get above T_g for the sand. You can now buy commercial 3D glass printers, but I like this example because it's emission-neutral.

Photo of Marcus Kayser's Solar Sinter

The future of how far we push technologies like this will depend on how far we're able to push the properties of glass. In the next lecture we're going to discuss a few different ways to control glass properties, but you only need today's lecture and an understanding of those silicate groups to understand the key link between chemistry and why this matters.

Why this employs

Corning is one of the biggest and most well-known glass makers in the world. That video I mentioned in the lecture above that I showed in class, about Prince Rupert's Drop, that was from the "Corning Museum of Glass" educational series. They are really, really into glass. And they're big: their 2018 revenue was $\$11.4\text{ B}$ and they've got 51,500 employees currently. On their website if you click on the "engineering" section of the job openings page you'll find hundreds listings. They've also got a ton of internships for students:, "A Corning internship offers valuable hands-on experience for individuals in their chosen discipline to include but not limited to Material Science, Engineering, Research, Manufacturing, IT, HR, Marketing, Finance and Supply Chain." It's a cool place that has made it big out of glass and made glass into a big deal.

Corning works on a wide range of applications of glass, but let's focus on just one of them: fiber optic cables. Most of the backbone of today's internet is served by fiber optics, which are made of silica glass, because they have so many advantages over (older) copper wiring. For example, fiber optic cables can carry much higher bandwidth over longer distances than copper, this means the need for signal boosters is lessened, and fiber optic cables are also less susceptible to interference from external electromagnetic fields so they don't need shielding, and finally they don't break down or corrode nearly as often so they're much less expensive to maintain. It's no wonder that major U.S. companies like Comcast FiOS and Google Fiber are working to get fiber optic cables beyond being just the internet backbone, but into literally every single building in the country. Unlike Corning which many of us may have heard of already, some of the top fiber optics companies are less known even while being huge companies (meaning: lots of jobs!). Take OFS Optics, which makes fiber optics cables for over 50 different application spaces. They have over $\$250\text{M}$ in annual revenues, and in one of their job postings for an "RD Engineer" states that they are looking for someone to, "lead the development of manufacturing processes for the next generation of glass optical fiber products." Cool.

Or how about going international to companies like Prysmian (based in Italy), which has over $\$1\text{ B}$ in annual revenue, has a "Graduate Program" for recent grads to immerse them quickly with a mentorship program and also has the coolest name for a fiber with their "BendBright" brand. Or there's YOFC based in China with over $\$1\text{ B}$/year in revenue, and nice slogan, "Smart Link Better Life," or Fujikura with $\$7\text{ B}$ annual sales and a claim to be, "Shaping the Future with Tsunagu Technology." (that means "connecting"). These and so many more companies are working on making next-generation fiber-optic cables, and if you dig a few layers deep into any of them, you'll see how complicated the production of fiber optic cables is, how many different ways it can be done today and will be done in the future, and how many jobs there are that directly relate to knowledge of $\mathrm{SiO_2}$ glass!

It's not just all about processing: there is fundamental chemistry research to be done on silica glass, too. By doping silica glass with other elements, its properties can be changed. For example, by adding Erbium ions, the glass transforms from a passive light carrier to an amplifier capable of making the signal several orders of magnitude higher. And if you're interested in coding, there's a lot of work to be done to simulate how light travels in media like glass, and how it interacts with these dopants.

Extra practice

1. You obtain the following free volume vs temperature curves for a material cooled at three different rates. Label all instances of the following phenomena on the plot (and the axes!):

a) T_g

b) T_m

c) glassy regime

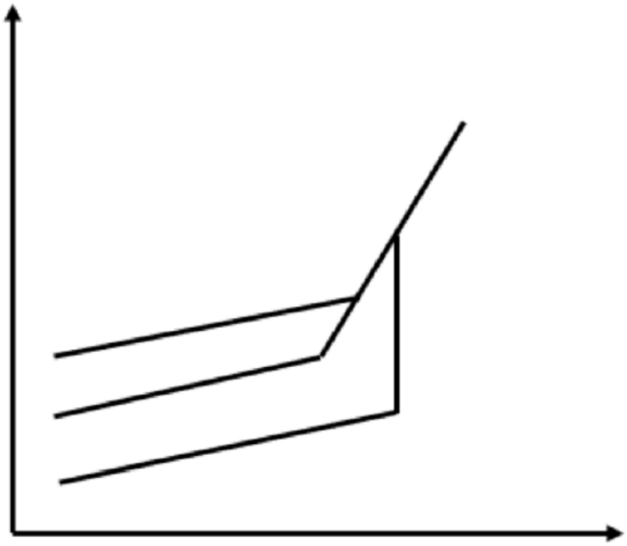
d) crystalline regime

e) fastest cooling rate

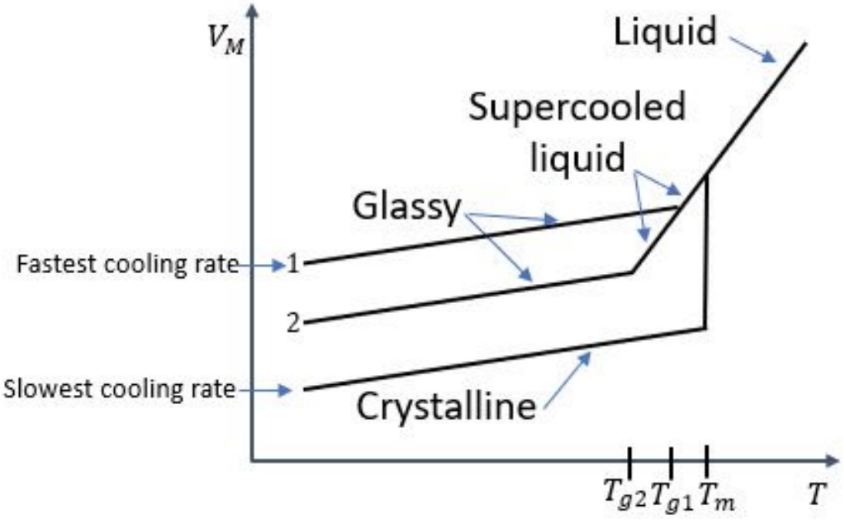
f) slowest cooling rate

g) liquid

h) supercooled liquid



Answer



Lecture 26: Engineering Glass Properties

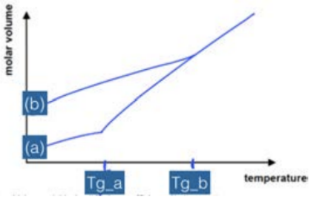
Summary

What does it mean to engineer glass? It can mean adding impurities that change properties like the glass transition temperature (T_g), the solubility, the durability, etc. What unites most of these glass modifiers is that they are **oxide donors**, meaning they give up an O^{2-} ion. This implies that these modifiers have stable cations, so often metals are good. For example:

$$\mathrm{CaO} \rightarrow \mathrm{Ca}^{2+} + \mathrm{O}^{2-} \quad \mathrm{Na_2O} \rightarrow 2\mathrm{Na}^{+} + \mathrm{O}^{2-} \quad \mathrm{Al_2O_3} \rightarrow 2\mathrm{Al}^{3+} + 3\mathrm{O}^{2-}$$

The donated O^{2-} ion attacks the $\mathrm{Si}-\mathrm{O}-\mathrm{Si}$ bond and breaks it into two. It's like a knife that cuts the glass bond, and so this process is called chain scission. The O^{2-} is able to insert itself into the bond and with its two extra electrons satisfies the charge state of the oxygen atoms that now "cap" the chains on each end. So we have that $\mathrm{Si}-\mathrm{O}-\mathrm{Si}+\mathrm{O}^{2-} \rightarrow \mathrm{Si}-\mathrm{O} \mid \mathrm{O}-\mathrm{Si}$ with negative charge on each O. As shown in the figure, the $\mathrm{Na}+$ ions hang around the oxygen. The effect of chain scission on the properties of glasses is enormous. Just take the melting temperature as an example: for crystalline $\mathrm{SiO_2}$ (quartz) the Tm is greater than $1200^{\circ}\mathrm{C}$. For soda-lime glass, the glass transition temperature is typically around $500^{\circ}\mathrm{C}$. If the silicate chains are cut, then the material is much less viscous, and it can find better packing more easily, leading to lower volume per mole and also a lower glass transition temperature (more supercooling).

The base chemistry of the solid, which in the case described above is $\mathrm{SiO_2}$, is the **network former**. The oxide donor is called the **network modifier**. Adding network modifiers is another way to change a glass cooling curve. For example, curve (b) to the right could be obtained using $\mathrm{SiO_2}$ with $5\%\mathrm{PbO}$ and curve (a) using $\mathrm{SiO_2}$ with $10\%\mathrm{PbO}$. The reason is that more cutting of the chains makes the material less viscous, which means it can find better packing and be supercooled more.



We discussed two ways that mechanical properties are engineered in glass. First, the glass can be **tempered**: molten glass is cooled down with air and if the outside of the glass solidifies while the inside is still a liquid, then the outside has a completely different volume per mole than the inside. the hot melted $\mathrm{SiO_2}$ solidifies but since it cannot have the smaller volume that it would like to have, it puts a inward pressure (**compressive stress**) on the already-solid outside layer. The second method of glass strengthening is called **ion exchange**. It involves swapping ions left in glass by network modifiers with ions of different size, which creates compressive stress.

Why this matters

The ability to engineer glass with wide-ranging properties has led to its use in a whole lot more than windows. How about: doors, façades, plates, cups, bowls, insulation, food storage, bottles, solar panels, wind turbines, mirrors, balustrades, tables, partitions, cook tops, ovens, televisions, computers, phones, aircraft, ships, windscreens, backlights, medical technology, optical glass, biotechnology, fiber optic cables, radiation barriers. And on top of that, glass is almost fully recyclable. The main reason glass has become so ubiquitous in all of these different ways is because of its massive chemical tunability as discussed in this lecture.

But here I want to focus on one particular property: strength. We talked today about using compressive stress to make glass stronger. But what if glass could be made stronger still? What if it could be made stronger than major structural materials like steel? In research labs, that is exactly what is happening. For example, in a Nature Materials paper from 2011 (doi:10.1038/nmat2930), the authors made a certain type of metallic glass stronger than steel and critically also tougher than steel. That means that not only does it have a high Young's modulus, but when it breaks it can deform plastically as opposed to shattering. They created this new material through its chemistry, by adding a touch of palladium and a dash of silver to the mix. It already had a bit of phosphorus, silicon, and germanium, but by adding the palladium and silver, the glass was able to surpass steel in both hardness and toughness. Since then, many more demonstrations of mechanically super-strong glass have been made (often trying to avoid Palladium which costs $50,000 per kg. Here's a plot from that same paper, showing the fracture toughness vs. the yield strength of different materials. Again, the yield is related to how much force the material can withstand without breaking, and the toughness is how much it can break without shattering. Going up on both axes can be very appealing for many applications. I love plots like this (called "Ashby plots") since we can right away compare a bunch of different materials, in this case oxides, ceramics, polymers, metals, and of course their own new stuff (shown as "x" marks on the plot). Note how strong regular old oxide glasses are but also how little toughness they have (when they give, they shatter). But notice also how much tougher they can get by engineering their chemistry. This could put amorphous materials on a trajectory to becoming some of the most if not the most damage tolerant materials in the world!

Why this employs

In the last lecture for this section I listed glass manufacturing and companies working on innovating in glass chemistry. For this chapter on engineered glass, let's talk about smarts. In particular, "smart glass." For now, that label means one specific type of silicate-based glass: switchable glass. It has been around for a long time, as even in the 1980's you may have noticed (ok, your parents may have noticed) people wearing the sunglasses that automatically tinted and de-tinted in response to the sun (that used what are called "thermochromic" materials embedded in the glass, which change color based on temperature. They never worked all that well, staying a little too shaded inside and a little too unshaded outside, but the idea was there. But now we've gone from thermo- to electro-chromic glass, and the possibilities are seriously exciting. With a tiny applied voltage, glass can be engineered to go back and forth between near full transparency and near full-opacity. Apart from being extremely cool, this type of technology can have a lot of positive sustainability-related benefits, since the glass can be programmed to automatically dim and brighten in response to outdoor light conditions — that can in turn dramatically reduce a building’s energy needs.

This type of smart glass is still on the early side although a number of companies are taking off, and that means jobs. These will be jobs at either mid or early-range start-ups, but in some cases they’ve closed mega (>$100M) fund-raising rounds so definitely growth is strong. Some companies in this space include Kinestral, Smartglass, View, Suntuitive, Gentex, Intelligent Glass, or Glass Apps. A lot of the investment in these companies is coming from the bigger ones like Asahi Glass or Corning, which have of course also started their own smart glass programs. Taken together all of this spells jobs in the future of glass. And its future looks very bright, far beyond switching the color or transparency, as the thermal, electronic and optical properties of the material continue to be engineered. We may or may not be living in the “Age of Glass,” as Corning likes to say, but we sure are living in an exciting time for this material.

Example Problems

1. The 2-D structure of soda-lime glass (used in windows) is shown below.

a) What compounds were used to make this glass? Do these compounds serve as network formers or network modifiers?

Answer

SiO_2 : network former
CaO : network modifier
Na_2O : network modifier

b) How do each of the added compounds impact the bond structure in the glass?

Answer

Ca_O : breaks one bond/creates two network modifiers (coordinated with $1Ca^{2+}$ ion)
Na_2O : breaks one bond/ creates two network modifiers (coordinated with $2Na^{+}$ ions)

3. If they are cooled at the same rate, would you expect silica glass with 14% $Na2O$ or 25% $Na2O$ to have a:

Higher molar volume?

Higher glass transition temperature?

Higher viscosity?

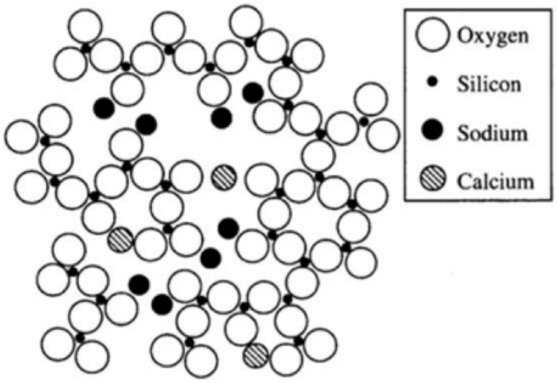


Figure 5.2 *Schematic drawing of a 2-dimensional structure for a soda – lime – silicate glass. A fourth oxygen would be located above each silicon in the 3-dimensional structure*

Answer

14% would have the higher molar volume
14% would have the higher glass transition temperature
14% would have the higher viscosity

4. If a silica glass is doped with MgO, and then ion exchange is performed such that Ca ions replace the Mg ions, how would the mechanical properties of the glass change?

Answer

Ca ions take up more space than the Mg ions, so the glass will be under internal compression (like the Prince Rupert's drop)

Lecture 27: Reaction Rates

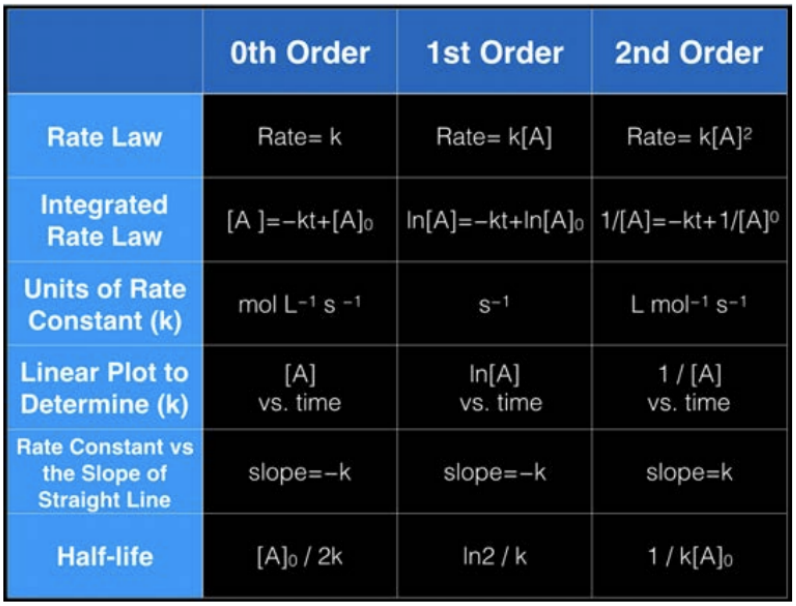
Summary

Chemical kinetics means the study of reaction rates, which correspond to changes in concentrations of reactants and products with time. Some terms to know: **concentration** $=$ moles / liter $=$ molarity $= []$, **rate** $= \mathrm{d}[]/\mathrm{dt}$, a **rate law** is some equation that relates the rate to [], an **integrated rate law** relates the [ ] to t (ime), and the Arrhenius equation gives us the rate vs. T(emperature)

Take a simple reaction where $aA \rightarrow bB:$ since mass is conserved, A disappears no faster than B appears, so the actual reaction rate is $= 1/\mathrm{bd}[\mathrm{B}]/\mathrm{dt} = -1/\mathrm{ad}[\mathrm{A}]/\mathrm{dt}$. In other words, the change in the concentration of B must equal the opposite of the change in concentration of A weighted by one over the molar coefficient a or b. We can have more than one reactant product and the same idea holds. For example, suppose we have 2 of each: $a\ \mathrm{A} + \mathrm{bB} \rightarrow \mathrm{cC} + \mathrm{dD}$. In this case the reaction rate would be:

$$\text{rate } = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

The general way to write an equation for the rate for the equation above is: rate $= \mathrm{k}[\mathrm{A}]^m[\mathrm{~B}]^n$, where $\mathrm{k} =$ rate constant and is dependent on conditions $(\mathrm{T}, \mathrm{P}$, solvent), m and n are exponents determined experimentally, $m+n$ is called the **reaction order**. Note that the rate units must always be M/s by definition, so this means that units of k depend on n and m. For this class we'll cover three different orders of reactions: 0^{th}, 1^{st}, and 2^{nd}.



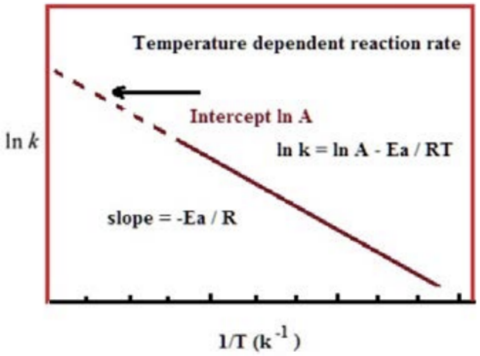
	0th Order	1st Order	2nd Order
Rate Law	Rate= k	Rate= k[A]	Rate= $k[A]^2$
Integrated Rate Law	$[A]=-kt+[A]_0$	$\ln[A]=-kt+\ln[A]_0$	$1/[A]=-kt+1/[A]^0$
Units of Rate Constant (k)	mol L^{-1} s^{-1}	s^{-1}	L mol^{-1} s^{-1}
Linear Plot to Determine (k)	[A] vs. time	ln[A] vs. time	1 / [A] vs. time
Rate Constant vs the Slope of Straight Line	slope=−k	slope=−k	slope=k
Half-life	$[A]_0$ / 2k	ln2 / k	1 / $k[A]_0$

To know the order of a reaction based on data tables like the one below, take any two rows of data: say the $\mathrm{t} = 26\ \mathrm{min}$ and $\mathrm{t} = 70\ \mathrm{min}$ rows. The concentration ratio between these two times is $0.0020/0.0034 = 0.5882$The rate ratio is $1.8/5.0 = 0.36$

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

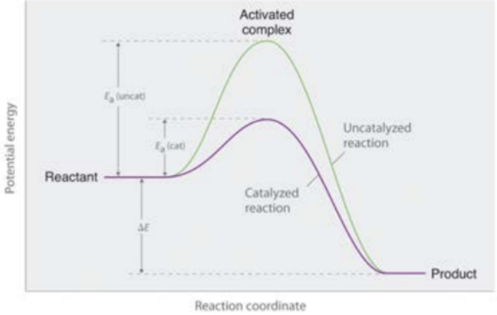
First of all the rate is changing so it can't be 0th order. Second of all, at two different times the ratio of concentrations is not equal to the ratio of rates, so it can't be 1st order. But if we square the ratio of concentrations, $(0.0020/0.0034)^2 = 0.35$which is very close to 0.36, so now we have our answer: from the data we can say the reaction is 2nd order!

To know the role of temperature in determining reaction rates, we must first learn about **collision theory**. Collision theory frames the reaction between molecules, say A and B, as follows: 1) a reaction can only occur when A and B collide, 2) not all collisions result in the formation of product, 3) there are two factors that matter most: the energy of the collision, and the orientation of molecule A with respect to B at the time of collision.



We can think of the energy required for A to react with B to be a kind of “activation energy” or E_a. As we learned in chapter 14 (phases), molecules at a given temperature have a distribution of kinetic energies with that temperature being the average. That means some molecules have much more energy than the average, while other have less. Reactions are similar in that it’s the part of the distribution higher than the activation energy that matters. This plot shows how this works: the distribution of energies for a given molecule at two different temperatures shows that for higher temperature more molecules will have energies above the activation energy than for the lower temperature.

The Arrhenius equation gives us an expression that summarizes the collision model of chemical kinetics. It goes as follows: rate = (collision frequency)*(a steric factor)*(the fraction of collisions with $\mathrm{E} > \mathrm{E}_a$). In math terms, that’s shown here for the equation for rate (k).



$\mathrm{A} =$ the frequency factor, and its units depend on the reaction order. For example if the reaction is first order then the frequency factor must have units of s^{-1} The activation energy, E_a, we've already discussed. If it's given in units per mole, like $\mathrm{J/mol}$, we use R as it's written, where R is the ideal gas constant $\mathrm{R} = 8.314\ \mathrm{J/K^*}$ mol. If the activation energy is given in units of eV, then the constant used would be the Boltzmann constant in units of eV $\left(8.61733 \times 10^{-5} \mathrm{eV/K}\right)$.

This relationship means that if we plot the natural log of the rate vs. $1/\mathrm{T}$ then it should be a straight line with slope $= -\mathrm{Ea}/\mathrm{R}$ and intercept $= \ln(\mathrm{A})$, as shown in the plot above.

So we’ve covered concentration, and now temperature. The last example of a way to change the rate of a reaction that we’ll mention (and unlike those other two, we’ll really just mention it and not go into detail) is the catalyst. A catalyst is a way to increase the rate of a reaction without having anything consumed as part of it. It’s a material that, in the language of our discussion on Arrhenius above, lowers the activation energy for the reaction.

Why this matters

Let's keep going with the catalyst theme for this section. It is estimated that $\approx 90\%$ of all commercially produced chemical products involve catalysts at some stage in the process of their manufacture! Some of these processes I've already highlighted in other Why This Matters moments, like the Haber-Bosch process for fixing N_2, or the depletion of O_3 by CFCs. At the time, we hadn't learned about reaction rates or catalysts, so I didn't go into it. But in both cases the role of the catalyst is absolutely essential (in fact, the big innovation of Haber-Bosch was not to discover the reaction (which had been known) but rather to discover a catalyst that lowers the temperature needed to make the reaction happen economically and at large scales.

Let's discuss another world-changing catalytically enhanced reaction: namely, the removal of most toxic emissions from cars and trucks. I know, you may be thinking that the tailpipe of a car smells pretty toxic. And that's because it is, but it's a whole lot better than it used to be, and the reason is the catalysts that are now part of every tailpipe in the form of what is called the catalytic converter. Why did we need these in the first place? It all goes back to the very first reaction we wrote on the first day of lecture: combustion. One example I gave was the combustion of methane:

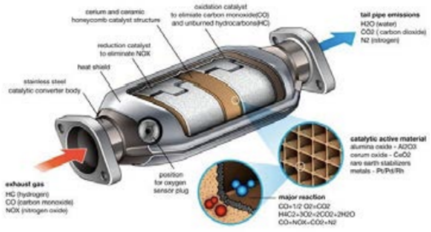
$$\mathrm{CH_4 + 2O_2 \rightarrow 2H_2O + CO_2}$$

It's true that $\mathrm{CO_2}$ is harmful to the environment for reasons of climate change, but there's nothing toxic in those products... so what's the problem?

Ah, if only cars burned pure methane! But gasoline is far, far away from a pure fuel source. And furthermore, even modern car engines are far, far away from being able to burn the fuel perfectly without side-reactions. Gasoline is a mixture of about 150 different chemicals, and these include not just those hydrocarbons that combust, but also a host of additives that range in purpose from corrosion inhibitors to lubricants to oxygen boosters. Since this complex chemical soup doesn’t burn cleanly, we get both direct products and by-products that go far beyond the pure case of $\mathrm{H_2O}$ and $\mathrm{CO_2}$. Many of these products are pollutants and some are really bad ones. An incomplete list would include: carbon monoxide (CO) which is poisonous, nitrogen oxides (like NO and $\mathrm{NO_2}$, or “NOX” as they’re called) which cause smog and have many adverse health effects, sulfur oxides (yes, you guessed it, “ SOX”) which cause acid rain, and unburned hydrocarbons or volatile organic compounds (VOCs) which cause cancer.

Similar to the removal of CFC's from refrigerants, cleaning up the tailpipe represents a fantastic example for how policy and regulation can make the world better. It was the Clean Air Act that Congress passed in 1970 that gave the newly-formed EPA the legal authority to regulate this toxic mess that came out of cars. As a result, today's cars are $\approx 99\%$ fewer emissions compared to the 1960s! The fuels are also cleaner (lead was removed and sulfur levels lowered), and taken together cities have much healthier air. Take a look at this picture of New York city from 1973 (left) compared to 2013 (right). In the 1970's, smog from car exhaust overwhelmed most major U.S. cities.

The key technology that enabled this dramatic clean-up is the catalytic converter. Inside a catalytic converter there are actually multiple catalysts, each enhancing different reactions. Most cars today use what is called a "three-way" catalyst, which just means that it tackles all three of the biggest pollutants: NOX, hydrocarbons, and CO. The key materials used as the catalysts are a combination of platinum, palladium, and rhodium. Inside a catalytic convertor one typically has a honeycomb mesh just to get a large surface area. Since the temperature gets quite high (and in fact needs to be high for the catalysts to operate, which is why cold engines pollute more than hot ones), the honeycomb mesh is made out of a ceramic material like alumina so it can handle $\mathrm{T = 500^\circ C}$ without cracking or degradation. The Pt, Pd, and Rh metals coat the $\mathrm{Al_2O_3}$ mesh, and the exhaust flows through.



Take a look at this catalytic converter schematic. You can see two different chambers, one where the metal acts as a "reduction catalyst" for the NOX removal and the other where a different metal (or combination of metals) acts as an "oxidation catalyst" to treat CO and unburned hydrocarbons. In the reduction catalyst chamber, the reaction we're trying to accelerate is

$2NO \rightarrow N_2 + O_2$. In order to do so, the catalyst binds the NO molecule to it, and is then able to pull off the nitrogen atom from NO and hold it in place. Then another N atom that also got pulled off of a different NO molecule gets stuck to the catalyst somewhere nearby, and those Likewise, the oxygen can form O)2. The whole point is that the catalyst finds a different way to carry out the same reaction with much lower barriers. The oxidation catalyst burns CO and hydrocarbons using remaining O2 gas, for example to get this reaction to go: $2CO + O_2 \rightarrow 2CO_2$. Again, that reaction would not occur at a high rate normally, but the catalyst breaks it down into steps (like splitting CO) that occur much more easily.

Why this employs

The rate of a reaction is of course of central importance to anything one does that involves a reaction. And how many different types of jobs do anything involving a reaction? A ton! We could be talking about any sort of chemical synthesis job, or in drug design where reaction rate is crucial to the drug's effectiveness and safety, or how about food making (even beyond beer) where rates determine anything from how long to let dough rise to how fast that dough browns in an oven vs. the apples inside turning mushy (I just made an apple pie in case you couldn't tell), to how quickly to food goes bad. The point is that making stuff is inherently about rates.

And so instead of focusing on any one of these things that we make, I'd like to use this Why This Employs section to mention the fact that in nearly everything we make today, far too much natural capital is expended, and it doesn't have to be that way. A single computer chip takes more than 600 times as much mass to make it and tremendous amounts of both water and energy (including annealing multiple times at temperatures over 1000°C. Cement is a wonderful material ("liquid stone") but it takes baking calcium silicate at very high temperatures to make the tiny particles called "clinkers" that give it the ability to take on any shape in an instant and then dry and set so quickly after. Why is it that, time and time again, we fail to do what nature does so well? Animals can build incredibly strong and complex structures without going a single degree over room temperature. Spiders spin silk stronger than steel without lighting a fire. How can we do better? Much of it comes down to reaction rates. We use these massive amounts of energy and high temperatures and harsh chemicals because we want to make stuff quickly and because we need to make stuff in almost unimaginable quantities. China alone produced 2.5 trillion kilograms of cement last year!

There are more sustainable ways to make stuff, especially if we can get a handle on the reaction rates. Ten years ago I remember reading articles about the new revolution of "green chemistry" (check out for example this 2010 article in Scientific American, https://www.scientificamerican. com/article/green-chemistry-benign-by-design/. I remember thinking then that this field was ready to take off. Well, it didn't really happen with a bang, but slow and steady this idea of benign design is taking hold. If you search for green chemistry jobs, you'll find many companies now investing in this area substantially and that spells new jobs. The idea of green chemistry on the job market ranges quite broadly, from finding ways to synthesize materials without toxic chemicals, to making the drug discovery process biodegradable, to lowering the temperatures needed in a manufacturing step. Whatever it is, it's all about the rates.

Example problems

1. Acetic acid is made from carbon monoxide and methanol according to the following equation:

$$CO(g) + MeOH(g) \rightarrow AcOH(g)$$

Your company wants to know how to improve this reaction: they present you, a chemical consultant, with the following data. Propose a rate law for the reaction.

CO pressure	MeOH pressure	Acetic acid formed
21.5 atm	15.0 atm	980 mol/hour
11.1 atm	15.0 atm	499 mol/hour
11.1 atm	10.0 atm	502 mol/hour

Answer

The rate is fairly insensitive to changing $MeOH$, but the rate drops by about half when the pressure of CO is halved. Therefore, the rate is 0^{th} order in methanol, but 1^{st} order in CO:

$rate = k[CO]$

Lecture 28: Equilibium and Solubility

Summary

Many of you have probably heard the expression, “like dissolves like”. . . but let’s add a little bit more chemistry to that phrase. What is really meant by the word “like” is “similar bonds,” so the expression could also be said, “similar bonds dissolve similar bonds.” **Solubility** is a metric that tells us how much the **solute** (the solid being dissolved) can break apart and dissolve into the **solvent** (the liquid in which the solid is dissolving). When the solubility is **miscible** that means that it can be full mixed together at any concentration.

Intermolecular forces play a huge role in solubility. Water is called a **polar solvent** (also called **hydrophilic**) because it’s a solvent with large dipole moments, while hydrocarbons are examples of **nonpolar solvents** (also called **hydrophobic**) since the dominant IMF is London. Polar solvents are in general immiscible with nonpolar solvents.

What’s really going on at the scale of the molecule and its various IMFs, is that if a molecule can lower or keep similar its energy by welcoming a different molecule into its bonding environment, then it will do so. If on the other hand the other molecule cannot bond in the same way (as in the example of the longer hydrocarbon chaining having much more London forces than H-bond ability) then it would raise the energy of the system for the solvent to bond to it over itself.

Particles in a solution that re-join the solid are said to be **precipitating**. both dissolution and precipitation occur simultaneously and at the point of saturation, or maximum solubility, they happen at exactly the same rate. This is called dynamic equilibrium.

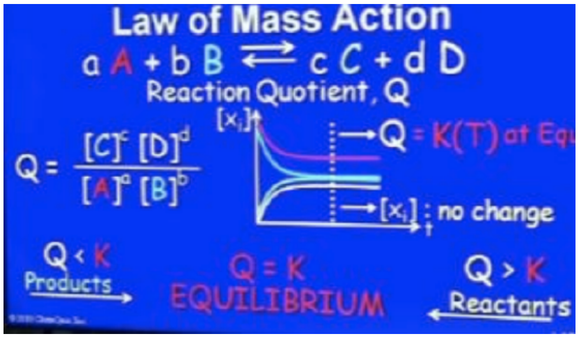
We know from our previous lectures on ionic solids that these are cations and anions in the solid, which is the basis of the ionic bond. When dissolved in water, they also remain ions, just now in solution, where they interact strongly with water. We can understand why, since we know from our IMF lecture that the ions will interact with the dipole of the water molecule. The reason there is a trend in the solubility of these salts is related to the strength of the bond between ions in the solid relative to those the liquid. As the ionic bonding becomes stronger (from weakest at NaI to strongest at NaF), less of it dissolves.

Suppose the general reaction has already reached its dynamic equilibrium:

$$aA + bB \leftrightarrow cC + dD$$

This means that the four different concentrations, $[\mathrm{A}]$, $[\mathrm{B}]$, $[\mathrm{C}]$, and $[\mathrm{D}]$ are not changing even though the reaction is still going in both directions. Below is a nice picture of what might happen to these concentrations as a function of time. At first during the reaction the concentrations change, and then they all flatten out. At that point, when they're all flat, the system has reached dynamic equilibrium. We define the reaction quotient, Q, as the ratio of

$$\frac{[C]^c[D]^d}{[A]^a[B]^b}$$



Law of Mass Action

$$a\,A + b\,B \rightleftarrows c\,C + d\,D$$

Reaction Quotient, Q

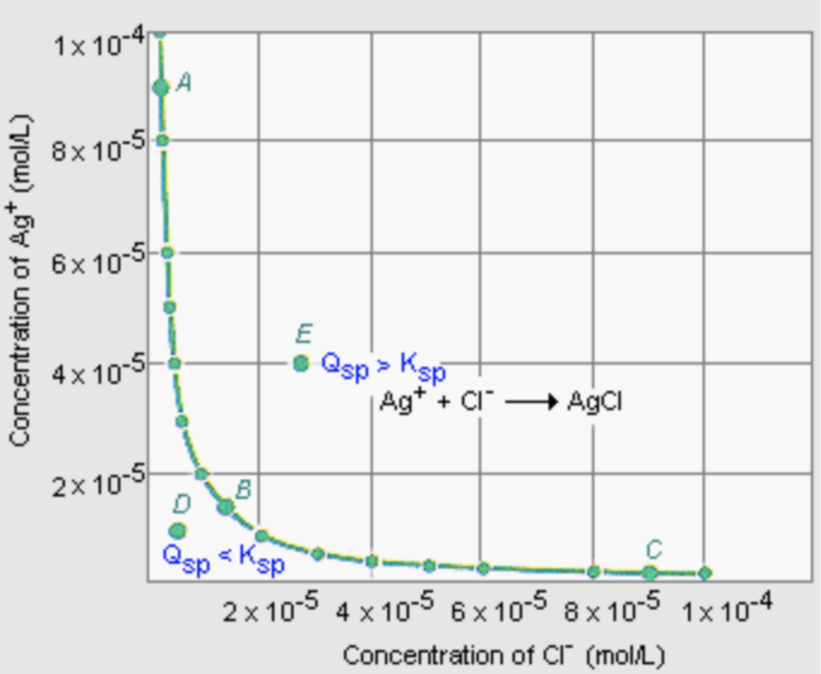
$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

Q < K
Products →

Q = K
EQUILIBRIUM

Q > K
← Reactants

This expression for Q can be evaluated at any point during the reaction, whether the system has reached equilibrium or not. BUT, we have a special way to call Q once the system is in dynamic equilibrium, and that's with the letter K, or the equilibrium constant for the reaction. Often, we put a subscript "eq" on the K just to make sure we know what it refers to, so $\mathbf{K}_{eq} = \mathbf{Q}$ (for the reaction quotient in equilibrium). The Keq for a solid dissolving in water is the solubility product $(\mathbf{K}_{sp})$

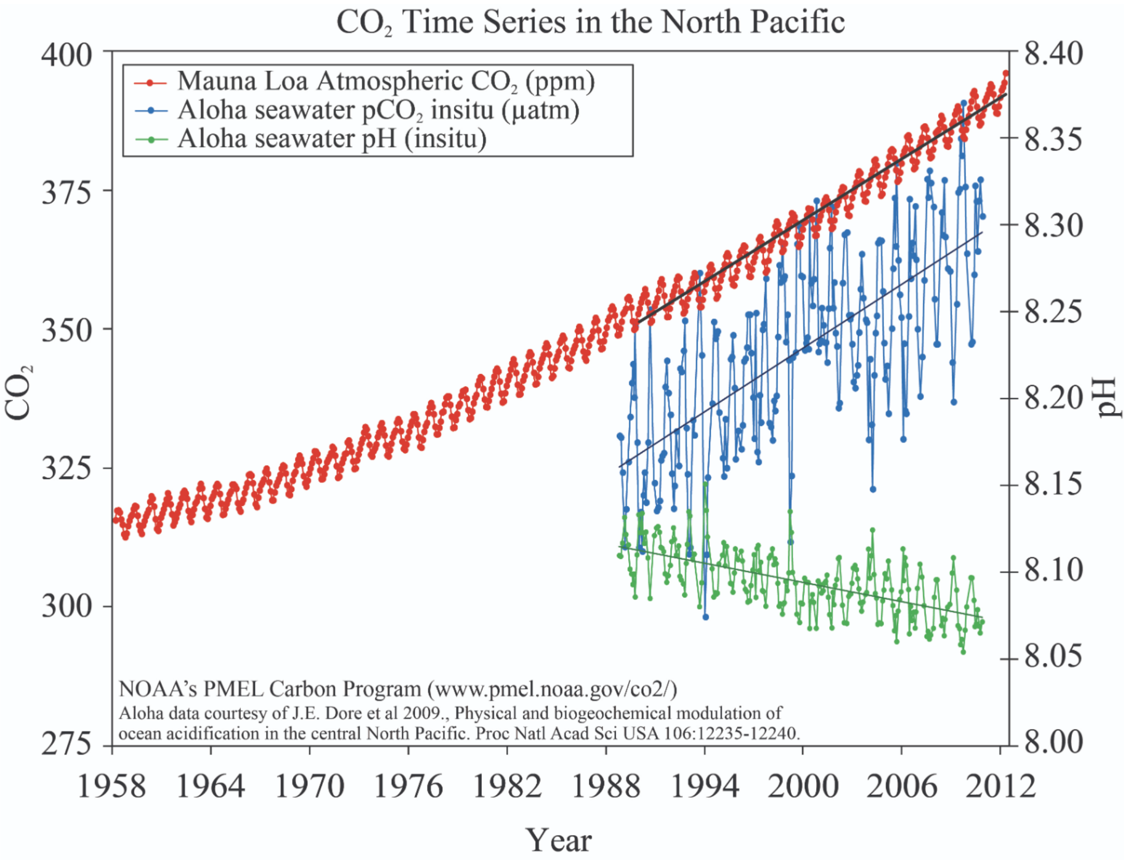


By comparing the value of Q to the equilibrium constant, Keq, for the reaction, we can determine whether the forward reaction or reverse reaction will be favored.

If $Q = K_{eq}$, the reaction is at equilibrium. If $Q < K_{eq}$, like at point D, then the reaction will move to the right (in the forward direction) in order to reach equilibrium. If $Q > K_{eq}$, like in point E, then the reaction will move to the left (in the reverse direction) in order to reach equilibrium. Le Chatelier coming at us in graphical form!

Why this matters

From examining the tiny bubbles trapped in ice cores, we know that the level of CO_2 currently in the atmosphere is more than it has been in over a million years, and the amount is growing exponentially. But while this incredibly important greenhouse gas has received tremendous attention for its role in climate change, there is a much less frequently discussed impact that CO_2 is having on our planet. Maybe that’s because it’s happening in the oceans, which we don’t live in so it’s harder to make as big of a deal about the changes occurring. But we will feel these changes soon enough. The ocean has absorbed more than 500 billion tons of CO_2 from the atmosphere, as it quietly captures roughly a quarter of what’s being emitted day in and day out (today we humans crank out 1,200,000 grams of CO_2 per second). So why does this matter?



The problem with all that extra CO_2 in the oceans is that it makes the water more acidic. Over the past 200 years alone, ocean water has become 30 percent more acidic. This change in acidity is faster than any known change in ocean chemistry over the last 50 million years! In geological terms, this is an extremely abrupt perturbation, and without dramatic changes in human behavior we are only seeing the beginning.

Unfortunately, one of the most important defenses for ocean creatures - the shell - cannot survive increased acidity. Here's a picture of what happens to the shell of a pteropod, a type of mollusk only a few cm long, after 45 days in a solution of $pH = 7.8$. Now, the oceans aren't quite that acidic yet (current ocean pH is 8.1), but they're well on their way. Pteropods are one of only a few basic types of sea creature that sits at the very bottom of the ocean food chain, right above plankton and seaweed, which means that if their numbers are reduced, everything higher on the food chain is impacted, from krill to salmon, to herring and birds, to seals and polar bears, and of course, to us.

In the goodie bag that goes with these lectures, you'll be able to see this dissolution in action. We make it go faster than 45 days since I don't want you to wait that long, but the chemistry at play is the same. I wanted you to touch and feel this precious calcium carbonate loss, so that you can get a glimpse into what is beginning to happen to 2/3 of our planet.

Why this employs

In order for drugs to have a physiological effect on the human body, they must be in solution. In particular, they must be dissolved in solution if they start out in solid form, like tablets do. Now, the rate of the dissolution is extremely important since determines how fast the drug is absorbed in the body. Rates were discussed in the last chapter. But solubility itself (i.e. regardless of how fast it dissolves, what is its ability to fully dissolve at all?) is also of crucial importance in drug design. If the drug is not very soluble, formulations can lead to difficulties in the use of the drug which may otherwise have very beneficial effects. If a drug has low solubility that means it will likely have a low level of what is called "bioavailability," which basically just means that it won't get enough exposure in the body.

In pharmaceutical companies that do most of the new drug development, it is estimated that a whopping 40% of all new chemicals (possible new beneficial drugs) are practically insoluble in water, making them effectively useless. And what is it that these companies do to try to increase solubility, especially for otherwise promising candidates? Chemical modification, of course! And so it is that all of the large pharmaceutical companies are looking for people who know about solubility! In terms of where to look for jobs, the thing about drug design companies is that you don't have to look very far. Within just 1 mile of campus, there are dozens of both large and small companies specializing in drug design. More broadly, Kendall Square now has the largest biotechnology industry per square foot, with over 120 companies within a mile.

In terms of which ones of these companies have jobs related to solubility, well because of how important solubility is, it's pretty much all of them. Check out for example, the job postings at Takeda, Novartis, Alnylam, Sanofi, Pfizer, and Genentech just to get started, and then walk down the street to go learn more about the companies, what they do, and meet with them in person!

Example Problems

1. Calcium fluoride has a K_{sp} of 5.3×10^{-9} . How much calcium fluoride can dissolve in $1\mathrm{L}$ of water?

Answer

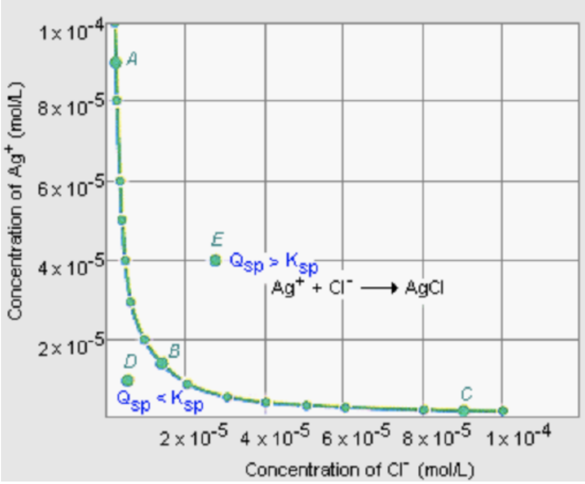
$$k_{sp} = [Ca][F]^2$$

For every mole of Ca that dissolves, twice as many moles of F must dissolve since the chemical formula is $\mathrm{CaF_2}$. Assuming x moles of Ca dissolve:

$$K_{sp} = [x][2x]^2$$
$$5.3 \times 1-^{-9} = 4x^3$$
$$x = 0.00109M$$
$$78\frac{g}{\mathrm{mol}}\frac{0.00109\ \mathrm{mol}}{L} = 85.9\mathrm{mg}/1\ \mathrm{L}$$

Lecture 29: Common Ions and Acids/Bases

Summary



Le Chatelier's principle states that the position of equilibrium moves to account for changes to the system, such as the introduction of a new ion to a solution. But what happens if we add a new compound that has one ion in common with an existing solution? The equilibrium curve for the AgCl dissociation is shown to the right. Suppose we add NaCl: it will dissociate completely into ions $\mathrm{Na^+(aq)}$ and $\mathrm{Cl^-(aq)}$. We can use an ICE table to determine the shift in equilibrium: if we start at point B and add $0.1\mathrm{M NaCl}$, we can use the equilibrium constant for $\mathrm{AgCl}, \mathrm{K}_{sp} = 1.7 \times 10^{-10}$. As $\left[\mathrm{Cl^-}\right]$ increases, $\left[\mathrm{Ag^+}\right]$ must decrease to keep K_{sp} constant.

	$[AgCl]$	$[Ag^+]$	$[Cl^-]$
I	(all solid)	1.3×10^{-5}	1.3×1^{-5}
C	+ x precipitates	$-x$	$+0.1 - x$
E	More solid	$1.3 \times 10^{-5} - x$	$+0.1 - x$

$$K_{sp} = [\mathrm{Ag}^+][\mathrm{Cl}^-] = (0.1 - x)(1.3 \times 10^{-5} - x)$$
$$K_{sp} = 0.1(1.3 \times 10^{-5} - x) = 1.7 \times 10^{-10} \quad x = 1.7 \times 10^{-9}$$

This is called the common ion effect: the solubility of one constituent is repressed by the addition of a second solute.

For a generic case of any acid, call it "A" we write its dissolution reaction as follows: $\mathrm{HA} + \mathrm{H_2O} \rightarrow \mathrm{H^+} + \mathrm{A^-} + \mathrm{H_2O}$. Although we write $\mathrm{H^+}$ to make the proton dissociation explicit, we never actually mean that if it's in water. That's because the $\mathrm{H^+}$ion is not stable in $\mathrm{H_2O}$, instead it always becomes $\mathrm{H_3O^+}$. The first person to define acids and bases in any sort of more concrete chemical way was good old Svante Arrhenius. According to him, an acid is a substance that dissolves in water to produce $\mathrm{H}+$ ions, and a base is a substance that dissolves in water to produce hydroxide $(\mathrm{OH^-})$ions.

Arrhenius defined acids and bases in terms of the presence of $\mathrm{H^+}$ or $\mathrm{OH^-}$ions in solution: for example, $\mathrm{HCl}(aq) \rightarrow \mathrm{H^+}(aq) + \mathrm{Cl^-}(aq)$ is an "Arrhenius acid" while $\mathrm{NaOH}(s) \rightarrow \mathrm{Na^+}(aq) + OH^-(aq)$ an "Arrhenius base."

Sorenson came up with the "power of hydrogen" scale, or "pH" scale for short. $\mathrm{pH} = -\log[\mathrm{H^+}]$. The pH scale runs from 0 to 14 , with 0 being extremely acidic and 14 being extremely basic. We can do the same thing for the concentration of $[\mathrm{OH^-}]$: the power of $\mathrm{OH^-}$ in solution, or the "pOH" $= -\log[\mathrm{OH^-}]$, with the opposite definition.

A strong acid like HCl fully dissociates: $\mathrm{HCl} + \mathrm{H_2O} \rightarrow \mathrm{H^+} + \mathrm{Cl^-} + \mathrm{H_2O}$, so $0.1\mathrm{M HCl}$ has $[\mathrm{H^+}] = 0.1$, so $0.1\mathrm{M HCl}$ solution has $\mathrm{pH} = -\log[0.1] = 1.0$.

Some materials can be both acids and bases. None other than water itself is one such material! When a molecule can either give $[\mathrm{H}+]$ ions or $[\mathrm{OH}-]$ ions into solution, it's called amphoteric: $\mathrm{H_2O}(l) + \mathrm{H_2O}(l) \leftrightarrow \mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq)$. K_{sp} for water is called K_w : $K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$. If an acid is added to pure water the hydrogen ion concentration increases (and the OH ion concentration decreases) A base goes the other way, adding hydroxide ions into the pure water solution. All of the tricks we learned for K_{sp} apply to K_w, which is especially useful in the context of acids and bases.

Arrhenius' definition of acids and bases has two key limitations: first, because acids and bases were defined in terms of ions obtained from water, the Arrhenius definition applied only to molecules in aqueous solution. Second, and more important, the Arrhenius definition predicted that only materials that dissolve in water to give $\mathrm{H^+}$ and $\mathrm{OH^-}$ions can have the properties of acids and bases. But there are many examples where this is not true! We need to go beyond Arrhenius to understand some acids and bases.

Why this matters

Now that we're armed with the concepts of the Common Ion Effect and Le Chatelier's principle, we can go into more detail on the chemistry that's causing the possible catastrophe discussed in the previous Why This Matters: ocean acidification and its impact on the fate of calcium carbonate. It's all about equilibrium and how $\mathrm{CO_2}$ is shifting it in the oceans. The first reaction we consider is what happens when the oceans encounter more $\mathrm{CO_2}$ from the atmosphere: namely, the $\mathrm{CO_2}$ dissolves in the $\mathrm{H_2O}$ to form carbonic acid:

$$\mathrm{CO_2} + \mathrm{H_2O} \leftrightarrow \mathrm{H_2CO_3}$$

So more $\mathrm{CO_2}$ getting dissolved in the ocean means there's more carbonic acid in the ocean, which then produces dissociated ions as follows:

$$\mathrm{H_2CO_3} \leftrightarrow \mathrm{HCO_3^-} + \mathrm{H^+}$$

But on the other hand, we've got solid $\mathrm{CaCO_3}$ which is the calcium carbonate, that is in a nice equilibrium with the following dissociation reaction:

$$\mathrm{CaCO_3} \leftrightarrow \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}}$$

The equilibrium constant for the dissolution of $\mathrm{CaCO_3}$ is $\mathrm{k}_{sp} = 5 \times 10^{-9}$. That means not a whole lot of it will dissociate in "normal" (i.e. last > 50 million years) ocean conditions. The reason this equilibrium is getting thrown off is that there are now extra $\mathrm{H^+}$ions that come from the $\mathrm{CO_2}$ reaction above. These $\mathrm{H^+}$ions consume (react with) $\mathrm{CO_3^{2-}}$ to form $\mathrm{HCO^{3-}}$ which lowers the concentration of $\mathrm{CO_3^{2-}}$. Ah, but we just learned about that with the Common Ion Effect: if we add or take away some molecule that's part of a balanced equilibrium, then we will drive that equilibrium to counter whatever we've done. In this case , $\mathrm{CO_3^{2-}}$ is getting consumed more than before, which in turn drives more dissolution of the $\mathrm{CaCO_3}$. That's why the shells are dissolving, and it's why I want you to experience this chemistry directly in your goodie bag. What you're seeing is those experiments is an accelerated version of what is happening in the oceans.

Acidity is measured by " pH," which is a logarithmic scale. Since the Industrial Revolution, the pH of the oceans has decreased by ≈ 0.1 to 8.07, which is equivalent to a $\approx 30\%$ increase in the oceans' acidity. I showed that trend in last lecture's Why This Matters. Estimates are that at our current rate of $\mathrm{CO_2}$ emissions, the acidity of the oceans will reach a whoppingly more acidic state of $\mathrm{pH} = 7.7$ by 2100 . That would represent a > 5-fold increase in acidity compared to pre-industrial levels, and that would also pretty much do it in terms of wiping out most ocean life.

The ocean has absorbed roughly 525 billion tons of $\mathrm{CO_2}$ from the atmosphere over the past 200 years, at a pace of ≈ 22 million tons per day. The change that this induces is the fastest known chemical change the ocean has experienced over the past 50 million years and probably much longer. Around 250 million years ago, at the end of what is known as the "Permian era," records show that there was a sudden change in the oceans, and geologists refer to what happened as, "The Great Dying." This is because more than 90% of all marine life disappeared from the fossil record. Most scientists who study this kind of thing relate the mass extinction to a huge spike in volcanic activity, which put vast clouds of acidic dust into the atmosphere, which then fell into the oceans and raised their acidity.

The reason the dissolution of calcium carbonate is so important is that it is essential not just to the pteropods I showed before, but to so many other “base” elements of the ocean’s food chain, like phytoplankton, shell fish (mussels, oysters, lobsters, crayfish, etc), and of course coral, to name only a few examples. The calcium carbonate structures in these sea creatures are highly sensitive to slight changes in acidity, and without them the health of the oceans will fail. I’ll end this Why This Matters with a thought-provoking quote from Ken Caldeira who is a climate scientist at Stanford. In trying to help people get perspective on what we’re doing, he said, “Well, if the Romans had industrialized, it now would be two thousand years later. The seas would still be rising and still be completely acidified, and, yes, maybe they would have got a century or so of higher G.D.P. than they would have otherwise.” The point being: the deleterious changes we’re on track to make in the oceans won’t just impact our kids, and our kids’ kids; it will impact tens and more likely hundreds of generations to come.

Why this employs

I talked about ocean acidification in this lecture since we’re introducing acids and bases, and what’s going on in the oceans is a good example of the effects of chemistry happening on a planetary scale. But what if you want to actually work on this problem, like as a job? Well, that’s not as straightforward as you might think, or for that matter may have hoped, but there are some things you can do.

For one thing, there are many, many academic or state-run programs that are studying ocean chemistry, and many of them have postings for jobs. This ranges from a random ocean acidification project at the University Di’ Bologna, Italy, to the National Oceanic and Atmospheric Administration Cooperative Science Center for Earth System Sciences and Remote Sensing Technologies (yes, thankfully they go by NOAA-CESSRST), to other government agencies such as the EPA or any agency working in conservation and policy, to Washington State’s Department of Ecology, to Stony Brook University who is currently seeking an, “Ocean Acidification Monitoring Associate.” There are many faculty positions in this area, and I believe there will be more in the future. So if you’re interested in both this topic as well as a career in academia, then the path of research in scientific centers is a good one. There are a number of different specializations that would lead to studying (and hopefully helping to save!) the oceans, from marine biologist to environmental engineer to a “chemical oceanographer,” who is kind of like an oceanographer but specializing in the chemical composition of the oceans rather than their ecology, biological life and geology.

Example problems

1. Hydrofluoric acid reacts with calcium carbonate according to the following equation:

$$\mathrm{2HF}(aq) + \mathrm{CaCO_3} \rightarrow \mathrm{H_2O}(l) + \mathrm{CO_2}(g) + \mathrm{CaF_2}$$

If $100\ \mathrm{mL}$ of a $10\mathrm{mM}$ solution of HF is added to $100\ \mathrm{mL}$ of a $10\mathrm{mM}$ solution of $\mathrm{CaCO_3}$, how much $\mathrm{CaF_2}$ will precipitate? Assume the reaction goes to completion.

Answer

In this problem, the first clue is that the reaction "goes to completion:" this indicates that we don't need to worry about equilibrium. When a $10mM$ solution of HF is added to a $10mM$ solution of $\mathrm{CaCO_3}$, the final solution has a different concentration.

The original solutions each contain $1\mathrm{mmol}$ of material, since $0.1L * 10\mathrm{mmol}/L = 1\mathrm{mmol}$ The final solution, therefore, has $1\mathrm{mmol Hf}$ and $1\mathrm{mmol CaCO_3}$ in $0.2\ \mathrm{L}$ of water, so the concentration of the final solution is $5\mathrm{mM}$ in both reactants.

Next, we need to think about how much $\mathrm{CaF_2}$ we can form: if we start with $1 \mathrm{mmol}$of HF and 1 mmol $\mathrm{CaCO_3}$, you can check that the limiting reagent is $\mathrm{CaCO_3}$, since we need twice as much HF as $\mathrm{CaCO_3}$ to form $\mathrm{CaF_2}$. We'll end up with $0.5 \mathrm{mmol CaF_2}$ and leave behind $0.5 \mathrm{mmol CaCO_3}$

Next, we need to determine how much will dissolve. We can use an ICE table and the common ion effect. We start with $0.5 \mathrm{mmol}$of calcium ions in $0.2 \mathrm{~L} = 0.25 \mathrm{mM}$

	$\mathrm{CaF_2}$	$\mathrm{Ca^{2+}}$	$2F^-$
I		$2.5 \mathrm{mM}$	$0 \mathrm{mM}$
C		$+\mathrm{x}$	$+2\mathrm{x}$
E		$2.5+\mathrm{x}$	$2\mathrm{x}$

$$\begin{aligned} 5.3 \times 10^{-9} &= (.0025+x)(2x)^2 \\ x &= 0.000649 \end{aligned}$$

Therefore, $0.649 \mathrm{mM}$will be soluble, leaving $2.5 \mathrm{mM} - 0.649 \mathrm{mM} = 1.85 \mathrm{mM} CaF_2$will precipitate.

$$1.85 \mathrm{mmol}/L * 0.2L = 0.37 \mathrm{mmol}$$

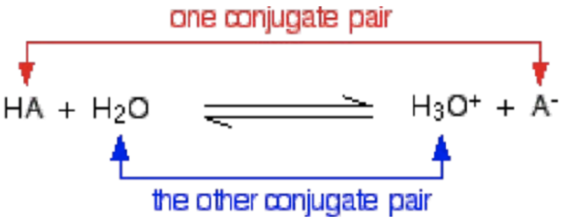
$$0.37 \mathrm{mmol} * 78.07 \mathrm{~g/mol} = 28.9 \mathrm{mg CaFC_2}$$

Therefore, $28.9 \mathrm{mg}$of $\mathrm{CaF_2}$ will precipitate.

Lecture 30: Bronsted-Lowry Acids/Bases and Neutralization

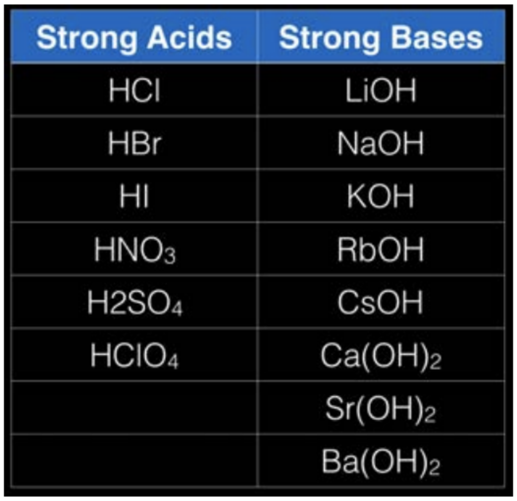
Summary

In this lecture, we started by considering what happens if you combine an acid and a base directly: for example, $\mathrm{NaOH(aq)} + \mathrm{HCl(aq)} \rightarrow \mathrm{H2O(l)} + \mathrm{NaCl(s)}$. Each of these products, the water and the salt, find an equilibrium of their own. So the arrow goes both ways $\mathrm{H++OH-} \leftrightarrow \mathrm{H_2O(l)}$ and water gives the usual neutral ion concentrations of $\mathrm{H+}$ and $\mathrm{OH-}$. Salt also will have its equilibrium reaction to form ions $\mathrm{Na+}$ and $\mathrm{Cl-}$ in solution. Sometime the $\mathrm{Na+}$ and $\mathrm{Cl-}$ ions called "spectators" when in solution, since they don't participate in making the solution either acidic or basic. The reaction of an acid with a base to make water and salt is called a neutralization reaction.



Bronsted and Lowry defined acids and bases more broadly: a Bronsted-Lowry acid is anything that releases $\mathrm{H^+}$ions. A Bronsted-Lowry base is anything that accepts $\mathrm{H+}$ ions. A "conjugate pair" is a nice way to keep track of the proton transfer that happens in acid/base chemistry. If we consider the generic reaction $\mathrm{HA + H_2O}$, where we label the A for "acid" and purposefully write the H separately since we know as an acid it will be giving that H up as a $\mathrm{H^+}$ion, the molecule left the other conjugate pair over after giving up the $\mathrm{H+}$ ion into solution, $\mathrm{A-}$, is called its conjugate pair. Similarly, if it reacted with $\mathrm{H_2O}$, then the $\mathrm{H_2O}$ gained the $\mathrm{H+}$ to become $\mathrm{H_3O^+}$, and those two molecules are conjugate pairs. According to Bronsted-Lowry, an acid base reaction is essentially just a proton transfer reaction.

A general way to write an acid mixing with a base would be: $\mathrm{HA + B \rightarrow BH^+ + A^-}$ where here it is very clear that the acid transfers a proton to the base.



Strong Acids	Strong Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H2SO4	CsOH
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

How do we know why and when an acid or base is "strong" vs. "weak?" This table lists common strong acids and bases. Acids other than these six are essentially all weak acids. The only common strong bases are the hydroxides of the alkali metals and the heavier alkaline earths (Ca, Sr, and Ba; any other bases are likely to be weak. We can quantify why these molecules are considered "strong" by considering their acid dissociation constants. For HCl, the acid dissociation constant, or in other words the equilibrium constant for the acid, $K_a = \left[H_3O^+\right]\left[Cl^-\right]/[HCl] \approx 106$ - this is huge, and it means effectively full dissociation. A strong acid like HCl is in fact strong because it fully dissociates. And the opposite is true too: if an acid fully dissociates, then it is a strong acid. The same applies for strong bases.

For example, suppose you have a $1.0M$ solution of CH_3COOH. That means that there's 1 mole of CH_3COOH in a liter of water. Since $K_a = 10^{-5}$, that means that $\left[H_3O^+\right]$ for this $1M$ solution is around 0.003, which in turn means that the pH of $1M CH_3COOH$ is about 2.5. Note that if there's 0.003 moles of $\left[H_3O^+\right]$ that can from 1 mole of CH_3COOH, then that means that only 0.3% of it dissolved. That's not a lot of dissolution compared to the near 100% for the strong acids!

Here's another example: will the salt formed from the following reaction have a pH greater than, less than, or equal to $7? CH_3COOH(aq) + NaOH(s) \leftrightarrow Na^+ + CH_3COO^-(aq) + H_2O(l)$ To answer this we don't even need to do any math. That's because if a weak acid is mixed with a strong base (as is the case here), we automatically know that it will be basic.

In general, when the following are mixed, the results are:

- Weak acid mixed with weak base: $pH < 7$ for $K_a > K_b$; $pH = 7$ if $K_a = K_b$; $pH > 7$ for $K_a < K_b$
- Strong acid mixed with string base: $pH = 7$
- Strong acid mixed with weak base: $pH < 7$
- Strong base mixed with weak acid: $pH > 7$

Why this matters

It might feel a bit on the hot side at $470^\circ C$, and you'd be surrounded by sulfuric acid most of the time. That's what it would be like if you lived on Venus. Here's a nice picture from a Russian space probe back in the 1970's that landed on the surface, showing what a stroll would be like over there. These temperatures and acidic atmospheres may sound crazy, but many materials require similar conditions for processing. A lot of aspects of our industrial revolution have effectively relied on reproducing the conditions of Venus! In fact, today, nearly 250 million tons of sulfuric acid is produced per year, which makes it one of the largest chemicals produced worldwide. The liberated $H+$ ions that come from $H2SO4$ are put to use in a wide range of industries, from detergents to lead-acid car batteries to dyes to metal processing, it is in the production of fertilizers where its use dominates: roughly 50% of all sulfuric acid is used to make fertilizer!

In one of our earlier Why This Matters, we discussed the Haber-Bosch process, which uses a catalyst, high temperatures (like $\approx 400^\circ C$), and high pressures (like ≈ 180 atm.) to fix N_2 molecules and turn them into ammonia, NH_3. But the thing is, that's only one of the three most important ingredients plants need to grow: the other two are phosphorus and potassium. Phosphorus, in particular, is typically made with vast amounts of sulfuric acid. Why is this the case? You already know the answer, it's the chemistry.

found in sedimentary deposits, meaning that they formed by deposition of phosphate-rich materials in marine environments. Here's a picture of a phosphate rock formation being mined in Utah. But if you take phosphate rock and grind it up into a powder, it still won't be very soluble in water (we now have some knowledge about what that means!). This means that if you put the mineral directly into fertilizer, it will not be useful to plants. It's just like for the case of N_2 in the air: even though there's plenty of N_2, plants have no way of absorbing it. Rather, they need to work with NH_3 in order to take in nitrogen. The same thing is true for phosphorus: tricalcium phosphate, $Ca_3(PO_4)_2$, which is what phosphate rock mostly consists of, is not able to give phosphorus to plants because it doesn't dissolve enough in water. The K_{sp} for this ionic salt is a whoppingly low 2.07×10^{-33}! By the way, it's a pretty good thing that this doesn't dissolve very much since it's a key ingredient in bones and teeth.

That's where sulfuric acid comes in: it's a fairly simple way to liberate the phosphoric acid H_3PO_4 from the phosphate rock. In particular, the H_2SO_4 from the phosphate rock. In particular, the H_2SO_4 gives up its hydrogen in exchange for the calcium to form calcium sulfate, as follows:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4$$

Once the phosphoric acid is produced in this manner, it can then be made into different types of fertilizer that are now water-soluble, so the plants can absorb it. These are generally termed "phosphates," or salts of phosphoric acid, which in the context of fertilizers include ammonium phosphates, calcium phosphates, and sodium phosphates. Bottom line: we feed the world because of our knowledge of acid/base chemistry!

Why this employs

Acids and bases are used so much in industry and in life: it's not hard to find jobs that involve acids and bases. You could check out DuPont, for example, which sells phosphate fertilizer plants that do just what we discussed above (for example, see http://cleantechnologies.dupont.com/ industries/phosphate-fertilizer/). http://cleantechnologies.dupont.com/...atefertilizer/. BASF was one of the very first companies to make and sell sulfuric acid on large scales, and they still do and have many job openings related to acid chemistry. There's Sigma Aldrich, which is a massive company with 10,000 employees and nearly $\$3$ B in annual revenue: their "acids and bases" category shows hundreds of products (btw, another company, Merck, bought them recently for $\$17$ B). Or how about Cabot Laboratories, which doesn't make acids and bases explicitly but uses them to make every one of the cool chemical products they do make, whether elastomers or aerogels or "advanced carbons."

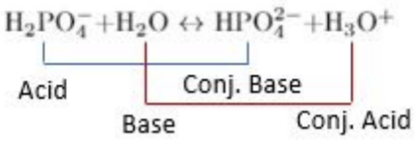
You could take any one of many different acids, look up its name, and likely find a market for it, and then all the companies that either make it or use it, many of which will have jobs related to it. Take formic acid: it's getting more interest from a range of different industries because it's easier to handle than other acids (see for example this article about it in C&EN (https://cen.acs.org/articles/93/i48/Chemical-Makers-Eyes-Formic-Acid.html), and is used heavily in the textiles industry. BASF and Eastman Chemical are big on formic acid, but a lot of other companies are getting interested. Speaking of textiles, that's another industry that uses massive amounts of acids, including formic acid but also citric, acetic, hydrochloric, and nitric acid. Textiles also rely heavily on bases like sodium hydroxide and baking soda for dyeing, cleaning, and fire-proofing clothes to name a few uses. All just to say that acids and bases and truly a bedrock of industry, and knowing how to make them or how to use them leads to massive job opportunities.

Example Problems

1. Identify the conjugate acid/base pairs in the following reactions:

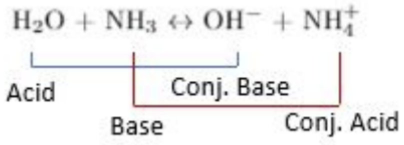
a) $H_2PO_4^- + H_2O \leftrightarrow HPO_4^{2-} + H_3O^+$

Answer



b) $H_2O + NH_3 \leftrightarrow OH^- + NH_4^+$

Answer



2. Calculate the K_a of an 0.2M aqueous solution of propionic acid $(\mathrm{CH_3CH_2CO_2H})$ with a pH of 4.88. The dissociation can be expressed as

$$\mathrm{CH_3CH_2CO_2H + H_2O \leftrightarrow H_3O^+ + CH_3CH_2CO_2^-}$$

Answer

This problem can be solved with an ICE table:

	$\mathrm{CH_3CH_2CO_2H}$	$\mathrm{H_3O^+}$	$\mathrm{CH_3CH_2CO_2^-}$
I	0.2	0	0
C	−x	+x	+x
E	0.2 − x	x	x

$$-pH = \log\left[H_3O^+\right] = -4.88$$

$$\left[\mathrm{H_3O^+}\right] = 10^{-4.88} = 1.32 \times 10^{-5} = x$$

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{CH_3CH_2CO_2^-}\right]}{\left[\mathrm{CH_3CH_2CO_2H}\right]} = \frac{x^2}{0.2 - x} = \frac{\left(1.32 \times 10^{-5}\right)^2}{0.2 - 1.32 \times 10^{-5}} = 8.69 \times 10^{-10}$$

Further Reading

Lecture 21: Bragg’s Law and x-ray Diffraction

- More Bragg’s Law:

  https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Analytical_Sciences_Digital_Library/JASDL/Courseware/ Introduction_to_X-ray_Diffraction_(XRD)/03_Basic_Theory/02_Diffraction__and_Bragg%E2% 80%99s_Law

- How to do an XRD experiment:

  https://serc.carleton.edu/research_education/geochemsheets/ techniques/XRD.html

- History of science: Rosalind Franklin, X-ray Diffraction, and the structure of DNA:

  https: //doi-org.stanford.idm.oclc.org/10.1119/1.5020051

Lecture 22: From x-ray Diffraction to Crystal Structure

- Laue condition (beyond-the-scope of 3.091):

  http://www.physics.udel.edu/~yji/PHYS624/ Chapter3.pdf

- Nice visualizations:

  http://web.pdx.edu/~pmoeck/phy381/Topic5a-XRD.pdf

Lecture 23: Point Defects

- Schottky and Frenkel defects, plus some beyond-the-scope stuff:

  http://ww2.chemistry.gatech. edu/class/6182/wilkinson/nonstoi.pdf

- How defects give different gemstones their distinctive looks:

  https://www.tf.uni-kiel.de/ matwis/amat/iss/kap_6/advanced/t6_1_1.html

Lecture 24: Line Defects and Stress-Strain Curves

- Defects summary:

  https://chemed.chem.purdue.edu/genchem/topicreview/bp/materials/ defects3.html

- Animation of moving edge dislocation:

  https://www.tf.uni-kiel.de/matwis/amat/def_en/ kap_5/illustr/a5_1_1.html

- Video on stress-strain curves:

  https://www.khanacademy.org/science/in-in-class11th-physics/ in-in-mechanical-properties-of-solids/in-in-stress-strain-and-modulus-of-elasticity/ v/stress-vs-strain-curve

Lecture 25: Amorphous Materials: Glassy Solids

- Crystalline vs. amorphous solids:

  https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chemistry_(Averill_and_Eldredge)/12%3A_Solids/12.1%3A_Crystalline_and_Amorphous_ Solids

- Record for image of thinnest glass:

  https://news.cornell.edu/stories/2013/09/shattering-records-thinnest-glass-guinness-book

Lecture 26: Engineering Glass Properties

- Inside a Corning factory:

  https://www.youtube.com/watch?v=gZPeyErbqz4

- 3D printing glass:

  https://www.youtube.com/watch?v=IvcpbtpWpGY

Lecture 27: Reaction Rates

- Summary of reaction rates:

  https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Reaction_Rates/Reaction_Rate

- More on catalytic converters:

  https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Case_Studies%3A_Kinetics/Catalytic_Converters

Lecture 28: Equilibrium and solubility

- Solubility product practice:

  https://www.chem.purdue.edu/gchelp/howtosolveit/Equilibrium/ Solubility_Products.htm

- A method for making more medicines soluble:

  https://www-chemistryworld-com.stanford. idm.oclc.org/health-tech/dissolving-insoluble-drugs/3008720.article

Lecture 29: Common Ions and Acids/Bases

- Worked out common ion effect example:

  https://www.khanacademy.org/science/chemistry/ acid-base-equilibrium/copy-of-solubility-equilibria-mcat/v/solubility-and-the-common-ion-effect

- Video on pH:

  https://www.khanacademy.org/science/chemistry/acids-and-bases-topic/ acids-and-bases/v/introduction-to-definition-of-ph

Lecture 30: Bronsted-Lowry Acids/Bases and Neutralization

- The Bronsted concept of acids and bases:

  https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Acids_and_Bases/Acid/Bronsted_Concept_of_Acids_and_Bases

- Acids and bases in cooking:

  https://www.livestrong.com/article/431096-acids-bases-in-cooking/

CHAPTER OVERVIEW

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6.1: Balancing Reactions, Yield, and Limiting Reagents

Balancing reactions

A *chemical reaction* involves rearranging elements in compounds to make different substances. They are usually written as a sum of *reactants*, which when combined yield a sum of *products* :

$$A + B \rightarrow C + D$$

Here, A, B, C, and D represent chemical compounds. The fundamental principle guiding the process of balancing a reaction is conservation of mass: a chemical reaction cannot create or destroy mass! This has several implications that can be used to determine whether a reaction is valid:

1. The mass of the reactants must equal the mass of the products
2. Every element that is in a reactant must be in a product
3. The number of each type of atom in the reactants must equal the number of each type of atom in the products

Example: Ethylene and oxygen gas are combined to make water and carbon dioxide. If you start with 4 moles of $\mathrm{O_2}$ gas, how many moles of water and carbon dioxide can you make? The unbalanced equation is given below:

$$\mathrm{C_2H_4} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$$

First, we must balance the reaction. One method to do this is by using a table:

	C	H	O	C	H	O
Initial (unbalanced):	2	4	2	1	2	3
Need: even number of oxygens Try: $2 \times \mathrm{H_2O}$ on the right	2	4	2	1	4	4
Need: even number of carbons Try: $2 \times \mathrm{CO_2}$ on the right:	2	4	2	2	4	6
Need: more oxygen on the left Try: $3 \times \mathrm{O_2}$ on the left	2	4	6	2	4	6

Once there are the same number of each elements on both sides of the reaction, we're done balancing! The final reaction is

$$\mathrm{C_2H_4} + 3\mathrm{O_2} \rightarrow 2\mathrm{CO_2} + 2\mathrm{H_2O}$$

The greatest common factor between the coefficients in front of each compound is 1, so this is the simplest form.

Yield

The *yield* of a reaction is the maximum amount of products that can be made with the reactants that are put in. For example, consider a s'more, which consists of a marshmallow, a piece of chocolate, and two graham crackers. If you had 5 marshmallows, 4 pieces of chocolate, and 6 graham crackers, you could make 3 full s'mores (with 2 extra marshmallows and 1 extra marshmallow). We combine chemical compounds in the same way!

Example: Ammonia $(\mathrm{NH_3})$ is produced when nitrogen gas $(\mathrm{N_2})$ is combined with hydrogen gas $(\mathrm{H_2})$. Write a balanced equation for this reaction, and determine how much ammonia can be produced if you start with 5 moles of hydrogen gas.

First, let's balance the reaction. We can try some coefficients by inspection and verify they satisfy conservation of mass:

$$\mathrm{N_2} + 3\mathrm{H_2} \rightarrow 2\mathrm{NH_3}$$

This balanced reaction tells us that for every three moles of H_2 gas, we can make two moles of ammonia. Therefore, if we start with 5 moles of H_2:

$$5 \text{ moles of } H_2 \times \frac{2 \text{ moles of } \mathrm{NH_3}}{3 \text{ moles of } \mathrm{H_2}} = 3.33 \text{ moles of } \mathrm{NH_3}$$

Limiting reagents

If we don’t start with the right stoichiometric ratios of reagents, there might be some reactant left over after we have formed the products. If we go back to the s’mores example, we were able to make three full s’mores, with extra chocolate and marshmallow. Since all of the graham crackers were used before the other reactants, they are the *limiting reagent*. The limiting reagent is specific to the initial amount of reactants available.

Example: The Kroll process for making titanium metal out of titanium chloride is:

$$\mathrm{TiCl_4 + Mg \rightarrow MgCL_2 + Ti}$$

You react 25 kg of Mg with 200 kg of $\mathrm{TiCl_4}$.

a) Balance the reaction, b) determine the limiting reagent, and c) determine the yield of Ti in this reaction.

Answer

a) To balance the reaction, we can start by looking at the Cl atoms: we need to double the $\mathrm{MgCl_2}$ on the right to equal the left. Then, we just need to balance the Mg atoms: we need double on the right to account for the extra we just created on the left. The balanced reaction is therefore

$$\mathrm{TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti}$$

b) To find the limiting reagent, we need to find the molar mass of the reactants:

$$\mathrm{TiCl_4} : 47.87 + 4 \times 25.45 = 189.7\ \mathrm{g/mol}$$
$$Mg : 24.3\ \mathrm{g/mol}$$

Next, we can convert from grams to moles:

$$200\ \mathrm{kgTiCl_4} \times \frac{1000\ \mathrm{gTiCl_4}}{1\ \mathrm{kgTiCl}l_4} \times \frac{1\ \mathrm{molTiCl_4}}{189.7\ \mathrm{gTiCl}l_4} = 1054\ \mathrm{molTiCl_4}$$
$$15\ \mathrm{kgMg} \times \frac{1000\ \mathrm{gMg}}{1\ \mathrm{kgMg}} \times \frac{1\ \mathrm{molMg}}{24.3\ \mathrm{gMg}} = 1029\ \mathrm{molMg}$$

The balanced reaction tells us we need twice as many moles of magnesium as moles of titanium chloride. We don't have enough Mg to react with all of the $\mathrm{TiCl_4}$, so Mg is the limiting reagent.

c) The yield is determined by the initial amount of the limiting reagent. The balanced reaction tells us we get two moles of $Mg\mathrm{Cl_2}$ and 1 mole of Ti per mole of Mg we react, so the yield is

$$1029\ \mathrm{molMg} \times \frac{1\ \mathrm{molTi}}{2\ \mathrm{molMg}} \times \frac{47.87\ \mathrm{gTi}}{1\ \mathrm{molTi}} = 24.7\ \mathrm{kg\ of\ Ti}$$

6.2: Avogadro and Moles, Periodic Table, Isotopes, and Combustion

Avogadro and moles

When balancing a reaction or determining its yield, it was really important to keep track of the number of each kind of atom before and after the reaction. Atoms can be difficult to account for in real life due to their minuscule size. Instead, we usually keep track in *moles* : a mole consists of Avogadro's number of atoms (or molecules), or 6.022×10^{23} atoms or molecules per mole.

Critically, we can convert from moles to a value that is easy to measure in a lab: mass. The *molar mass* of a a substance is defined to be the number of grams in one mole of that substance. The molar mass of a single element is also called the atomic mass; the molar mass of a compound can be obtained by summing the molar mass of the constituent elements.

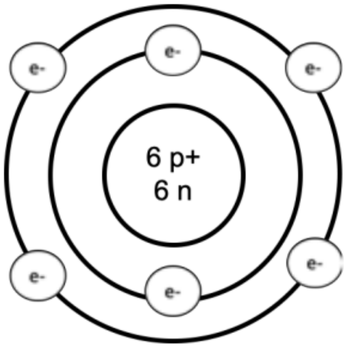
Example: How many moles of nickel are in 102 g of nickel? How many moles of H_2O are in 50 g of water?

$$102 \text{ gNi} \times \frac{1 \text{ molNi}}{58.69 \text{ gNi}} = 1.74 \text{ molNi}$$

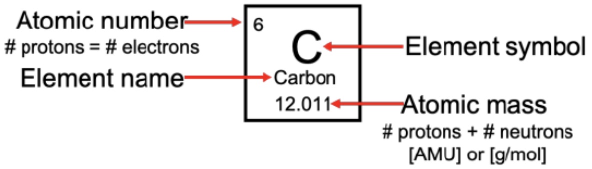
$$50 \text{ gH}_2\text{O} \times \frac{1 \text{ molH}_2\text{O}}{(15.999 + 2 \times 1.0107)\text{gH}_2\text{O}} = 2.77 \text{ molH}_2\text{O}$$

Periodic table

The periodic table is our key to solving problems! It contains a wealth of information that we can use to understand and calculate the properties of materials. The elements are organized by the number of protons: the rows are called *periods*, and the columns are called *groups*. Atoms are made up of positively charged protons, neutral neutrons, and negatively charged electrons. Protons and neutrons live at the center of the atom: together, these are the main source of mass. Electrons orbit around the protons and neutrons (more on this later). An example Bohr model of carbon is shown here:



We can read off many properties of atoms from the periodic table: An atom has the same number of protons and electrons. The atomic mass is the sum of the number of protons and neutrons: it is the average mass of one atom of each element. The units of atomic mass are AMU (atomic mass units, $= 1/12$ the mass of a carbon-12 isotope), or equivalently (due to a convenient convention), the number of grams in a mole of a substance.



Isotopes

You may have noticed that the atomic masses on the periodic table aren't integers, even though the number of protons + neutrons must be an integer. The number represented as atomic mass is really the *average* atomic mass, where a weighted average is taken over the possible isotopes of an atom. An *isotope* is an atom that has a few extra (or missing) neutrons, and therefore a different atomic mass. Isotopes are usually written like this:

$$^{A}_{Z}X$$

Here, X is the element symbol, Z is the atomic number, and A is the atomic mass. The number of neutrons in the isotope is just

$$\#\text{ neutrons } = A - Z$$

Example: Complete the following table:

Isotope	Abundance	Atomic mass (amu)
$^{28}\mathrm{Si}$	92.18%	28
$^{29}\mathrm{Si}$	?	29
$^{x}\mathrm{Si}$	3.12%	?

From the periodic table, the average atomic mass of silicon is $28.0855\,\mathrm{amu}$. First, we can solve for the percentage of ^{29}Si by using the fact that the total abundance must sum to 100%:

$$\begin{gathered}100\% = 92.18\% + 3.12\% + y \\ y = 4.71\%\end{gathered}$$

Then, we can use a weighted average to calculate the atomic mass and determine what the third isotope is:

$$\begin{gathered}28.0855 = 0.9218 \times (28amu) + 0.0471 \times (29amu) + 0.0312x \\ x = 30\end{gathered}$$

Combustion

A combustion reaction occurs when a substance reacts with oxygen gas, producing light and heat.

Example: If you put 400 g of sugar (glucose) into a 1 m^3 box, light it on fire, and quickly seal the box, would there be enough oxygen to completely combust the sugar? Write a balanced reaction; determine the limiting reagent and yield.

> *Density of air:* $1.225\ \mathrm{g/L} = 1.225\ \mathrm{kg/m^3}$
> *Oxygen weight percentage in air:* 23.2%
> *Chemical formula of glucose:* $\mathrm{C_6H_{12}O_6}$

We can try to match the number of moles in the glucose by adjusting the coefficients on the right side. This gives the right number of C and H. Finally, we can adjust the coefficient on the oxygen to get a balanced reaction:

$$\mathrm{C_6H_{12}O_6} + 6\mathrm{O_2} \rightarrow 6\mathrm{CO_2} + 6\mathrm{H_2O}$$

To determine the limiting reagent, we need to figure out how many moles of each reactant we have:

$$400\text{ g glucose} \times \frac{1\text{ mol glucose}}{(6 \times 12.0107 + 12 \times 1.01 + 6 \times 15.999)\text{ g glucose}} = 2.22\text{ mol glucose}$$

Next, we need to determine how much oxygen is in the box:

$$1m^3\text{ air } \times \frac{1.225\text{ kg air}}{1m^3\text{ air}} \times \frac{1000g}{kg} \times 0.232 \times \frac{1\text{ mol oxygen}}{2 \times 15.999\text{ g oxygen}} = 8.88\text{ mol oxygen}$$

where the multiplication by 0.232 to account for the fact that air is 23.2% oxygen.

We need 6 times as much oxygen as glucose to fully react, and $6.66/2.22 \leq 6$, so oxygen is the limiting reagent. We can use the limiting reagent to calculate the yield:

$$8.88\text{ gO}_2 \times \frac{1\text{ molH}_2\text{O}}{1\text{ molO}_2} \times \frac{(2 \times 1.01 + 15.999)\text{gH}_2\text{O}}{1\text{ molH}_2\text{O}} = 158.8\text{ gH}_2\text{O}$$

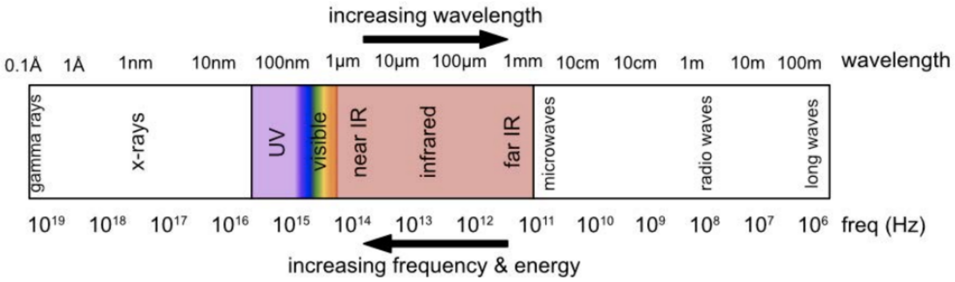
6.3: Waves, Photons, and Bohr Model

Waves and photons

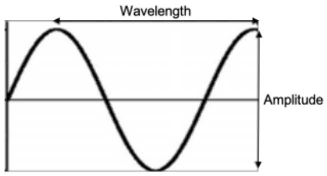
Photons are quanta of light: the energy of a photon with frequency ν (or wavelength λ) is given by the Planck-Einstein relation.

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

Here, h is Planck's constant, and c is the speed of light. The electromagnetic spectrum is shown here:



Recall that the equality above came from the fact that frequency and wavelength are related through the speed of light as $c = \lambda\nu$. It's also important to remember that the energy of a photon is independent of the amplitude of the wave:



The energy is set by the wavelength (or equivalently, frequency); the amplitude of the wave is related to its intensity: this can be thought of as the number of photons of a certain energy.

Example: A radio station broadcasts at $100.7 \mathrm{MHz}$ with a power output of $50 \mathrm{~kW}$. How many photons are emitted each second? Recall that $1W = 1J/s$.

The energy per second that leaves the radio station is

$$50 \mathrm{~kW} \times \frac{1000 \mathrm{~W}}{1 \mathrm{~kW}} \times \frac{1 \mathrm{~J/s}}{1 \mathrm{~W}} = 5 \times 10^{4} \mathrm{~J/s}$$

We can calculate the energy per photon with the Planck-Einstein relation:

$$E = h\nu = \left(6.626 \times 10^{-34} \mathrm{~J}^{*} \mathrm{~s}\right) \times \left(100.7 \times 10^{6} \mathrm{~s}^{-1}\right) = 6.672 \times 10^{-26} \mathrm{~J/ photon}$$

Finally, the number of photons per second is

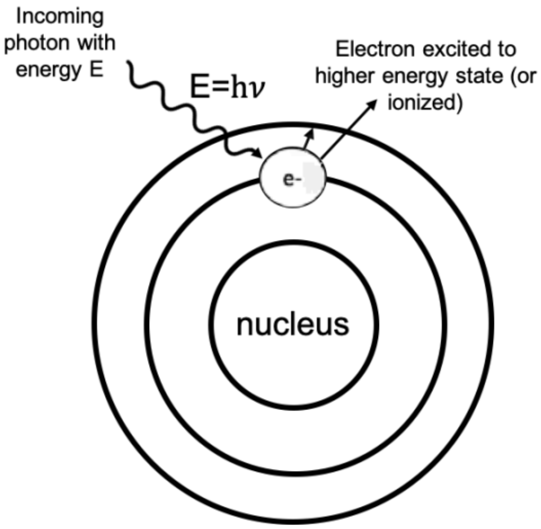
$$N = \left(5 \times 10^{-4} \mathrm{~J/s}\right) \frac{1 \text{ photon}}{6.672 \times 10^{-26} \mathrm{~J}} = 7 \times 10^{29} \text{ photons } / \mathrm{s}$$

Bohr model

The *photoelectric effect* tells us that shining light with enough energy on an atom can cause the emission of electrons. In 3.091, we'll use the Bohr model to model this process. In the Bohr model, an electron in a hydrogen atom can only live in discrete energy levels, which we label with n. The lowest energy level is the ground state, with $n = 1$. The change in energy corresponding to the transition from an initial energy level, n_i to a final energy level, n_f is given by

$$\Delta E = -13.6\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)[eV]$$

If a photon with just the right energy impinges on the atom, the photon can be absorbed and the electron excited to a higher energy level.



Conversely, if an electron relaxes from a higher energy level to a lower one within the atom, a photon with frequency $\nu = \Delta E/h$ is released.

Example: A power source emits 8×10^{18} photons/s at $10\ \mathrm{W}$. Determine how much energy each photon has. Then, calculate what state an electron in the ground state of a hydrogen atom would end up in if excited by a photon with this energy.

To calculate the energy of each photon, we can use dimensional analysis to get to Joules:

$$E = \frac{10\ \mathrm{J/s}}{5\times10^{18}\ \text{photons}\ /\mathrm{s}} \times \frac{1\mathrm{eV}}{1.6\times10^{-19}\ \mathrm{J}} = 12.5\mathrm{eV}$$

If the electron starts in the ground state, we need to solve

$$\Delta E = 12.5\mathrm{eV} = -13.6\mathrm{eV}\left(\frac{1}{n_f^2} - \frac{1}{1^2}\right) \qquad n_f = 3.51$$

Since the electron must live in an integer state, it must either go to the third or fourth level. It would take more energy than we have to get to the fourth energy level, the highest accessible energy level is $n = 3$.

6.4: Energy, Frequency, Wavelength, and Ionization

Energy, Frequency, and Wavelength

Last time, we discussed electromagnetic waves and how light is quantized as photons. We related the energy of a photon to its frequency and wavelength using the Planck-Einstein relation:

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

In 3.091, the most common units we will use for energy are joules (J) or electron volts (eV). A joule is equivalent to a $\mathrm{kg} \times \frac{\mathrm{m}^2}{\mathrm{s}^2}$, which is like a force integrated over a distance. Electron volts are also a unit of energy, but they are much smaller than a joule. An eV is literally the charge of one electron multiplied by one volt! We can convert between joules and electron volts using

$$1\mathrm{eV} = 1.6022 \times 10^{-19}\ \mathrm{J}$$

Depending on the problem, it may be easier to work in J or eV. Either one works - double checking how your units work out is a great way to check your answer.

The units of frequency (ν) are $1/s$, or equivalently, $\mathrm{Hertz}(\mathrm{Hz}$, and the wavelength (λ) has units of m. Now, we can consider the speed of light, c. Last time, we said $c = \lambda\nu$: using the units above, we see that the speed has units m/s as it should!

Frequently, we will use units like nanometers (nm) or microns (μm) for small length scales: these can be converted to meters using the following conversion factors:

$$1\ \mathrm{nm} = 10^{-9}\ \mathrm{m}$$
$$1\mu\mathrm{m} = 10^{-6}\ \mathrm{m}$$

The last piece of the Planck-Einstein relation is the h : Planck's constant! Planck's constant is

$$h = 6.626 \times 10^{-34}\mathrm{Js} = 4.136 \times 10^{-15}\mathrm{eVs}$$

It is important that you use the version of h with the units of energy in a problem!

Example: What is the energy and wavelength of light that has a frequency of $440\mathrm{THz}$?

$$E = h\nu = \left(4.136 \times 10^{-15}\mathrm{eVs}\right)(440\mathrm{THz})\left(\frac{10^{12}\ \mathrm{Hz}}{1\mathrm{THz}}\right) = 1.82\mathrm{eV}$$
$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{8}\ \mathrm{m/s}}{440 \times 10^{9} 1/\mathrm{s}} = 6.81 \times 10^{-7}\ \mathrm{m} = 681\ \mathrm{nm}$$

Ionization

If a photon with sufficient energy is absorbed by an atom, the atom can become *ionized* : it loses an electron! In fact, when we discussed Bohr's model, the factor $-13.6\mathrm{eV}$ is actually the *first ionization energy* of the hydrogen atom! That means it takes $13.6\mathrm{eV}$ of energy to ionize an electron in the ground state- that is, to excite an atom in the $\mathrm{n} = 1$ state so much it leaves the atom. The final energy state of a Bohr model electron that is ionized can be thought of as the limit as $n_f \rightarrow \infty$:

$$\Delta E_{\text{ionize}} = \lim_{n_f \rightarrow \infty}(-13.6[\mathrm{eV}])\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = \frac{13.6\mathrm{eV}}{n_i^2}$$

Example: A photon with a wavelength of $4.5\mu\mathrm{m}$ strikes a hydrogen atom with an electron in an unknown energy level. The electron is then ejected from the atom, and flies through space. Determine a) the minimum energy state the electron could have been in, and how much energy would have been leftover, b) the velocity of the electron right when it leaves. Then, c) assume a beam of $4.5\mu\mathrm{m}$ light shines on many hydrogen atoms in the state you determined in part a). If the beam power is $25\ \mathrm{mW}$, how many photons are ejected each second?

Answer

a)

$$\begin{aligned} E_{\text{photon}} &= \frac{hc}{\lambda} = \frac{\left(4.14\times 10^{-15}\text{eVs}\right)\left(3\times 10^{8}\ \text{m/s}\right)}{4.5\times 10^{-6}\ \text{m}} = 0.2757\text{eV} \\ E_{\text{photon}} &= -13.6\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right) = 13.6\text{eV}\left(\frac{1}{n_i^2}\right) = 0.2757\text{eV} \end{aligned}$$

Solving this, we get $n_i = 7.02\text{eV}$. The electron would have to be just above the 7 th energy level – since it must be in an integer energy level, the lowest initial state is $n_i = 8$. The energy to ionize from the 8th energy level is

$$\Delta E_{8,\infty} = -13.6\left(-\frac{1}{8^2}\right) = 0.2125\text{eV}$$

It takes $0.2125\text{eV}$to ionize from $n_i = 8$. The remaining energy is leftover:

$$E_{\text{left}} = 0.2757\text{eV} - 0.2125\text{eV} = 0.063\text{eV}$$

The energy leftover is not absorbed by the atom, but it must go somewhere! One place it could go is to the kinetic energy of the electron that was ionized.

b) Assuming all the leftover energy becomes kinetic ene

$$E = \frac{1}{2}mv^2$$

We need to convert to Joules to get a velocity in reasonable units:

$$\begin{aligned} 0.063\text{eV}\,\frac{1.602\times 10^{-10}\ \text{J}}{1\text{eV}} &= 1.009\times 10^{-20}\ \text{J} = \frac{1}{2}\left(9.11\times 10^{-31}\ \text{kg}\right)v^2 \\ v &= 1.5\times 10^{5}\ \text{m/s} \end{aligned}$$

c) First, let's break down the beam power:

$$25\ \text{mW}\left(\frac{1\ \text{W}}{1000\ \text{mW}}\right)\left(\frac{1\ \text{J/s}}{1\ \text{W}}\right) = 0.025\ \text{J/s}$$

We can then solve for the energy of each photon in joules:

$$\begin{aligned} E = \frac{hc}{\lambda} &= \frac{\left(6.626\times 10^{-34}\text{Js}\right)\left(3\times 10^{8}\ \text{m/s}\right)}{4.5\times 10^{-6}\ \text{m}} = 4.4\times 10^{-20}\ \text{J/ photon} \\ \frac{\text{photons}}{\text{s}} &= \frac{\frac{\text{J}}{\text{s}}}{\frac{\text{J}}{\text{photon}}} = \frac{0.025\ \text{J/s}}{4.4\times 10^{-20}\ \text{J/ photon}} = 5.68\times 10^{17}\ \text{photons /s} \end{aligned}$$

6.5: Quantum Numbers

Quantum numbers

Every electron localized in an atom can be described by four quantum numbers. The *Pauli Exclusion Principle* tells us that no two electrons can share the exact same set of quantum numbers

Principal quantum number

The principle quantum number, n, represents the energy level of the electron, much like the n used in the Bohr model. Energy is related to the principle quantum number by

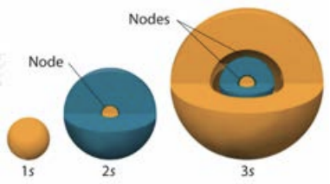
$$E = -\frac{13.6\text{eV}}{n^2}, \quad n > 0$$

Orbital angular momentum quantum number

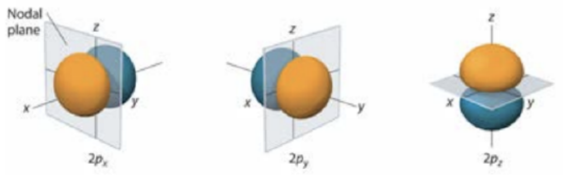
The orbital angular momentum quantum number, l, provides information about the shape of an orbital. Unlike the description of early models of the atom, electrons in atoms don't orbit around the nucleus like a planet around the sun. However, they do have *angular momentum*, and the shape of the probability cloud around the nucleus depends on the value of the angular momentum. The magnitude of the angular momentum is related to the orbital angular momentum quantum number by

$$L = \hbar\sqrt{l(l+1)}, \quad 0 \leq l \leq n-1$$

The orbital angular momentum quantum numbers correspond directly to letters commonly used by chemists to describe the orbital subshells: for example, $l = 1$ corresponds to the s orbitals, which are spherical:



$l = 2$ corresponds to the p orbitals, which are lobed: Visualizations of the higher orbitals, like the d$(l-2)$



and $f(l=3)$ can be found in Chapter 6 of the Averill textbook.

Magnetic quantum number

The magnetic quantum number, m, distinguishes the orbitals available within a subshell. The projection of the angular momentum onto the z-axis is related to the magnetic quantum number by

$$L_z = m\hbar, \quad -l \leq m \leq l$$

Spin quantum number

The spin quantum number, m_s, gives the spin angular momentum of each electron. Each electron can either be spin up or spin down. The magnitude of the spin is either $+1/2$ (spin up) or $-1/2$ (spin down). The magnitude of the angular momentum associated with spin is

$$|S| = \hbar\sqrt{s(s+1)}$$

and the spin projection onto the z-axis is given by

$$S_z = s\hbar$$

The restriction on the allowed values of spin is

$$s = \pm\frac{1}{2}$$

Example: What is the electronic configuration of carbon? Write out the quantum numbers for each electron.

Answer

Carbon has six valence electrons. We'll start filling up the quantum numbers by following the rules above. Starting with $n = 1$, the only possible value of l is $l = 0$, since $0 \leq l \leq n - 1$. When $l = 0, m$ must also be 0 . There are two possible spins that could go with these quantum numbers. There aren't any more available quantum numbers with $n = 1$, so we must go up to a higher shell. For $n = 2$, the lowest energy state corresponds to the lowest magnitude of angular momentum, $l = 0$, which again requires $m = 0$.

For the last two electrons, we have to remember Hund's rule. Every orbital in a subshell must be singly occupied with electrons of one spin before adding electrons of the other. So the $l = 1$ electrons must have different values of m, but the same value of m_s. The quantum numbers are summarized in the table below.

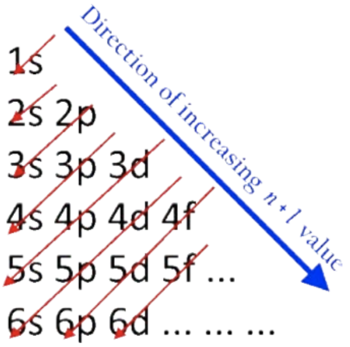
n	l	m	m_s
1	0	0	$1/2$
1	0	0	$-1/2$
2	0	0	$1/2$
2	0	0	$-1/2$
2	1	0	$1/2$
2	1	-1	$1/2$

6.6: Aufbau Principle, Electron Filling, Box Notation, and Photoelectron Spectroscopy

Aufbau principle

Quantum numbers are a handy way to account for the electrons that fill up atomic shells, but they can be tricky to keep track of. Instead, we often utilize shorthand to label the quantum numbers:

The Aufbau principle is a trick to keep track of the order each subshell is filled in:



The superscript after each subshell indicates the number of electrons in the subshell: each should be full except for the outermost shell, which is filled based on the number of valence electrons.

Example: Write down both the full electronic configuration and the noble gas notation of Br.

Br has 35 valence electrons, so we can fill up all the way to Argon. The full configuration, which mostly follows Aufbau, is

$$1\,\mathrm{s}^2 2\,\mathrm{s}^2 2\mathrm{p}^6 3\,\mathrm{s}^2 3\mathrm{p}^6 3\,\mathrm{d}^{10} 4\,\mathrm{s}^2 4\mathrm{p}^5$$

Note here that the $3\,\mathrm{d}^{10}$ and $4\,\mathrm{s}^2$ occur in an unexpected order: there are some exceptions to the Aufbau principle. We don't expect you to memorize these exceptions for 3.091, but know that they are noted in the periodic table! The noble gas configuration just shows the electrons beyond the last full shell:

$$[\mathrm{Ar}] 3\,\mathrm{d}^{10} 4\,\mathrm{s}^2 4\mathrm{p}^5$$

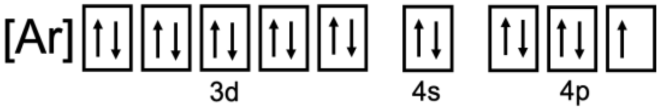
Electron filling and box notation

We can note the configuration and orientation of the electrons visually using box notation. It’s usually easiest to use the Aufbau principle (or the periodic table!) to write down the electronic configuration and then translate it to box notation. It’s important to recall *Hund’s rule* : every orbital in a subshell must be singly occupied before any orbital is doubly occupied.

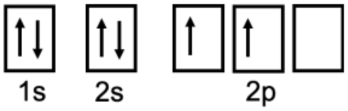
Example: Draw the electronic configuration of Br and C in box notation.

Answer

We wrote the noble gas configuration above, so we can just give the box notation of the valence electrons here:



For carbon, the electronic configuration is $1s^2 2s^2 2p^2$. In box notation, we fill up the $1s$ and $2s$ states, and populate the $2p$ according to Hund's rule:



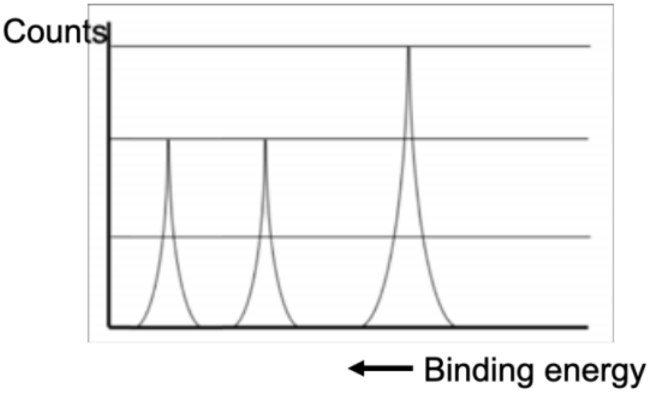
Photoelectron spectroscopy (PES)

Photoelectron spectroscopy (PES) is an experimental method used to determine electronic structure. First, a sample is bombarded with high energy photons to ionize the atoms. Then, the kinetic energy of the electrons that are emitted is measured. The binding energy can be determined using

$$E_{binding} = h\nu - KE_{e-}$$

By plotting the relative counts of electrons emitted with various binding energies, the elemental composition of a sample can be determined using PES!

Example: Determine which element corresponds to the following PES spectrum:



Answer

On this plot, the binding energy increases to the *left*. The electrons closer to the nucleus should have the highest binding energy, so the left-most peak must correspond to the $1s$ electrons. The relative height of the peak corresponds to the relative frequency at which the electrons are emitted: since there are two 1s electrons, the height of the left-most peak must correspond to two electrons. The middle peak must correspond to two $2s$ electrons. Then, since the right-most peak is 1.5 times taller, it must represent 3 electrons in the $2p$ subshell. The electronic configuration for the element in this PES diagram must be $1s^2 2s^2 2p^3$, which corresponds to nitrogen.

6.7: Periodic Trends, Lewis Dot Diagrams, and Formal Charge

Periodic trends

Inside an atom, negatively-charged electrons are attracted to the positively-charged nucleus, but they repel each other. Electrons close to the nucleus can *shield* the outermost electrons from Coulomb forces between the electrons and the nucleus.

Going across a row in the periodic table, each element has one extra electron *and* one extra proton. The additional proton has a strong effect on the electrons, as the number of inner shielding electrons does not change. However, when going down a period, there are more and more shells of electrons with increasing energy and average radius from the nucleus. Therefore, atomic radius decreases from left to right across the rows of the periodic table, and increases from top to bottom.

When atoms become *ionized*, their atomic radius changes as the charge state balance changes. If an atom gains electrons to become negatively charged, it is called an anion. If an atom loses electrons to become positively charged, it is called a *cation*. Cations are typically smaller than the neutral version of the atom, while anions are typically larger. An ionic solid contains cations and anions in a ratio that maintains charge neutrality.

Example: Arrange Al, C, and Si in order of increasing atomic radius.

Answer

Carbon is in the second period of the periodic table, while Al and Si are in the third: C must be the smallest. Al is in group III, while Si is in group IV, so Al is likely larger than Si due to relatively strong effect of the extra proton Si has.

$$\text{(smallest)} \quad \mathrm{C} \rightarrow \mathrm{Si} \rightarrow \mathrm{Al} \quad \text{(largest)}$$

Lewis Dot Diagrams

Lewis dot diagrams are a tool used to visualize the valence electrons in atoms. Then, by pairing up electrons, we can visualize possible ways that bonds can be formed between two atoms.

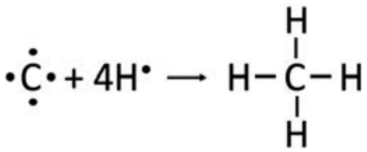
There are a couple of rules of thumb that come in handy when drawing Lewis dot diagrams. The *octet rule* tells us that atoms gain, lose, or share electrons in order to have a full valence shell of 8 electrons (2 for H and He). Also, the number of valence electrons in an atom is equal to the group number. We can generally start by following these steps:

1. Determine the number of valence electrons in each atom in the compound
2. Place a bonding pair between adjacent atoms
3. Starting from terminal atoms, add electrons to form octets

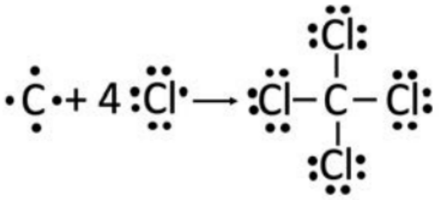
Example: Draw Lewis dot diagrams for the following compounds: $\mathrm{CH_4}$, $\mathrm{CCl_4}$, $\mathrm{CO_2}$, and $\mathrm{OH^-}$

Answer

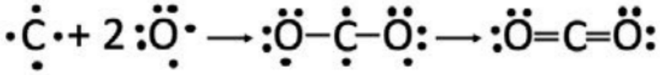
$\mathrm{CH_4}$: C has 4 valence electrons (group IV), while hydrogen just has one. Sharing four electrons between the C and H's yields an octet on the carbon atom and a complete shell of two electrons on the hydrogen. Note that it's often convenient to put the atom that has the most unpaired electrons in the middle.



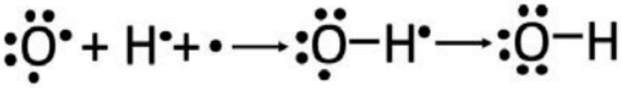
$\mathrm{CCl_4}$: Again, C has 4 valence electrons, and Cl has 7. Cl can only gain one additional electron to have a full octet, so each Cl only makes one bond. Therefore, we can put C in the middle again and surround it with Cl atoms, and every atom has a full octet.



CO_2: C has 4 valence electrons, while O has 6. We can start by placing the C in the middle and forming a bond with each O. The structure that results is unstable, because each O is left with an unpaired electron. C also has two unpaired electrons leftover. We can use them to form double bonds between the C and each O without violating the octet rule. Note that each O is left with two lone pairs.



OH^-: Here, the oxygen brings 6 valence electrons and the H brings just one, but there is an additional electron in play because of the structure's overall negative charge. After forming a single bond between the O and the H, we're left with unpaired electrons, so we need to rearrange some more. We can't make a double bond to the hydrogen, as it can only support two electrons. Moving the extra electron to the oxygen to join a lone pair does the trick.



Formal charge

Above, we discussed the steps for constructing Lewis dot diagrams: by following these rules, we can determine *stable* electronic configurations of molecules. We can also quantify this stability by calculating the *formal charge*.

$$\text{Formal Charge } = \# \text{ valence } e^{-}\text{s} - \left(N + \frac{b}{2}\right)$$

where the number of valence electrons refers to the neutral atom in isolation, $N =$ the number of nonbonding valence electrons and $b =$ the number of valence electrons participating in bonds. Formal charge should be calculated for each atom in the molecule.

Example: Determine the formal charge of CO_2.

Answer

Oxygen: the neutral oxygen atom in isolation has 6 valence electrons. Each oxygen in CO_2 has 4 nonbonding electrons and 4 electrons stored in bonds.

$$\text{Formal Charge (Oxygen) } = 6 - \left(4 + \frac{4}{2}\right) = 0$$

Carbon: the neutral carbon atom in isolation has 4 valence electrons. Each carbon in CO_2 has 8 electrons stored in bonds.

$$\text{Formal Charge (Carbon) } = 4 - \left(\frac{8}{2}\right) = 0$$

6.8: Resonance, and Formal Charge (cont.)

Resonance

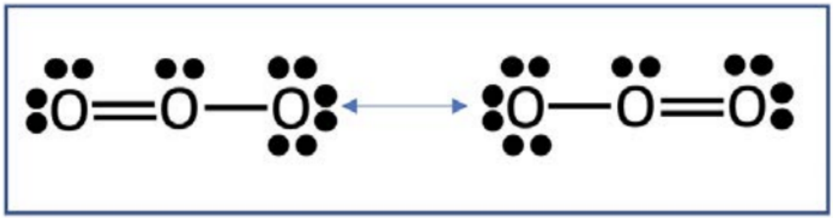
Often, there are many ways that electrons can be arranged around a molecule. The existence of multiple electronic configurations that are stable leads to *resonance*, which describes the delocalization of electrons in covalently bonded molecules. To be considered resonance structures, molecules must meet the following criteria:

1. Atoms must be in the same orientation relative to each other
2. All resonance structures must have the same number of valence electrons
3. The octet rule must be satisfied, with a few exceptions:
    - Not followed by some elements in periods three and higher, including $\mathrm{Cl}, \mathrm{Br}, \mathrm{I}, \mathrm{P}, \mathrm{Si}$
    - Sulfur can have up to $12\mathrm{e}^-$
    - Boron can have $6\mathrm{e}^-$
4. Formal charge should be on the most electronegative atoms

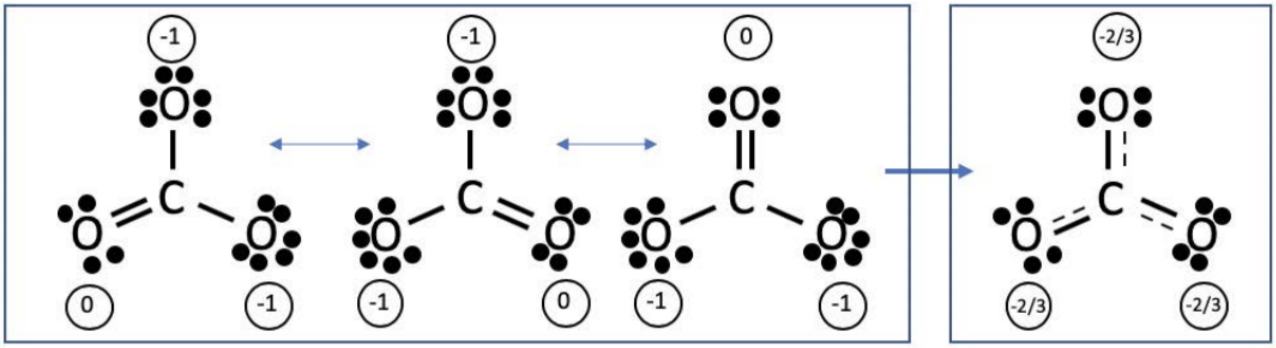
Example: Draw resonance structures for ozone (O_3) and CO_3^{2-}.

Answer

Ozone consists of three oxygen atoms, for a total of 18 valence electrons. These can be equivalently distributed in two ways:



CO_3^{2-} consists of a central carbon atom which brings 4 valence electrons, and four oxygen atoms that each bring 6 electrons, and two additional electrons that yield the additional 2^- charge. The resonance structures can be represented as follows:



These equivalent structures can be combined into one compact picture (shown above on the right) that is an average of the possible structures. All of the resonance structures are equally likely, as they equivalently satisfy the guidelines for stable Lewis structures.

Formal charge (again)

In the CO_3^{2-} example above, the formal charge on each atom is shown in circles. The formal charge only appears on the oxygen, as oxygen is more electronegative than carbon. In the average structure, the formal charge is averaged over all of the oxygen atoms. We can check that we have the most stable resonance structure by evaluating the formal charge on various options. The resonance structure with the lowest formal charge on each atom is the most stable and will occur with higher probability over other resonance structures. As a reminder, formal charge is calculated using

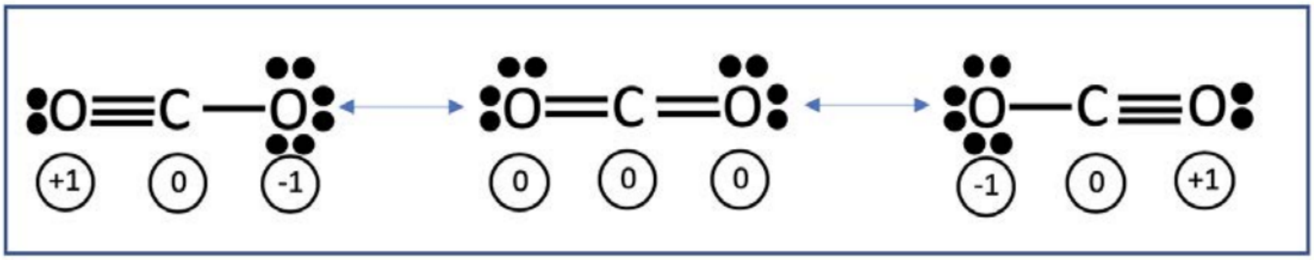
$$\text{Formal Charge} = \#\text{ valence } e^{-}\text{s} - \left(N + \frac{b}{2}\right)$$

where the number of valence electrons refers to the neutral atom in isolation, $N =$ the number of nonbonding valence electrons and $b =$ the number of valence electrons participating in bonds. Formal charge should be calculated for each atom in the molecule.

Example: Find three resonance structures of CO_2, and determine which is the most stable.

Answer

Last recitation, we drew one possible electronic structure of CO_2. Two more are given here:



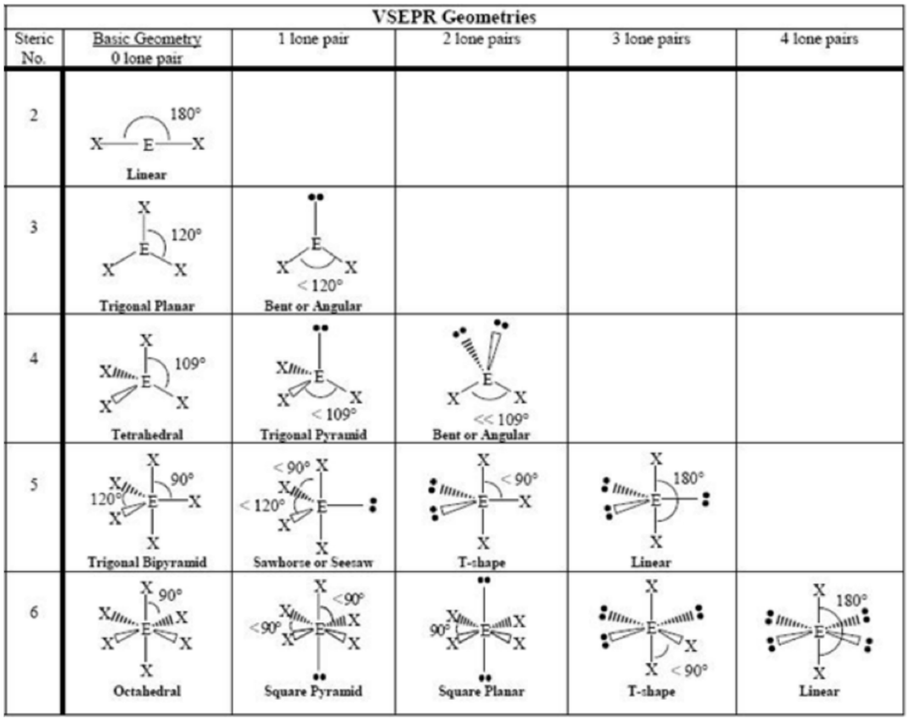
The formal charge on each atom in each of the three viable resonance structures is shown. Though each resonance structures satisfies the rules of valid Lewis dot diagrams and viable resonance structures, the central structure is the most stable as the formal charge is lowest.

6.9: VSEPR and Polarity

VSEPR

Lewis dot structures are a great tool to visualize how electrons can be arranged in molecules. Further, drawing resonance structures and determining the formal charge can help us determine which structures are most stable. However, neither of these tools provide much insight into the physical configuration of a molecule in 3D space. For this, we turn to **V**alence **S**hell **E**lectron **P**air **R**epulsion theory, or VSEPR.

Once we draw a viable Lewis structure, we can use the following chart to translate the 2D representation to a 3D geometry:



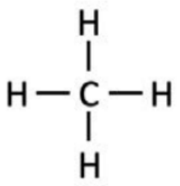
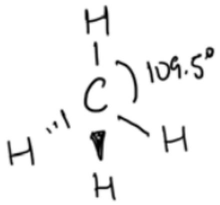
VSEPR Geometries					
Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal Planar	< 120° Bent or Angular			
4	109° Tetrahedral	< 109° Trigonal Pyramid	<< 109° Bent or Angular		
5	90° 120° Trigonal Bipyramid	< 90° < 120° Sawhorse or Seesaw	< 90° T-shape	180° Linear	
6	90° Octahedral	<90° <90° Square Pyramid	90° Square Planar	< 90° T-shape	180° Linear

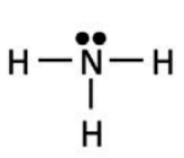
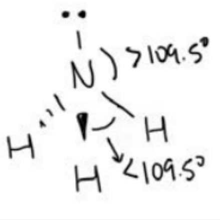
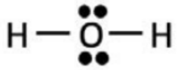
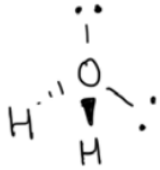
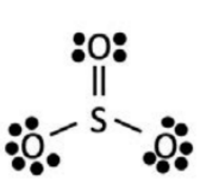
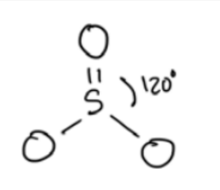
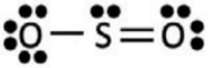
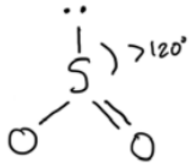
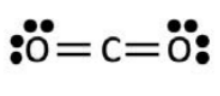
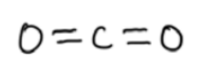
Chart courtesy of Boundless.com. License: CC BY-SA. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/fairuse.

Example: Draw Lewis dot diagrams and determine the 3D VSEPR geometry of the following molecules:

$$CH_4, NH_3, H_2O, SO_3, SO_2, CO_2$$

Answer

	Lewis dot diagram	Electrons around central atom	VESPR description	Sketch of 3D model
CH_4		- 4 groups of electrons in bonds - 0 lone pairs	tetrahedral	

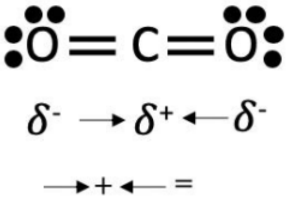
	Lewis dot diagram	Electrons around central atom	VESPR description	Sketch of 3D model
NH_3		-3 groups of electrons in bonds -1 lone pair	trigonal pyramidal	
H_2O		- 4 groups of electrons in bonds - 0 lone pairs	bent	
SO_3		- 4 groups of electrons in bonds - 0 lone pairs	trigonal planar	
SO_2		- 4 groups of electrons in bonds - 0 lone pairs	bent	
CO_2		- 4 groups of electrons - 0 lone pairs	linear	

Polarity

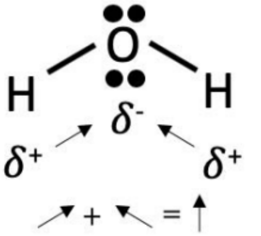
The difference in electronegativity across a molecule can generate electric dipole moments. Dipole moments are vector quantities, and by convention point from a more positive region of charge to a more negative region. If individual dipoles within a molecule cancel, there is no net dipole.

Example: Determine whether CO_2 and H_2O have a net dipole moment.

Answer



In CO_2, the two electronic dipoles are exactly opposite and cancel each other, so there isn't a net dipole. Carbon dioxide is not a polar molecule.



In H_2O, the electronic dipoles don't fully cancel, so there is a net dipole moment. Water is a polar molecule!

6.10: Hybridization, Atomic Orbitals, and Molecular Orbital Theory

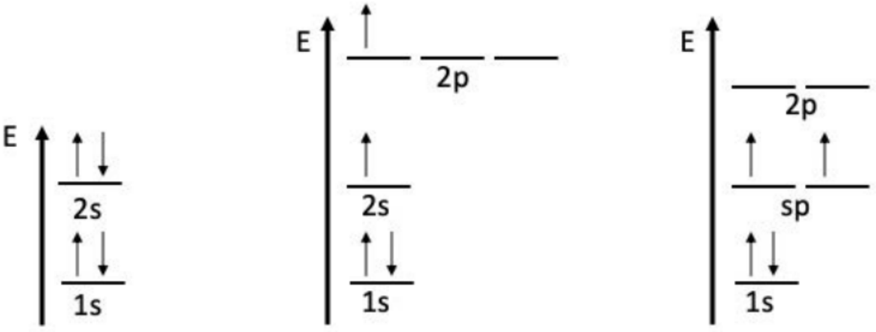
Hybridization and atomic orbitals

Lewis dot diagrams and VSEPR are powerful tools to think about electronic configuration and molecular shape, but neither tool offers a way to predict bond stability. The strength of a covalent bond is proportional to the amount of overlap between electronic orbitals.

Consider $\mathrm{BeH_2}$: beryllium contributes 2 valence electrons, and each of the two hydrogen atoms contribute one valence electron.

$$\mathrm{H-Be-H}$$

As a reminder, the electronic configuration of hydrogen is $1\,s^1$, while the electronic configuration of beryllium is $1\,s^2 2\,s^2$. The valence shell of Be $\left(2\,s^2\right)$ is full: it has two electrons, the maximum that can live in an s-orbital. There aren't any singly-occupied orbitals available to form bonds with hydrogen, even though we predict from the Lewis dot diagram above that there should be single bonds between each H and the Be. We can draw the electronic occupation of energy states in the Be atom as a function of energy, and then apply the principle of hybridization:



energy levels of Be atom $\rightarrow$ promotion $\rightarrow$ sp hybridization

To get around the issue of the full $2\,s$ shell, an electron could be promoted to the $2\,s$ subshell, leaving two electrons that are ready to form bonds. However, the $2\,s$ and $2p$ electrons aren't equal: if this were the case, the two $\mathrm{H-Be}$ bonds would be unequal, which has no physical basis. Instead, consider the third picture: by combining the $2s$ orbital with one of the $2p$ subshells, an intermediate sp-hybridized energy level is created. This sp orbital has two equal-energy subshells that allow for two equal energy bonds to be formed with the Be atom. This is not unique to $\mathrm{BeH_2}$: sp hybridization occurs any time a $2p$ subshell combines with the $2\,s$ subshell. Further, if there are more electrons available to participate in bonding, sp^2 hybridization (3 equal bonds), sp^3 hybridization (4 equal bonds), or higher order hybridization involving d-orbitals can take place.

Hybridization directly correlates to molecular geometry! The following table shows the equivalence:

Molecular geometry	Hybridization
linear	sp
trigonal	$\mathrm{sp^2}$
tetrahedral	$\mathrm{sp^3}$
trigonal bipyramidal	$\mathrm{sp^3\,d}$
octahedral	$\mathrm{sp^3\,d^2}$

Molecular orbital (MO) theory

We can use molecular orbital theory to gain a better understanding of how electrons form bonds and to predict properties such as bond stability and magnetic character. In 3.091, we'll apply MO theory to dimers. Recall that all electrons are negatively charged: in free space, electrons would feel a repulsive force from other nearby electrons. However, there are additional forces within an atom that create an environment that allows for the concentration of electron density into *bonds*. When considering how two electrons in a solid may interact, it is useful to think about wave nature of electrons. Two electrons can constructively interfere to form a *bonding* MO, or destructively interfere to form an *antibonding* MO.

MO diagrams are a convenient tool to keep track of the bonding and antibonding orbitals, and therefore the bond strength. We can quantify the bond strength by calculating *bond order:*

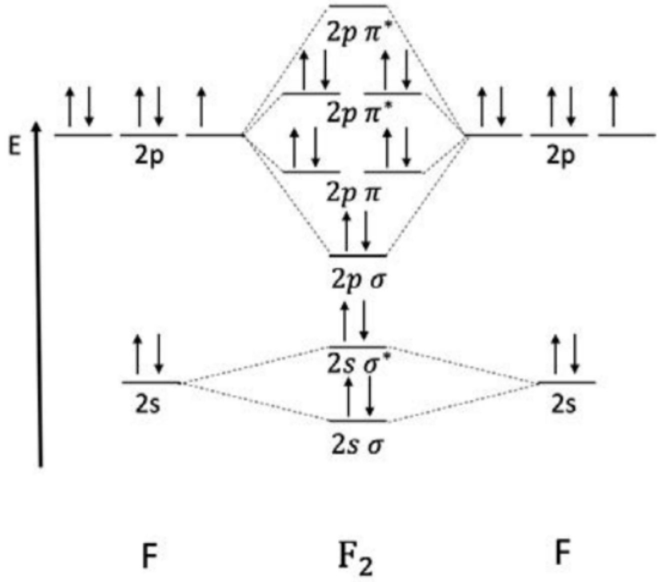
$$\text{Bond order} = \frac{1}{2}\ (\#\text{ electrons in bonding orbitals } - \#\text{ electrons in antibonding orbitals})$$

If the bond order is greater then zero, a stable dimer forms.

If a dimer has any unpaired electrons, it is *paramagnetic:* these unpaired electrons align with applied magnetic fields and are weakly attracted to the applied field. If all the electrons are paired, the dimers are repelled by applied magnetic fields, and the dimers are called *diamagnetic*.

Example: Draw a molecular orbital diagram for the F_2 dimer. Calculate the bond order, and determine whether it is paramagnetic or diamagnetic.

Answer



We start here by drawing the AO diagrams of the valence electrons of each F involved in the F_2 dimer. Recall that F (Group VII) has 7 valence electrons. Then, we populate the σ bonding and σ^* antibonding orbitals associated with the 2s valence shell. Then, we draw the 2pσ bonding, π bonding, π^* antibonding, and σ^* antibonding orbitals. Populating from the lowest energy to the highest energy, there are enough electrons to fill the $2p\pi^*$ antibonding orbitals.

We can calculate the bond order using the formula from above. There are eight electrons in bonding orbitals and six electrons in antibonding orbitals:

$$\text{bond order } = \frac{1}{2}(8-6) = 1$$

All of the electrons are paired, so the F_2 dimer is diamagnetic.

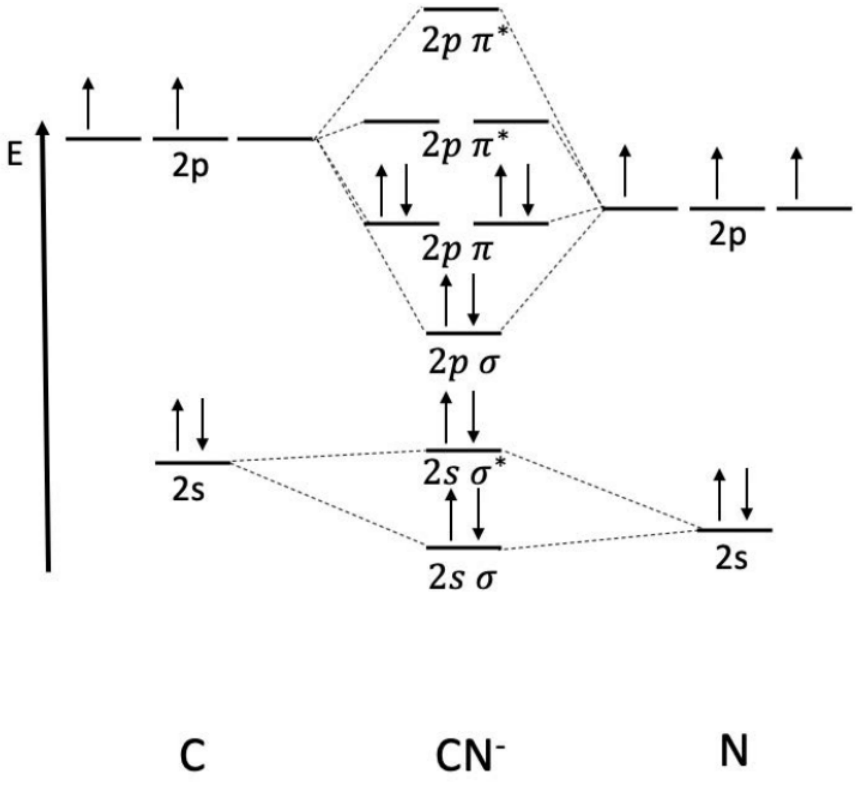
6.11: More Molecular Orbital Theory and Intermolecular Forces

More MO Theory

So far we've discussed MO diagrams with homogeneous dimers: both atoms are the same. But there can also be heterogenous dimers involving two different atoms, and these dimers can be charged! When we construct a MO diagram for a heterogeneous dimer, it is the same principle as for a homogeneous dimer: draw electronic orbital diagrams for each atom, populate the electronic states, and then fil in the sigma and pi bonding and antibonding states formed. The only difference in the case of the heterogeneous dimer is that we must consider the **relative energy** of each set of atomic orbitals. This often yields asymmetric MO diagrams. Typically, the more electronegative atom is lower in energy.

Example: Draw the MO diagram of CN^{-}. Determine the bond order.

Answer



Nitrogen is lower along the energy axis because it is more electronegative than carbon, yielding an asymmetric MO diagram. There are 8 electrons in bonding orbitals and 2 electrons in antibonding orbitals, so the bond order is

$$\text{bond order } = \frac{1}{2}(8-2) = 3$$

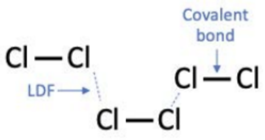
A dimer with bond order 3 is triple bonded! You may recognize this molecule as cyanide.

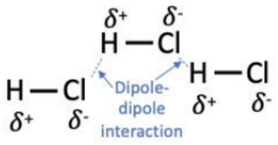
Intermolecular Forces (IMFs)

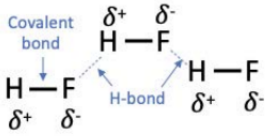
London Dispersion Forces (LDFs) exist in all molecules. As the electrons distributed across a molecule fluctuate in time, they generate small electric fields. Then, electrons in other molecules or atoms that are in close proximity rearrange in response to the generated electric fields. Molecules with more electrons experience stronger LDFs.

Dipole-dipole interactions are IMFs characterized by electrostatic force between *polar* molecules. The more polar the molecule, the stronger the interaction.

Hydrogen bonds (H-bonds) are a particular type of dipole-dipole interaction that occur in molecules with a hydrogen atom (H) bonded directly to a fluorine, oxygen, or nitrogen atom (F, O, or N).



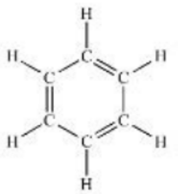




Generally, LDFs are weaker than dipole-dipole interactions, and H-bonds are strongest of all. However, there is no way to apply a one-size-fits-all classification of IMF strength, as they depend on specific molecular geometry, steric bulk (how big the molecule is), arrangement of atoms, polarity, and other factors. If a substance contains molecules with stronger IMFs, it requires more energy to break apart the molecules, which generally means that materials with stronger IMFs have higher melting points and higher boiling points.

Example: Will it H-bond? Circle the molecules that form hydrogen bonds in solution.

1



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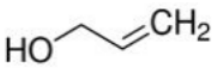

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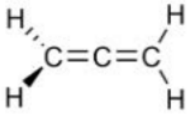

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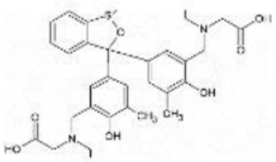

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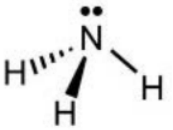


6

Answer

1. This molecule has a ring of carbons, and each carbon is also bonded to one hydrogen. There are no $H-F$, $H-O$, or $H-N$ bonds, so this molecule does not form H-bonds.

2. Here, the molecule is shown in a notation typical of organic chemistry: each vertex along the line connecting HO and CH_2 contains a carbon atom + hydrogen atoms to complete the octet, and the lines connecting the vertices represent bonds. Written another way, this molecule is $HO-CH_2-CH=CH_2$. None of the $C-H$ bonds participate in hydrogen bonding, but the HO groups will form H-bonds with the other HO groups!

3. Similar to the first one, this molecule only contains bonds between C and H atoms. It will not form H bonds.

4. There is a lot going on with this molecule. The rings here are the same sort of structure as the ring in 1: you can imagine filling in a C at each vertex and then populating with H to fill out the octets. This molecule contains N, but all of the N atoms are bonded only to C: these $N-C$ groups won't form H bonds. However, there are some OH groups: these *will* form H-bonds with the OH groups on neighboring molecules!

5. You might recognize this molecule as ammonia. Here, the N atom is directly bonded to hydrogen. These $N-H$ end groups *will* form H-bonds.

6. Finally, this hydrofluoric acid molecule is just $H-F$. Therefore, it will form H-bonds.

6.12: Band Diagrams, Semiconductors, and Doping

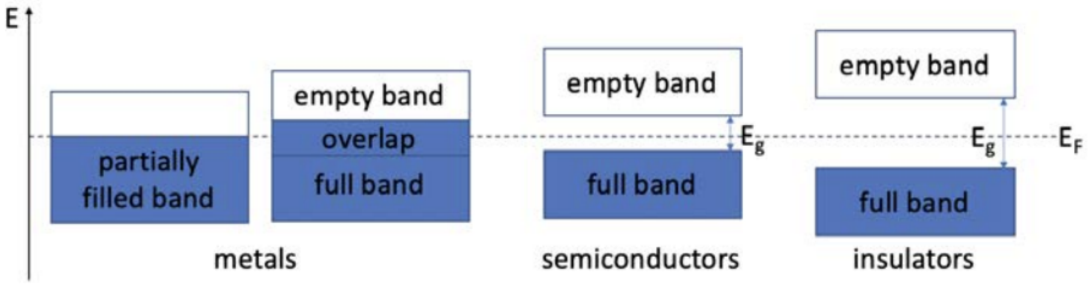
Band diagrams

As we saw for hydrogen in lecture, band diagrams can be thought of as the continuum limit of MO theory, allowing us to think about a long chain of bonds (or even a crystalline solid!) instead of just a dimer. To recap, let's imagine what building up a carbon solid - diamond- would be like. Start with just a few carbon atoms: with electronic configuration $1\,s^2 2\,s^2 2p^2$, they each bring 6 electrons, including two core electrons and four valence electrons. Remember - the core electrons live closest to the nucleus; they require the most energy to remove. The valence electrons live further away from the nucleus: these are the electrons that participate in bonding. Now, let's bring in some more atoms.

We know from previous weeks that carbon can form sp^3 hybridized bonds - these are tetrahedral, so every carbon is coordinated to bond with four other neighboring carbon atoms. The bonding happens between (hybridized) valence electrons: if we were working at $0\ \mathrm{K}$ - absolute zero temperature - we could imagine a rigid structure of nuclei and bonds. And remember, a diamond could have moles of electrons, meaning moles of bonds! The sp^3 hybridized valence electrons collectively form the valence band. Unlike a MO diagram, in which we drew one energy level for each type of bonding and antibonding orbital, the moles of electrons in a solid form distributions: all of the 1s electrons are distributed around a very low energy value, for example.

But what happens if we turn up the temperature? It turns out, several interesting things: for one, the thermal energy now available to the system allows for atoms to begin vibrating. Though the core electrons are too low in energy to be affected, some of the electrons in the tail of the valence band gain enough energy that they can *delocalize* (think back to our ionization days!), and become conducting electrons. The electrons that have been excited form the **conduction band**.

In a metal, it requires little thermal energy to excite a sea of electrons that readily carry charge (current). It happens at room temperature! This can occur in two ways: either a band is only partially full, so there are lots of states nearby in energy to be populated, or a full band overlaps with an empty band, so again it's easy for the electrons to hop between. In a semiconductor, the energy gap between the full valence band and the empty (at $0\ \mathrm{K}$) conduction band is a little bit larger: as the temperature increases, statistically, a few electrons gain enough energy to hop across the gap and conduct. Finally, in an insulator, the space between the highest full band and the lowest energy band is very large: it takes so much energy for an electron to jump to the conduction band that it doesn't happen under normal temperature and operating conditions.



Semiconductors

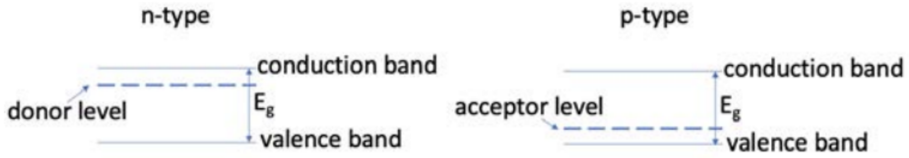
Semiconductors are defined by their name: they are kinda conductive. These materials have a *band gap*, but it’s not as big as that of an insulator. Often in the field, $3\ \mathrm{eV}$ serves as a rough cut-off: band gaps below this energy belong to semiconductors, while higher energy systems are considered insulating. Silicon is by far the most mature semiconductor technology: it is used in all sorts of applications and devices.

Semiconductors have a particularly interesting property that make them useful: they can function as transducors between electricity and light. If you shine light with sufficient energy on an semiconductor, it excites carriers inside the material: specifically, one photon excites an electron from the valance band up to the conduction band, where it is mobile. What happens to the atom that electron came from? It has essentially become electron-deficient, or ionized: it can be thought of as an extra positive charge in the valence band called a *hole*. Similar to electrons in the conduction band, holes in the valence band can move around: both carriers play a role in how conductive a material is! This is the operating principle of a solar cell: light shines on a material, and is converted into electricity. And what sets the relevant energy scale? The band gap, of course! Light with energy greater than the bandgap will be absorbed by the semiconductor and create carriers; light lower in energy than the bandgap will not be absorbed and will have no effect.

Similarly, semiconductors can transduce electricity to light as well: think of an LED! LEDs require a little more thought (and engineering) because while it’s easy for a passing photon to find an electron/hole pair to excite, it’s not quite as simple to bump an electron and a hole together so they *recombine* and emit light. The device used to engineer this process is called a PN junction.

Doping

Though we won't cover PN junction operation in 3.091, we will talk about the ingredients to make one. A PN junction is formed by stacking a p-type semiconductor next to an n-type semiconductor material. A $p-type$ semiconductor contains extra holes, while an $n-type$ semiconductor contains extra electrons. You may be wondering, extra carriers compared to *what?* A plain semiconductor material - a single material (like Si) or an alloy (like GaAs - is called *intrinsic*. The extra carriers are introduced via *doping:* adding a small fraction of a different type of atom to introduce new carriers. P-type materials are obtained by doping with atoms with fewer electrons: think doping a group IV semiconductor with group III atoms. N-type materials are obtained by doping with atoms with more electrons: think doping group IV with group V.



The extra carriers don't have quite the same energy structures as the lattice they are substituting into. Consider adding P into Si. P has 5 valence electrons, compared to 4 in a Si atom. Remember that the electronic bands in a material are really an extension of their MO diagrams: adding just one electron to an MO diagram had a drastic effect on the bonding! In the local environment of the n-type dopant, there is one too many electrons. This electron is much higher in energy than the other valence electrons: it forms a *donor level* within the band gap. The donor levels are often so close to the conduction band that thermal energy is enough to excite the extra carriers into the conduction band. Therefore, in n-type materials, the extra carriers are electron donors.

Now, consider adding Ga into Si. Ga is missing an electron compared to Si, so it creates an extra hole in the conduction band. Energetically, things would be much more favorable if there were an electron populating that site: the hole creates an *acceptor level* close to the valence band. The holes are readily excited to the valence band, where they conduct. In both of these processes, the band gap itself is unaffected by the doping: rather, the extra states within the band gap increase the carrier population at thermal equilibrium.

Example: If you dope 1 cubic meter of Ge with $2.43\mathrm{mgMg}$, how many carriers does each substitution yield and how many carriers are generated? What kind of doping is this?

Answer

We can determine how many carriers each substitution yields using the periodic table: Ge is group IV, while Mg is group II. Therefore, Ge has four valence electrons compared to Mg's two. Each substitution generates 2 extra carriers. Additionally, because we are doping with an electron-deficient material, this is p-type doping. Finally, let's set up the unit conversion to determine how many carriers are created:

$$2.43\mathrm{mgMg} \times \left(\frac{10^{-3}\ \mathrm{g}}{1\mathrm{mg}}\right)\left(\frac{1\ \mathrm{molMg}}{24.3\ \mathrm{gMg}}\right) = 10^{-4}\ \mathrm{molMg}$$

Then, since each Mg provides two holes:

$$\frac{2\ \text{holes}}{\text{Mg substitution}} \times 10^{-4}\ \mathrm{molMg} = 2 \times 10^{-4}\ \text{mol holes}$$

Finally, we can pull out Avogadro:

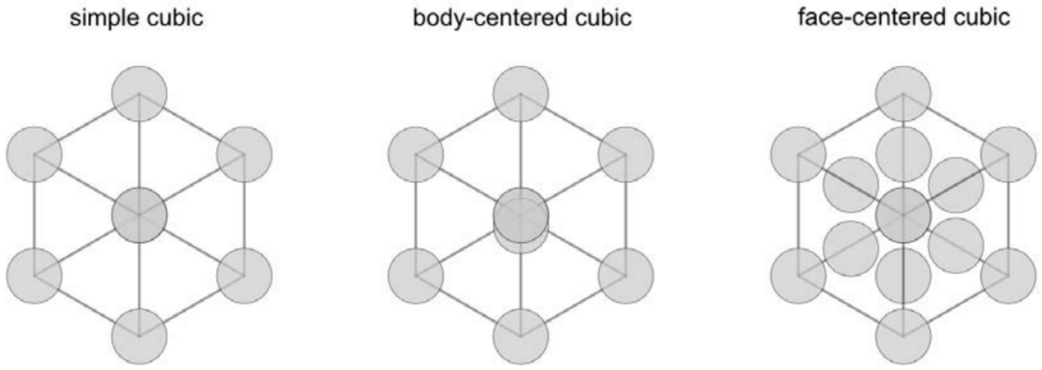
$$\left(2 \times 10^{-4}\ \text{mol holes}\right)\left(6.602 \times 10^{23}\ \frac{\text{holes}}{\text{mol holes}}\right) = 1.32 \times 10^{20}\ \text{holes}$$

6.13: Bravais Lattices and Crystal Packing

Bravais lattices

To describe a crystal you need two ingredients: a *lattice* and a *basis*. Put another way, the lattice describes how atoms are arranged spatially: in a crystal, it is a regular, ordered pattern that tiles 3D space. The basis is the unit that is copied over the pattern: it usually consists of one or more atoms. Crystallographers utilize a set of patters called *Bravais lattices* to describe the ways atoms can be arranged to form crystalline solids. In 3.091, we will focus on the subset of the Bravais lattices that are *cubic:* the scale in all three dimensions is the same.

There are three cubic lattices: simple cubic (SC), body-centered cubic (BCC), and face-centered cubic (FCC).



In the figure above, the grey grid shows the outline of the unit cell, while each circle represents an atom. For the atoms along the corners of the unit cell, each atom is shared amongst eight neighboring cells, so each cell contains $1/8$ of an atom. Similarly, each of the face atoms in the FCC unit cell are shared between two cells, so each contains $1/2$ an atom. We can calculate how many atoms are in each of the cubic unit cells:

$$N_{SC} = 8 \text{ corners} * \frac{1}{8} \text{ atoms per corner} = 1 \text{ atom per SC unit cell}$$

$$N_{BCC} = 8 \text{ corners} * \frac{1}{8} \text{ atoms per corner} + 1 \text{ central atom} = 2 \text{ atoms per BCC unit cell}$$

$$N_{FCC} = 8 \text{ corners} * \frac{1}{8} \text{ atoms per corner} + 6 \text{ face atoms} * \frac{1}{2} \text{ atoms per face} = 4 \text{ atom per } \mathrm{FCC} \text{ unit cell}$$

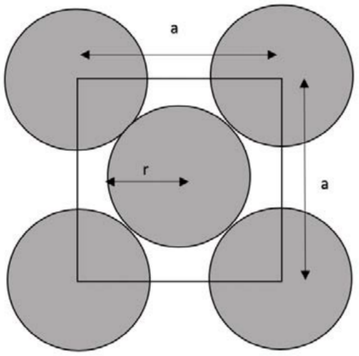
Crystal packing

We can now define some relevant metrics to describe the atomic density in different lattices and even along different directions within the crystal. We will talk about density both in terms of area and volume. To define a few terms:

- **packing density**: ratio of space occupied by atoms to total space available. Units are $\left[\frac{\text{atoms}}{nm^2}\right]$ (by area) or $\left[\frac{\text{atoms}}{nm^3}\right]$ by volume
- **atomic packing factor**: fraction of space occupied by atoms, in 2D (area ratio) or 3D (volume ratio). It is a unitless value between 0 and 1.

We also need to remember a few things from geometry: the area of a circle is πr^2, and the volume of a sphere is $\frac{4}{3}\pi r^3$. For a cubic system with side length a has face diagonal length $\sqrt{2} * a$ and body diagonal length $\sqrt{3} * a$. The trick to successfully solving packing questions is being able to relate the radius of the atoms (assuming they are hard spheres and as close packed as possible) and the side length of the unit cell. From there, it's just a bit of algebra to find the solution.

Example: Below is a section of an FCC unit cell: it is a cut-away of one face. First, find the relationship between the radius of the atoms, r, and the unit cell width, a. Then, determine how many atoms are in the $2\mathrm{D}$ unit cell. Finally, calculate the packing density of this plane (assuming $a = 3.5 \mathring{A}$), and the 2D atomic packing fraction.



Answer

First, we need to relate r to a. The easiest way to do this is usually to look along the closest packed direction: here, if we go down a diagonal, the atoms are always in contact along their center.

$$r+2r+r=\sqrt{2}*a$$

$$r=\frac{\sqrt{2}}{4}a$$

Then, we want to figure out how many atoms are enclosed in the square, 2 d unit cell. There is one full atom in the middle, and four corners which each contain $1/4$ of an atom.

$$4 \text{ corners } * \frac{1}{4} \text{ atoms per corner } +1 \text{ center atom } = 2 \text{ atoms per unit cell}$$

The packing density in two dimensions is the number of atoms per square nm. We can simply divide the number of atoms in the unit cell by the area of the unit cell:

$$\text{packing density } = \frac{2 \text{ atoms per unit cell}}{(3.5 \text{Å})^2 \text{ per unit cell}}\left(\frac{100 \text{Å}^2}{1 \text{ nm}^2}\right) \approx 16.33 \text{ atoms }/\text{nm}^2$$

The packing fraction in two dimensions is the fraction of space occupied by atoms:

$$\text{packing fraction } = \frac{\text{area occupied by atoms}}{\text{total area}} = 2[\text{ atoms } / \text{ unit cell }] * \left(\frac{\pi r^2[\text{ area per atom}]}{a^2[\text{ area per unit cell }]}\right)$$

$$= \frac{2\pi * \left(\frac{\sqrt{2}}{4}a\right)^2}{a^2} = \frac{\pi}{4} = 0.7854$$

6.14: Miller Indices and Interplanar Spacing

Miller indices

In crystallography, we use Miller indices to specify locations, directions, and planes in a crystal. Standard $\mathrm{x-y-z}$ Cartesian coordinates use a basis consisting of three orthogonal axes in three dimensions with unit length. In Miller index notation, we will rely on the lattice vectors of the unit cell as our basis. In 3.091, since we are working with cubic Bravais lattices, the crystallographic lattice vectors are all orthogonal and the same length (with the length specific to a particular solid). With this framework, we can specify an arbitrary point in terms of its projections onto the lattice vectors, much as you would with standard Cartesian coordinates:

$$\text{location } = h\vec{a_1} + k\vec{a_2} + l\vec{a_3}$$

where $\vec{a_i}$ are the unit vectors with some magnitude and direction, and the values of $h, k,$ and l specify how far to go along each lattice vector. We can express this in shorthand as (h, k, l), just like you would write an ordered pair of Cartesian coordinates! A quick note on notation: in Miller indices, the brackets and commas matter a lot! Here's a quick list of the options and what each signifies:

Notation	Representation
(h, k, l)	point
$[hkl]$	direction
$\langle hkl\rangle$	family of directions
(hkl)	plane
$\{hkl\}$	family of planes

Note that only points use commas! Finally, negative weights can be represented with a bar over the relevant number: travel in the negative $\vec{a_1}$ direction would be indicated by $[\bar{h}kl]$, for example.

Directions and planes can be specified algorithmically:

Directions

A crystalline direction is defined in the context of a unit cell, and the vector defining the direction always passes through the origin of the unit cell. The vector stretches from the origin to the location specified in terms of the lattice vectors

$$h\vec{a_1} + k\vec{a_2} + l\vec{a_3}$$

where it is our job to determine the values of $[hkl]$. To determine the crystallographic direction given a picture of a vector in a unit cell:

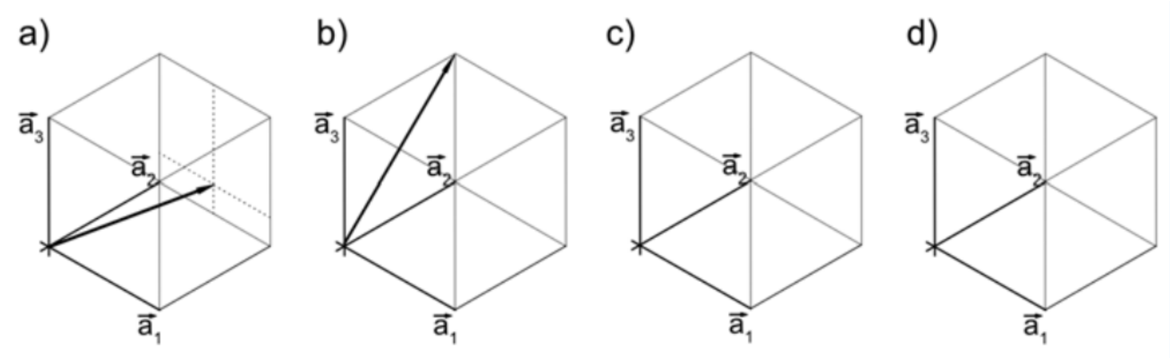
1. Shift the vector such that it intersects the origin of the unit cell (if it doesn't already)
2. Make a mark on the edge of the unit cell where the vector intersects the unit cell frame
3. Determine the fraction of each lattice vector traversed
4. Multiply the fractions by a common multiple to yield integer hkl values which define the direction

Of course you can go the other way as well, from a direction $[hkl]$ to a drawing. To represent a direction $[hkl]$ in a unit cell:

1. Divide through the vector $[hkl]$ by whichever of $h, k,$ and l is the largest to yield fractional values
2. Place the tip of the vector at the point on the edge of the unit cell defined by the fraction found previously
3. Connect the origin to the vector tip

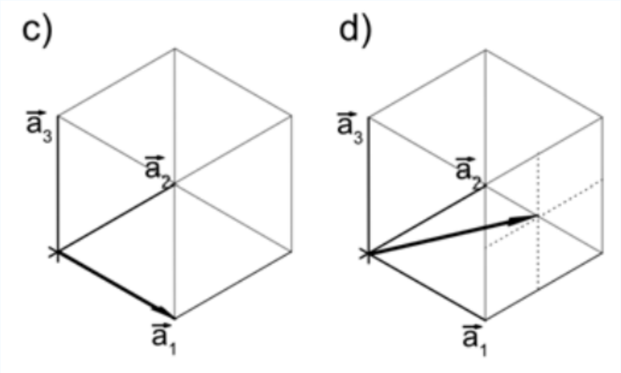
✓ Example 6.14.1

For a) and b), determine the crystallographic direction indicated on the unit cell. Then, for c) and d), sketch the direction on the axes provided. For c), sketch [100], and for d), sketch [211].



Solution

For a), we can see that the end of the vector is located at $\frac{1}{2}\vec{a_1} + 1\vec{a_2} + \frac{1}{4}a_3$. We can convert this to a crystallographic direction by multiplying through by 4 to get rid of the fractions while preserving the ratios. The direction shown in a) is therefore [241]. For b), the end of the vector is located at $1\vec{a_2} + 1\vec{a_3}$, which is represented as [011]. Finally, the [100] and [211] planes are shown below:



Planes

Similar to a crystalline direction a crystalline plane is usually represented in a unit cell, and determined in terms of the lattice vectors $\vec{a_1}$, $\vec{a_2}$, and $\vec{a_3}$. When given a picture of a plane to identify:

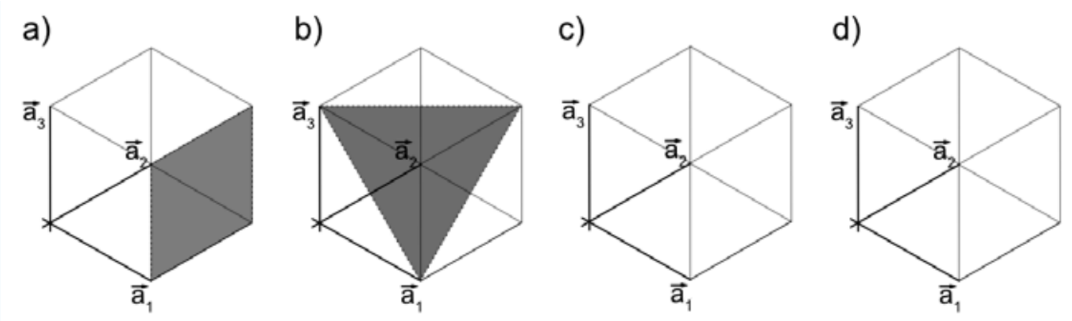
1. Make a mark on each edge of the unit cell where the plane intersects the unit cell frame
2. Determine the fraction of each lattice vector traversed. If the plane never intercepts a lattice vector, you can note it as intercepting at ∞
3. Take the reciprocal of each fractional intercept $\left(\frac{1}{\infty} = 0\right)$ to yield integer hkl values which define the plane

Finally, to sketch a plane given (hkl):

1. Find the reciprocal value of h, k, and l $\left(\frac{1}{0} = \infty\right)$
2. Mark the fractional values associated with h, k, and l on the $\vec{a_1}$, $\vec{a_2}$, and $\vec{a_3}$ axes
3. Connect the marks on the edge of the unit cell to form the plane

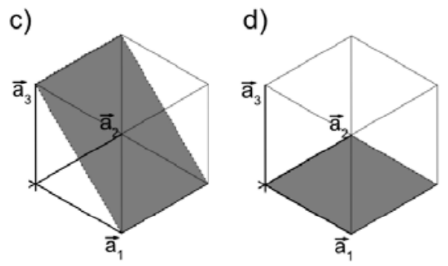
✓ Example 6.14.1

For a) and b), determine the plane shown in the unit cell. Then, for c) and d), sketch the given plane on the axes provided. For c), sketch the (101) plane. For d), sketch the (001) plane.



Solution

For a), the plane intersects $\overrightarrow{a_1}$ at the edge of the unit cell, which is 1. It is entirely parallel to $\overrightarrow{a_2}$ and $\overrightarrow{a_3}$, so we say it intercepts at ∞. Taking the reciprocals of these intercepts yields $\left(\frac{1}{1}\frac{1}{\infty}\frac{1}{\infty}\right)$, so this must be the (100) plane. For b), the plane intersects $\overrightarrow{a_1}$ at 1 and $\overrightarrow{a_3}$ at 1 . If we extend the plane along the positive $\overrightarrow{a_2}$ direction, it doesn't intercept the axis. But we have to remember to consider the other half of the crystal too: if we were to extend the plane backwards, it would intercept $\overrightarrow{a_2}$ at -1. Taking reciprocals, $\left(\frac{1}{1}\frac{1}{1}\frac{1}{1}\right)$ yields the (1111) plane. Finally, the (101) and (001) planes are shown below:



You might notice that some directions and planes in the crystal look the same: the atoms are spaced the same amount. This is due to symmetry in a crystal: for example, if you look down any of the diagonals in a cubic lattice, the atoms you "see" look the same! These equivalent directions and planes are called families. For example, the $\langle 100\rangle$ family of directions includes $[100], [010], [001], [00\bar{1}], [0\bar{1}0]$ and $[00\bar{1}]$ in a cubic crystal.

Interplanar spacing

To find the distance between neighboring parallel planes, we calculate the interplanar spacing, d_{hkl}.

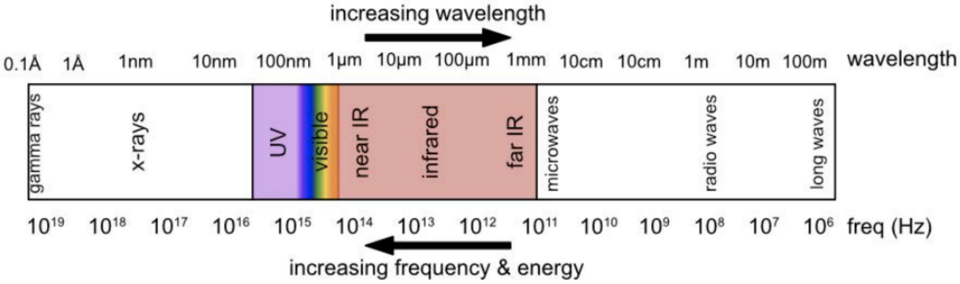
$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

Here, a is the lattice parameter, usually expressed in [nm].

6.15: X-ray Generation, Diffraction, and Bragg's Law

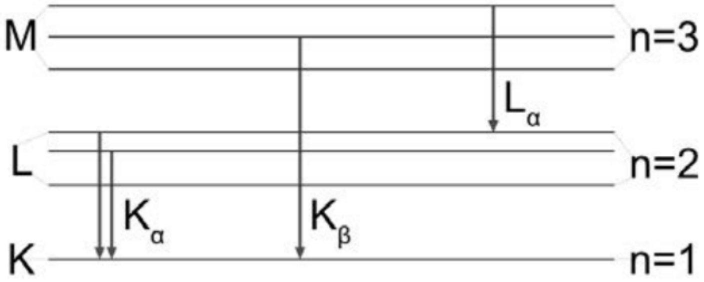
X-ray generation

X-rays are a form of high-energy electromagnetic radiation. We have talked about ways to generate EM radiation before: think back to semiconductors. The visible light emitted from LEDs has energy on the order of a few eVs. X-rays are much more energetic! They can range from hundreds to hundreds of thousands of eVs. Therefore, to generate x-rays, we need a much higher energy differential than the band gap of even an insulator.



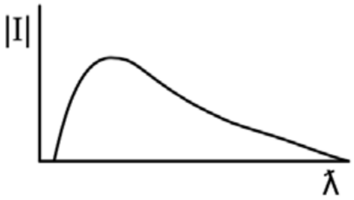
To achieve such a massive ΔE, we turn to another old friend: interatomic transitions! When we first went quantum, we talked about Bohr's model of quantization in the hydrogen atom. Though the Bohr model really only applies to the hydrogen atom, atoms with higher Z are roughly proportional to the Bohr model prediction by a factor of $(Z-1)^2$. Though the ionization energy of hydrogen was only $13.1\mathrm{eV}$, with the intra-atomic energy transitions even lower in energy, larger elements can have energy states separated by massive amounts of energy: enough to produce x-rays.

To actually generate x-rays, we need to excite an electron between two atomic energy levels within an atom. For historical reasons, the atomic transitions that produce x-rays are denoted in Siegbahn notation: the familiar our $\mathrm{n}=1, \mathrm{n}=2$, and $\mathrm{n}=3$ shells are called K, L, and M, respectively.



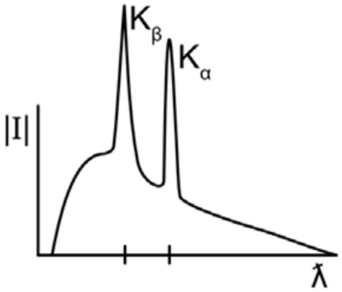
The x-rays that are emitted are named by a letter with a subscript: the letter tells us which shell the electron *ended* in, and the subscript tells us which shell the electron *started* in. For example, K_α radiation ends in the K shell $(\mathrm{n}=1)$, and the α tells us it started one shell higher, in the $\mathrm{n}=2$, or L shell. Similarly, K_β ends in the $\mathrm{n}=1$ shell, but comes from two shells up (β), or the M shell. Don't worry about the subshells; we'll just focus on transitions between principal energy levels. These x-rays are called characteristic x-rays, because their character (properties) are atom-specific.

Finally, we need to consider how this energy transition is excited. This is done with high energy electrons: the electrons are accelerated by applying high voltages. When they crash into a heavy element, x-rays are produced (if the electrons are energetic enough). The act of high-energy electrons colliding into a solid is enough to produce some x-rays: these are called Bremsstrahlung.



When the electrons collide with the solid target, they rapidly decelerate as they interact with the charged nuclei. Above all else, energy must be conserved: the excess kinetic energy dissipated through deceleration is emitted as a photon. These photons have a continuous spectrum, as shown in the plot above. However, there is a hard lower bound on the wavelength that can be emitted: since energy and wavelength are inversely proportional, this lower bound is determined by the energy of the incoming electrons (you can also think of it as an upper bound on energy/frequency).

In addition to the Bremsstrahlung, characteristic x-rays are emitted. They show up at specific wavelengths in the x-ray spectrum. We can determine which intraatomic transition the peaks correspond to by referencing the diagram above, and recalling that the energy levels get closer together as n increases.



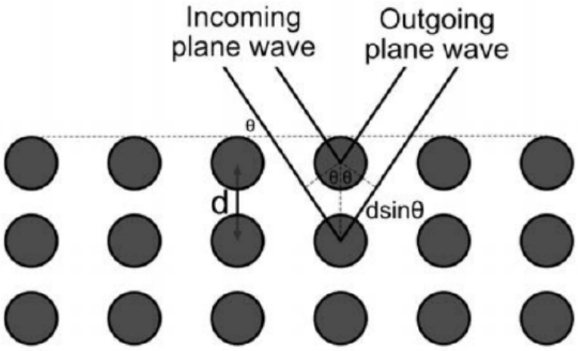
The K_β transition is larger in energy than K_α, so it occurs at a lower wavelength. The L_α would be the lowest energy (highest wavelength) of the three, and would appear to the right on this plot.

Diffraction and Bragg's Law

Next time we'll talk about what we can do with x-rays, but for now, we need to brush up on Bragg's law. The basic idea is that when light that is incident on a periodic structure satisfies the *Bragg condition*, it scatters coherently. The Bragg condition gives the angle at which coherent scattering occurs as a function of the wavelength of the incident light and the periodicity of the lattice:

$$n\lambda = 2d\sin\theta$$

This equation is the condition for constructive interference, and n is an integer ($n=1$ dominates for most lattices), λ is the wavelength of the x-rays, θ is an experimental knob, and d is the interplanar spacing, d_{hkl}.

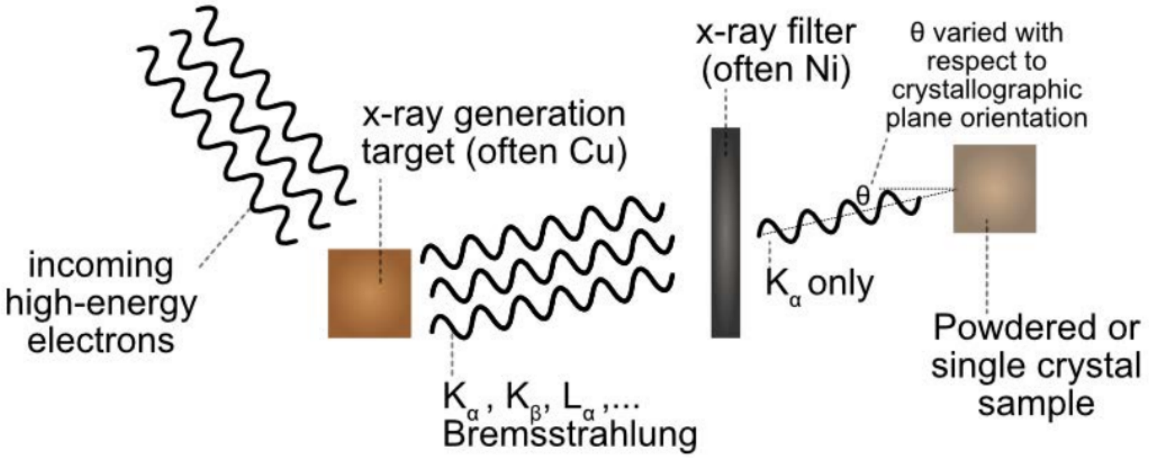


From the figure above, we can see that when the Bragg condition is fulfilled, what is actually happening is that the extra path length traveled by neighboring photons that scatter coherently is exactly $d\sin\theta$ as it comes in and again as it comes out. Therefore the incoming and outgoing waves constructively interfere, and light registers as bouncing off the crystal.

6.16: X-ray Diffraction and Selection Rules

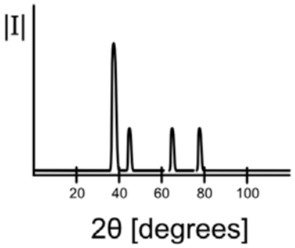
X-ray diffraction

Last time we discussed how to generate x-rays; now, let's talk about one application that plays a big role in materials characterization. X-ray diffraction is a tool that allows us to probe the crystal structure of a sample. Let's walk through the process:



First, we need to generate x-rays: this process is shown on the left. As we discussed, by shooting high energy electrons at a target made of heavy atoms (copper is a common choice), both characteristic x-rays and Bremsstrahlung are generated. Then, by bombarding an unknown sample with the x-rays, and measuring the scattered light as a function of incident angle, we can probe the interplanar spacing that exists within the crystal. However, recall that the Bragg condition is wavelength-dependent: to really do this effectively, we only want to keep a narrow band of wavelengths. This is accomplished by employing a filter, removing everything except the K_α x-rays, for example.

After all that, what is really measured in an XRD experiment is the intensity of scattered x-rays as a function of incident angle. A typical XRD spectrum looks something like this:



Plotted here is intensity/counts of x-rays on a detector as a function of 2θ, or twice the incident angle. It is helpful to utilize the following table to translate an XRD plot to a crystal structure/element:

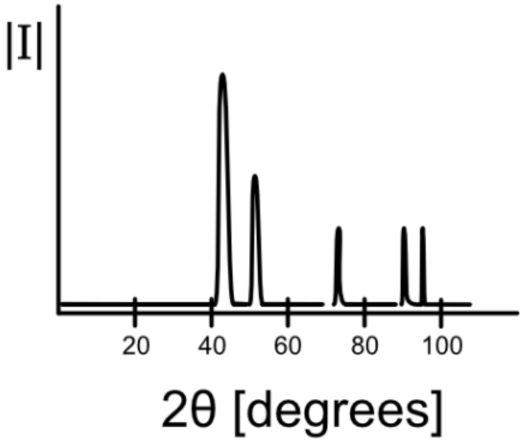
Peak #	2θ	θ	$\sin^2\theta$	normalized	integer	plane
	from graph	$\leftarrow \times \frac{1}{2}$	calculator	divide all $\leftarrow$ by $\leftarrow$ smallest of an integer	multiply $\leftarrow$ by (often 2 or 3)	$h^2+k^2+l^2=$ $\leftarrow$

Selection rules

As we discussed in lecture, we can apply selection rules to determine what kind of crystal structure a sample has. For each of the Bravais lattices, selection rules tell us which planes have coherent scattering and which do not:

Cubic crystal	Allowed planes (hkl)	Forbidden planes(hkl)
SC	any h, k, l	none
BCC	$h+k+l=$ even number	$h+k+l=$ odd number
FCC	h, k, l all even h, k, l all odd	h, k, l mixed even and odd

Example: Use the following XRD spectrum to determine the element that was investigated. It is either BCC or FCC. Copper K_α radiation was used, which has a wavelength of 1.54 Angstroms.



Peak #	2θ
1	44.51
2	51.90
3	76.45
4	93.02
5	98.50

We are given a plot and the values of 2θ, so next let's construct the chart as described above. The first two columns are given, and we can quickly calculate the next two:

Peak #	2θ	θ	$\sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434			
2	51.90	25.95	0.1915			
3	76.45	38.23	0.3829			
4	93.02	46.51	0.5263			
5	98.50	49.25	0.5739			

For the next column, normalized values, we simply divide all of the values in the $\sin^2\theta$ column by the *smallest* value in the $\sin^2\theta$ column, 0.1434

Peak #	2θ	θ	$\sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434	1		
2	51.90	25.95	0.1915	1.33		
3	76.45	38.23	0.3829	2.66		
4	93.02	46.51	0.5263	3.65		
5	98.50	49.25	0.5739	4		

Looking at the values in the normalized column, they seem to be approximately factors of $\frac{1}{3}$. To create integers, let's try multiplying each by 3 .

Peak #	2θ	θ	$\sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434	1	3	
2	51.90	25.95	0.1915	1.33	4	
3	76.45	38.23	0.3829	2.66	8	
4	93.02	46.51	0.5263	3.65	11	
5	98.50	49.25	0.5739	4	12	

Great, this created integers! The integers in this column should be the sum of h^2, k^2, and l^2 that form a particular plane. Let's try to match some planes:

Peak #	2θ	θ	$\sin^2\theta$	normalized	integer	plane
1	44.51	22.25	0.1434	1	3	(111)
2	51.90	25.95	0.1915	1.33	4	(200)
3	76.45	38.23	0.3829	2.66	8	(220)
4	93.02	46.51	0.5263	3.65	11	(311)
5	98.50	49.25	0.5739	4	12	(222)

It takes a bit of time to develop intuition as to how to combine the squares of three numbers to form integers, but it comes with practice. For now, you can double check that these (hkl) planes really do generate the integers in the neighboring column. Also note that any member of a planar family could generate the integer in question: it's ok to choose any plane within that family! For example, the (200), (020), and (002) planes all satisfy $h^2+k^2+l^2=4$, so any would work there.

Next, we should check the selection rules. We see that for each of the planes, the values of h, k, and l are either all odd or all even. Further the (111) plane is forbidden for BCC crystals, since $1+1+1=3$, which is odd. We can conclude that this must be an FCC structure!

Finally, we need to figure out which FCC element it is. We can combine some old principles to figure this out. We know the Bragg condition is

$$\lambda = 2d_{hkl}\sin\theta$$

where θ corresponds to one of the peaks above, which signify constructive interference. Recall also that the interplanar spacing is given by

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

By plugging in one of the entries from the table above, we can figure out what the lattice constant is. Let's use $\theta = 25.95$ degrees and the (200) plane:

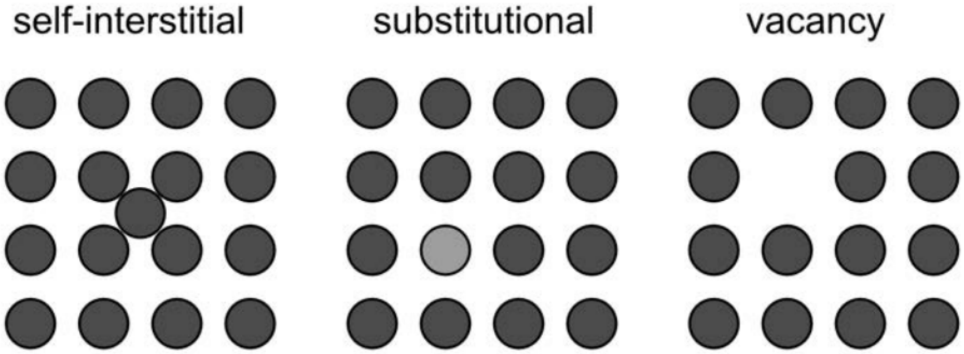
$$a = d_{hkl}\sqrt{h^2+k^2+l^2}$$
$$a = \frac{\lambda}{2\sin\theta}\sqrt{h^2+k^2+l^2}$$
$$a = \frac{1.54\text{Å}}{2 * \sin(25.95^\circ)}\sqrt{2^2+0^2+0^2} = 3.52\text{Å}$$

Looking at the periodic table, an FCC element with lattice parameter around 3.52Å is nickel!

6.17: Point Defects and Arrhenius-like Vacancy Activation

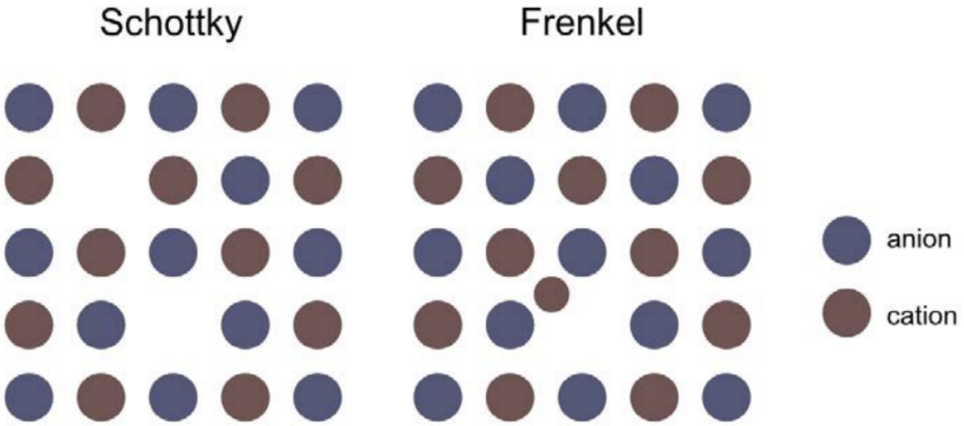
Point defects

Point defects are local, so-called zero-dimensional defects in a lattice. They consist of an atom and its immediate surroundings, no more than a few atomic layers away. In 3.091, we'll talk about three types of defects that occur in covalent solids, and two that occur in ionic solids. As a reminder, the individual atoms in a covalent solid have no charge relative to each other. The three defects are pictured below:



A *self-interstitial* occurs in crystals with atoms that are reasonably small compared to their spacing: it is sometimes possible for an atom to squeeze in between the atoms that are in their correct lattice position. A *substitutional defect* occurs when an atom in the homogeneous crystal is replaced by something else- think Ge in Si, for example. Finally, a *vacancy* occurs when one of the atoms in the crystal is missing from its standard lattice site. Remember also - though these are shown in 2D here, the real crystals they occur in are 3D Bravais lattices!

In an ionic crystal, all of the atoms have a relative charge: usually they are arranged to alternate, so the material retains both local and global charge neutrality. Therefore, it is important to account for charge neutrality when thinking about defects. Two ionic defects are shown below.



A *Schottky defect* occurs when there are two simultaneous vacancies – one anion and one cation – in close proximity. A *Frenkel defect* occurs when a cation vacancy neighbors an interstitial cation. Realistically, this occurs when a cation leaves its spot in the crystal lattice and becomes an interstitial. Recall that cations have a much smaller atomic radius than anions: it is much more practical for this sort of atomic migration to occur with a small cation than a huge anion!

Many, many defects occur in even the purest of crystals. In fact, they are entropically favorable! They can interact with each other, and even move around through the lattice in a thermally-activated process. In 3.091, it is sufficient to be able to identify them.

Example: How many oxygen vacancies are generated if you dope $\mathrm{ZrO_2}$ with 0.5 g of $\mathrm{Sc_2O_3}$?

Answer

In zirconia, each zinc is stoichiometrically matched with two oxygen atoms. Therefore, the charge on the zirconium atom must be Zr^{4+}. In scandium oxide, there are two scandium ions per three oxygen ions, so it must be coordinated as Sc^{3+}. If we dope zirconia with scandium oxide, the cations will substitute for the cations, and the oxygen will just go on oxygen sites. But each Zr^{4+} that is replaced by Sc^{3+} leaves a local charge imbalance in the lattice of one missing positive charge. This can be counteracted with oxygen vacancies in the lattice, effectively creating missing negative charge to balance things out. For every $2\mathrm{Sc}\,^{3+}$ atoms added, one V_O'' must be generated in order to maintain charge neutrality.

$$0.5\ \mathrm{gSc_2O_3}\left(\frac{1\ \mathrm{mol\ Sc_2O_3}}{137.9\ \mathrm{g}}\right)=0.0036\ \mathrm{molSc_2O_3}$$

$$0.0072\ \mathrm{mol\ Sc}^{3+}\ \text{added}\times\frac{1\ \mathrm{mol\ V}_O''}{2\ \mathrm{mol\ Sc}^{3+}}=0.0036\ \mathrm{mol\ V}_O''$$

$$\#\ \text{oxygen vacancies }=(0.0036\ \mathrm{mol\ V}_O'')\left(6.022\times 10^{23}\frac{\text{vacancies}}{\text{mol vacancies}}\right)=2.18\times 10^{21}$$

Arrhenius-like vacancy activation

Arrhenius provided a mathematical description for *thermally activated processes* which relates the rate at which a process occurs to temperature. The dependence is exponential and parameterized by energy: you can think of it as an "activation energy" to achieve a state.

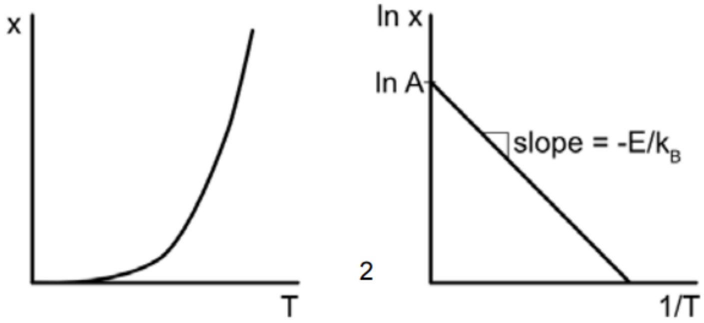
$$x\propto e^{-\frac{E_a}{k_BT}}$$

Here, E is the relevant activation energy in $[\mathrm{J}]$ or $[\mathrm{eV}]$, k_B is the Boltzmann constant (with units $[\mathrm{J/k}]$ or $[\mathrm{eV/k}]$ to match the energy), and T is temperature in Kelvin. If we call the constant of proportionality A, we can write this equation in a convenient linear form by taking the log of both sides:

$$\ln(x)=\ln\left(Ae^{-\frac{E}{k_BT}}\right)=\ln A-\frac{E}{k_BT}$$

$$\ln x=-\frac{E}{k_B}\frac{1}{T}+\ln A$$

Here we have a convenient slope-intercept form that allows us to read off the exponential rate and constant from a simple plot.



We'll come back to Arrhenius later in the course, but for now we will apply this exponential relationship to calculating the thermally-activated process of vacancy creation. Let's call the rate of vacancy formation r_{form} and the rate of vacancy annihilation $r_{destroy}$. We can describe these rates as Arrhenius processes:

$$r_{\text{form}}=A_{\text{form}}\,e^{-\frac{E_{a,\text{ form}}}{k_BT}}\qquad r_{\text{destroy}}=A_{\text{destroy}}\,e^{-\frac{E_{a,\text{ destroy}}}{k_BT}}$$

In equilibrium, the flux of vacancies that form must be equal to the flux of vacancies are destroyed. The flux of vacancies formed is simply the number of sites available to form a vacancy times the rate at which vacancies form, and the flux of vacancies destroyed is the number of sites already having a vacancy times the rate at which vacancies are destroyed. Let's say our crystal has N atoms and N_V vacancies, then in equilibrium:

$$N * r_{\text{form}} = N_V * r_{\text{destroy}}$$

$$\frac{N_V}{N} = \frac{r_{\text{form}}}{r_{\text{destroy}}} = \frac{A_{\text{form}}}{A_{\text{destroy}}} e^{-\frac{E_{\text{form}} - E_{\text{destroy}}}{k_B T^T}}$$

We can wrap the difference in formation and annihilation activation energies into a ΔE that we'll call E_V. Then finally, the fraction of vacancies as a function of temperature is

$$\frac{N_V}{N} = \frac{A_{\text{form}}}{A_{\text{destroy}}} e^{-\frac{E_V}{k_B T}}$$

Example: At room temperature (295k), a piece of Si has 3 vacancies per 10 million atoms. When it is heated to 400k, there are 15 vacancies per 10 million atoms. What is E_V?

Answer

Let’s start up by setting up the equations for the fraction of vacancies at each temperature:

$$\frac{N_{V,295}}{N} = \frac{A_{\text{form}}}{A_{\text{destroy}}} e^{-\frac{E_V}{295 * k_B}} \qquad \frac{N_{V,400}}{N} = \frac{A_{\text{form}}}{A_{\text{destroy}}} e^{-\frac{E_V}{295 * k_B}}$$

Here we essentially have two equations with two unknowns: one is E_V, the quantity we are looking for, and the other is $N\frac{A_form}{A_destroy}$, which we can treat as a constant. Here we are making an assumption that $\frac{A_form}{A_destroy}$ is temperature independent. We can divide the two equations to get rid of the constant we don't care about, and then solve for E_V:

$$\frac{\frac{N_{V,295}}{N}}{\frac{N_{V,400}}{N}} = \frac{\frac{A_{\text{form}}}{A_{\text{destroy}}}}{\frac{A_{\text{form}}}{A_{\text{destroy}}}} \frac{e^{-\frac{E_V}{295 k_B}}}{e^{-\frac{E_V}{40T}}}$$

$$\frac{N_{V,295}}{N_{V,400}} = e^{\frac{E_V}{k_B}\left(\frac{1}{400} - \frac{1}{295}\right)} = \frac{3}{15}$$

Taking the log of both sides

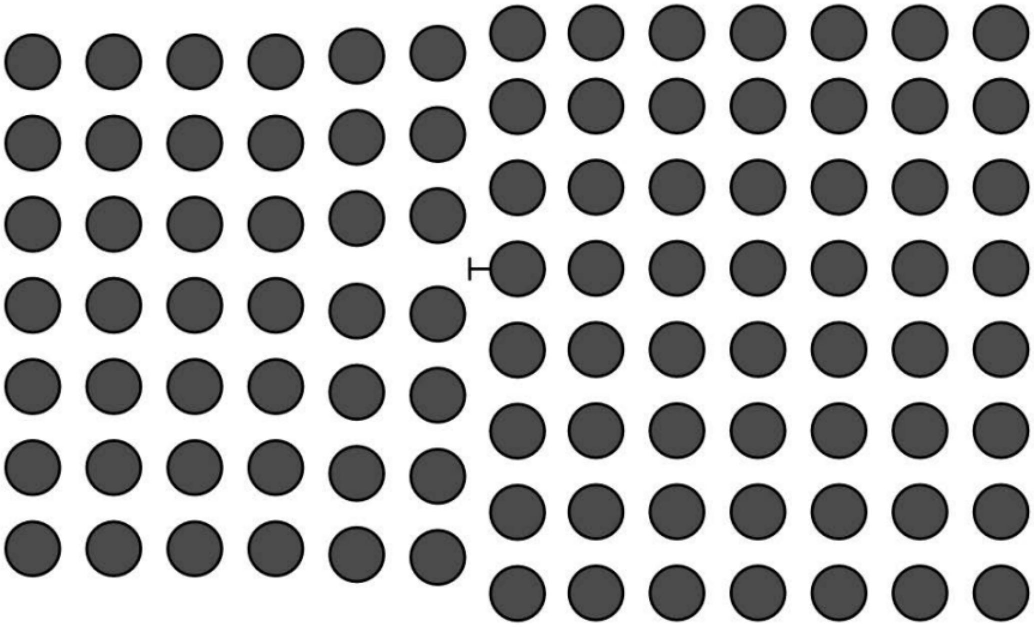
$$\ln\left(\frac{3}{15}\right) = \frac{E_V}{8.617 \times 10^{-5} \text{eV/k}} \left(\frac{1}{400} - \frac{1}{295}\right)$$

$$E_V = 0.16\text{eV}$$

6.18: Line Defects, Mechanics and Stress-strain Curves, and Slip

Line defects

In addition to point defects, crystals can have defects that cover larger areas and involve the coordination of more atoms than just one. Point defects are called 0D, or zero dimensional; in keeping with this nomenclature, line defects can be thought of as 1D defects (involving a line of atoms), and planar defects can be thought of as 2D defects (involving a plane). One important line defect is called a *dislocation*. A dislocation amounts to an extra line of atoms which persists part of the way through the crystal: the termination within the crystal is noted with a T shape as below:

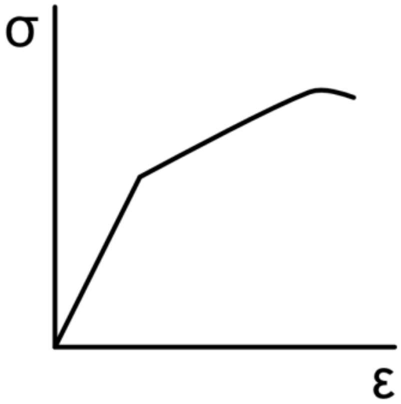


The bulk of the crystal maintains its equilibrium structure, well-aligned with the lattice. However, you can see that the region around the origin of the dislocation has been forced out of its equilibrium position in the lattice. The spacing between atoms is different around the end of the dislocation; the bonds are disrupted. It takes energy to generate a dislocation, but it also takes energy for it to move in the crystal. Therefore, even though they are not the most energetically favorable state, they are meta-stable in equilibrium once generated.

Mechanics and stress–strain curves

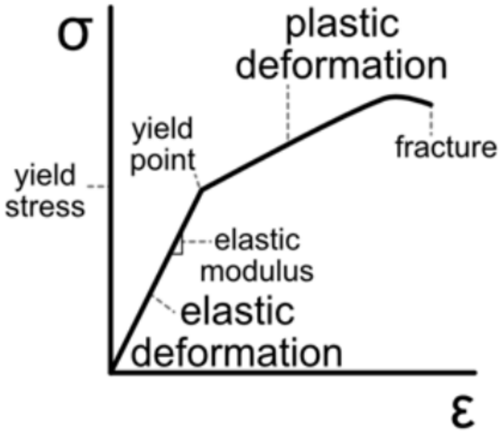
One of the most informative experiments to explore the mechanical properties of a material is generating a stress–strain curve. As we discussed in lecture, this is usually done with an Instron; the basic principle is to pull (or push) on a material in a carefully controlled way, and to measure its response.

Example: Label the plot with the following features of stress-strain curves: elastic deformation, plastic deformation, yield stress, elastic modulus, yield point, fracture



Answer

Elastic deformation refers to the linear response of a material to applied strain. This typically happens for low amounts of applied stress in crystalline materials. The slope of the stress-strain curve in the elastic region is called the *elastic modulus. Plastic deformation* refers to nonlinear strain response that is irreversible. The transition between elastic and plastic deformation is the *yield point*, and the stress at which the material yields is the *yield stress.* When the material is not able to stretch any more, it breaks: this is *fracture*. The relevant regimes are labeled below:



Slip

Even failure in crystalline materials is systematic: when significant force is applied to a material, enough to break bonds, the material can yield. Except in cases of high impact, this generally happens along *slip planes*. Slip planes are the most densely-packed planes in a lattice. Since the bond density within a slip plane is as large as it gets in the crystal, the out-of-plane density is lower: this means that fewer bonds must be broken for rows of atoms to move past each other as the material yields. As it yields, you can think of a planar face dividing sections of material forced in different directions. The directions that slip happens along are called *slip directions*, and with similar rationale, they are the most closely-packed directions in the crystal.

6.19: Glasses and Cooling Curves

Glasses

Sometimes, instead of possessing the carefully arranged crystalline bonds we've been talking about, materials end up partially or completely jumbled. In particular, elements that have flexibility in the rotational orientation of bonds can form these disordered structures, like long, interlinked chains frozen in a random orientation. We refer to these amorphous structures as *glasses*. In 3.091 we'll focus primarily on silica: a glass based on silicon dioxide.

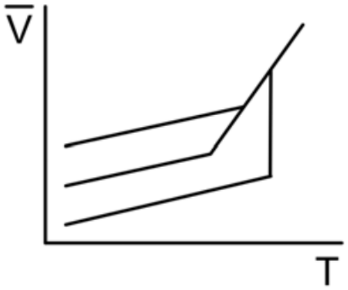
The scale from order to disorder is a spectrum. Single crystals have near-perfect order: everything is oriented the same way, and there is long-range order in the crystalline lattice. Then there are polycrystalline materials, which possess multiple crystalline regions arranged in grains. Near the grain boundaries, there are defects; the sudden change in crystal orientation can add local strain. Polycrystalline materials have short-range order, on the scale of the grains, but they lack the homogeniety of single crystals. At the other end of the spectrum are amorphous materials. These glassy materials lack any semblance of order: the complete rotational freedom of the silicon bond provides little constraint on the arrangement of bonds.

As it turns out, it is possible to control whether a melt forms a crystal or a glass by carefully engineering the cooling process. Although silica glasses are able to form, the regular structure of the crystalline lattice is still the most energetically favorable structure. In a crystal, the atoms are optimally arranged to minimize energy by balancing the Coulombic attraction between protons and electrons with the repulsion of like charges.

Cooling curves

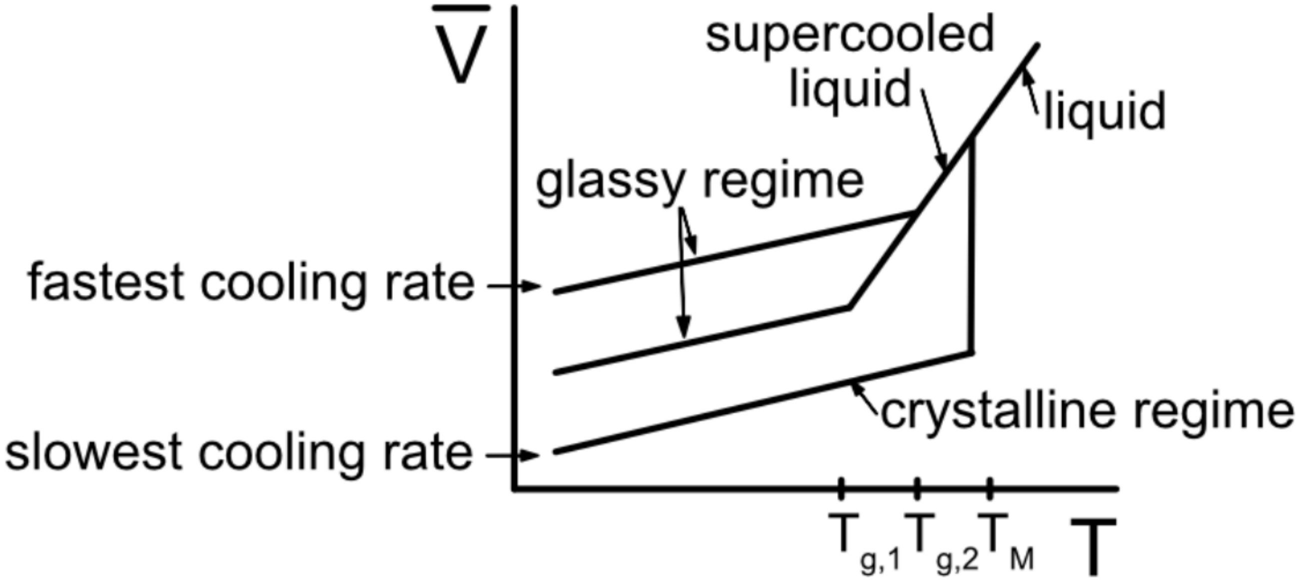
In summary, the primary knob we can turn to determine whether a melt ends up as a crystal or a glass is *processing*. One metric that allows us to keep track of the affect various processing steps have affected the melt is the *molar volume*. You can think of molar volume as a proxy for disorder. For the optimally-arranged crystal, the atoms are minimally spaced, and the molar volume is minimized. The more disordered the material becomes, the more space each atom takes up, and the larger the molar volume is! By measuring the molar volume as a function of temperature, we can compare how ordered or disordered different processing methods are.

Example: Label the plot with the following features of cooling curves: liquid, supercooled liquid, $\mathrm{T}_m, \mathrm{T}_g$, the crystalline and glassy regimes, and the curves with the fastest and slowest cooling rates



Answer

Liquid is the state of matter at high temperatures, when the material forms a melt. It has a higher slope than the solid regions because the coefficient of thermal expansion $\left(\frac{\partial \bar{V}}{\partial T}\right)$ is generally higher for liquids than solids. The melting point, T_m, can be determined by looking for a discontinuity in the plot: during the phase transition from liquid to solid involves a big change in molar volume at constant temperature. Correspondingly, the *crystalline regime* is the low temperature solid that follows the phase transition. *Supercooled liquid* is any liquid that remains at temperatures below the melting point- it has the same slope as the liquid above the melting point. The points in the supercooled liquid regime where the slope changes are the *glass transition temperatures*, T_g. Unlike the crystalline phase transition, the glass transition is continuous (but not smooth): you can think of the glass transition as just freezing the viscous liquid melt in place, as is. Remember that depending on the specifics of the processing, glasses with different T_g and different molar volumes can form. Below T_g, the glass becomes a solid: this is the *glassy regime*. Finally, it takes a long time atoms to rearrange into ordered structures, so crystals are processed with the *slowest* *cooling rates*. The glasses with the highest molar volumes are the most disordered: these melts have to freeze rapidly, and they have the *fastest cooling rates*.



Example: Which of the following samples will yield a glass with higher molar volume?

melt is very viscous	OR	melt is very fluid
melt is cooled rapidly	OR	melt is cooled slowly
equilibrium crystal structure is complex	OR	equilibrium crystal structure is simple

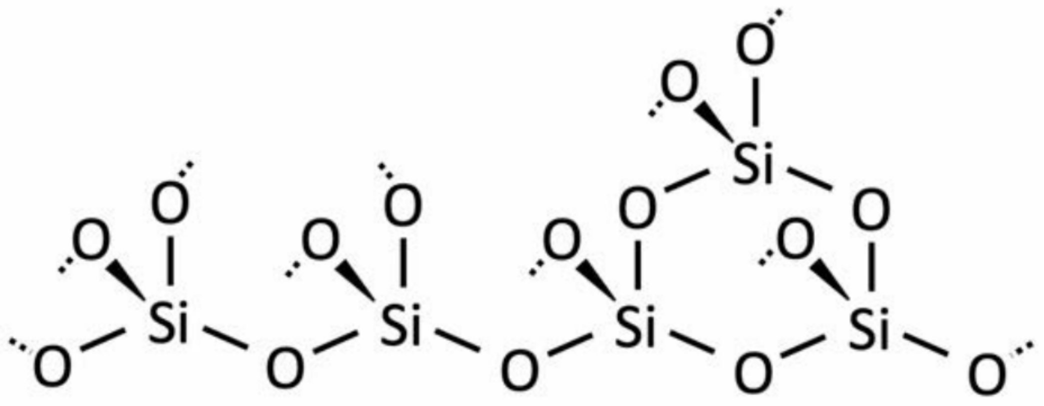
Answer

A viscous melt does not flow easily: it is more difficult for the atoms to move around than in a very fluid melt. Therefore, with all other factors held constant, **the viscous melt** should produce a glass with higher molar volume. Following the rationale from the previous section, **the melt that is cooled rapidly** will yield a glass with higher molar volume compared to a melt that is cooled slowly. Finally, if the equilibrium crystal structure formed by a melt is very complicated, it takes time for all of the atoms to make it to their optimal lattice sites. With all other factors held constant, **the melt with a more complex equilibrium crystal structure** will yield a higher molar volume glass than the melt with a simple equilibrium crystal structure.

6.20: Glass Formers and Network Modifiers

Glass formers

In 3.091, we focus on silica glass. The chemical composition of silica is SiO_2: you are now well equipped to check this compound is charge-neutral. Although the charges are balanced, if you were to draw a Lewis dot diagram for SiO_2, you might notice that there are lots of lone pairs of electrons that aren't involved in bonding. You may also recall that silicon, with its four valence electrons, typically forms tetrahedrally coordinated (or sp^3) bonds. What ends up happening when liquid silica solidifies is that oxygen atoms are shared between silicon atoms, acting like bridges: these are referred to as *bridging oxygens*. If we were to flatten crystalline silica to represent it in 2D, it might look something like this (not a true projection):



Here, the dotted lines represent half-bonds that would continue on throughout $3D$ space. Each oxygen atom is a bridging oxygen, because it is shared between adjacent silicon atoms. Though the stoichiometry is SiO_2, you can think of the tetrahedral structure as silicate groups $\left([SiO_4]^{4-}\right)$ where the oxygen ions are then shared with neighboring Si ions, yielding a charge-neutral compound.

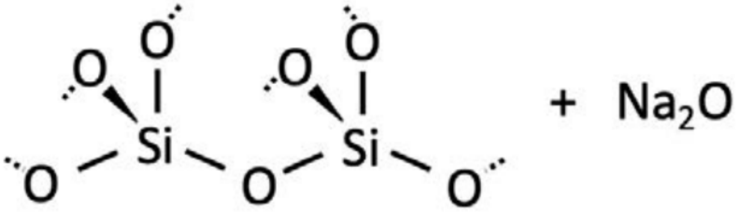
$$\mathrm{Si}+4\left(\frac{1}{2}\mathrm{O}\right)=\mathrm{Si}+2\mathrm{O}=\mathrm{SiO_2}$$

Although I've shown a crystalline representation above, the same concept applies for glasses: the difference is that in a glass, the arrangement of the bonds is not perfectly tetrahedral. In lecture and in Recitation 19 , we we talked about various processing methods that yield more disordered (glassy) or more ordered (crystalline) materials. Generally, when a glass forms instead of a crystal, the bonds do not have enough time (or energy) to become arranged in neat tetrahedrons: instead, they are rotated, stretched, and the long range structure is generally amorphous. The chemistry, however, remains the same: for silica glass, there are bridging oxygen atoms that connect neighboring silicon atoms, and a 2:1 ratio of oxygen atoms to silicon atoms. The resulting glass is like a large network of haphazardly-arranged $Si-O$ bonds: for this reason, silica is called a *network former.*

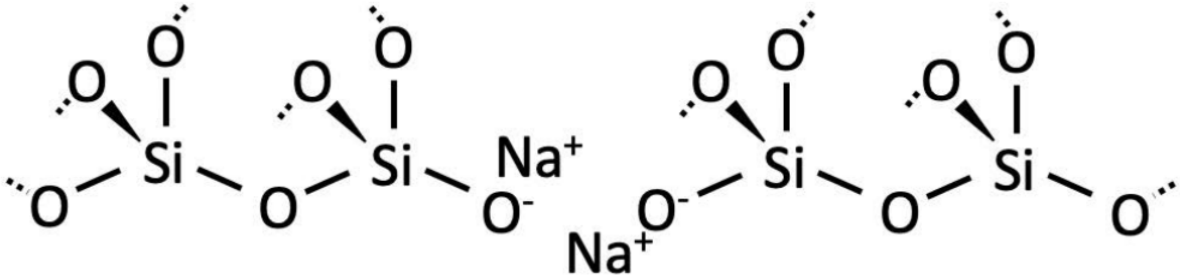
Network modifiers

In contrast to a network former, there can also be network modifiers: elemental defects introduced into the melt that disrupt the highly connected silica network. Some examples include Na_2O, CaO_2 and Al_2O_3. These ionic oxides dissociate inside the glass, and the strongly electropositive cations have an affinity for the electronegative oxygen atoms. Here's an example using Na_2O:

Let's focus in on one bridging oxygen. If we think of it like a chemical reaction, we can add a number of units of Na_2O.



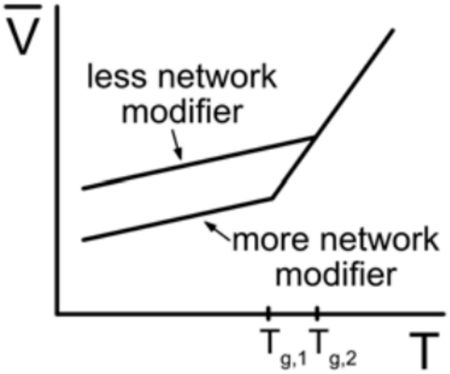
Each Na_2O in the melt dissociates into two sodium atoms and an oxygen atom. One of the covalent bonds connecting the bridging oxygen atom is broken by the sodium atoms. Of course, mass is conserved, and the oxygen from Na_2O can form a new covalent bond with the Si whose bond was broken. In the final state, the Na^+ atoms form ionic bonds with the newly nonbridging oxygen atoms. The network of silica has been split.



For other ionic salts, you can think of each O_2^{2-} that is added as breaking one bond, but creating two nonbridging oxygen atoms. The more network modifier that is added, the more this process happens, and the shorter the continuous chains of silica get! As the chains get shorter and shorter, they can slide past each other more easily during cooling. It's harder for them to get tangled. Therefore, the more network modifier is added, the lower the free volume of the glass that results (holding all other factors constant), because the shorter chains can pack more efficiently than the jumbled mess of pure silica glass.

Example: Sketch a glass cooling curve comparing a glass with a lot of network modifier added to a glass with little network modifier added, assuming the cooling rate is the same for both.

Answer



Note that the glass with more network modifier has a lower T_g!

6.21: Reaction Kinetics, Rate Laws and Rate Constants

Reaction kinetics

Not every reaction is the the same: early on, we talked about stoichiometry and how chemical equations give information about what is reacting and in what ratios. We learned how to determine which reactants would be limiting, and which would be in excess. The *rate* of a reaction is the change in concentration as a function of change in time. Reactants are consumed, so their rate is negative, and products are formed, so their rate is positive.

To determine the rate of a reaction experimentally, we simply measure and plot the concentration as a function of time. The *order* of a reaction refers to the relationship between concentration and rate. If the reaction rate is independent of the concentration of a reagent, the reaction is 0^{th} *order* in that reagent. If the reaction rate doubles when the concentration of a reagent is doubled, the reaction is 1^{st} *order* in that reagent. Finally, if the reaction rate quadruples when the concentration of a reagent is doubled, the reaction is 2^{nd} *order* in that reagent. Note that order is defined with respect to a specific reagent (usually for each reactant), not for a reaction as a whole!

When there are multiple reactants, it can be difficult to determine which reactant is causing the rate to change in what way. The best way to isolate the effect of changing concentration is to modulate the concentration of each reactant in turn, while holding the others constant.

Say we have a reaction of the following form:

$$a\,\mathrm{A}+\mathrm{bB}\rightarrow\mathrm{cC}+\mathrm{dD}$$

Conservation of mass allows us to write a generalized rate law, since we know that the rate at which the reactants disappear must equal the rate at which products appear:

$$\text{rate }=-\frac{1}{a}\frac{d[A]}{dt}=-\frac{1}{b}\frac{d[B]}{dt}=\frac{1}{c}\frac{d[C]}{dt}=\frac{1}{d}\frac{d[D]}{dt}$$

Say the dependence of rate on concentration is as follows:

	[A]	[B]	rate
Experiment 1	2M	1M	140mM/s
Experiment 2	2M	4M	560mM/s
Experiment 3	1M	1M	35mM/s

Notice that if we compare Experiments 1 and 2, the concentration of B quadruples, while the concentration if A is kept constant, and the rate also quadruples. This reaction must be first order in B! Comparing Experiments 1 and 3, the concentration of A halves, the concentration of B is constant, and the rate decreases by a factor of 4 . Since the reaction increases with the square of the concentration of A, this reaction must be second order in A. The *general* rate law can be expressed as

$$r=k[A]^2[B]$$

Here, the constant k is called the *rate constant*. The overall order of the reaction is given by the sum of the rates of the individual components. In our example above, the overall reaction rate is 3.

Rate laws and rate constants

The rate law for a 0^{th} order reaction is

$$r=k[A]^0=k$$

The units of the rate constant must therefore be units of rate, or $\mathrm{M/s}$. The integrated rate law can be found by integrating the rate law with respect to time, recalling that rate is change in concentration per unit time. For 0^{th} order, the integrated rate law is

$$[A]=[A]_0-kt$$

A similar analysis can be performed for first and second order reactions; the characteristics are summarized below:

	0^{th} order	1^{st} order	2^{nd} order
rate law	$\mathrm{r}=\mathrm{k}$	$\mathrm{r}=\mathrm{k}[\mathrm{A}]$	$\mathrm{r}=\mathrm{k}[\mathrm{A}]^2$
units of k	$M s^{-1}$	s^{-1}	$M^{-1} s^{-1}$
integrated rate law	$[A]=[A]_0-kt$	$\ln[A]=\ln[A]_0-kt$	$\frac{1}{[A]}=\frac{1}{[A]_0}+kt$

If you've had some diff eq, try to produce the integrated rate laws for each order for the rate laws given! You just need to separate variables and choose appropriate integration limits.

Example: You measure the rate at which reactants are consumed for the following reaction. Determine the overall order of the reaction and write the general rate law. What are the units of the rate constant k?

$$2\mathrm{NO}(g)+2\mathrm{H}_2(g) \rightarrow 2\ \mathrm{N}_2(g)+2\mathrm{H}_2\mathrm{O}(g)$$

Trial	[NO]	$[\mathrm{H}_2]$	rate
1	0.1M	0.1M	1.2mM/s
2	0.1M	0.2M	2.4mM/s
3	0.3M	0.1M	10.8mM/s

Answer

Comparing trial 2 to trial 1, the rate doubles while the concentration of H_2 doubles, so the reaction must be first order in $[\mathrm{H}_2]$. Comparing trial 3 to trial 1 , the concentration of NO triples and the rate increases by a factor of 9 $\left(=3^2\right)$. The reaction must therefore be second order in $[\mathrm{NO}]$.

The overall rate law for this reaction is

$$\text{rate }=-\frac{d[NO]}{dt}=-\frac{d\left[H_2\right]}{dt}=k[NO]^2\left[H_2\right]$$

The overall order of the reaction is the sum of the orders of the constituent reactants: in this case, $2+1=3$, so the overall reaction order is 3 . Finally, both sides of the rate equation must have the same units: the rate has units of M/s. We must choose the units of k such that the right hand side matches. The concentrations contribute M^3; therefore, the units of k must be $\mathrm{M}^{-2}\ \mathrm{s}^{-1}$ to match.

6.22: Equilibrium, Solubility Product, and Common Ion Effect

Equilibrium

Last time when we discussed reaction rates, we focused on the rate at which the *forward* reaction progresses– the rate at which reactants become products. Of course, reactions can progress in both the forward and reverse direction, and it is frequently thermodynamically favorable for this to happen. A reaction reaches a dynamic equilibrium when both the forward and reverse reaction are proceeding at the same rate.

The *equillibrium constant*, K_{eq}, is a ratio between the reverse reaction and the forward reaction in equilibrium. For a reaction

$$a[A]+b[B]\rightarrow c[C]+d[D]$$

the equilibrium constant is

$$K_{eq}=\frac{[C]^c[D]^d}{[A]^a[B]^b}\qquad(\text{use when system is in equilibrium})$$

Each reaction has an equilibrium constant, and here, the superscripts are the stoichiometric coefficients (unlike the rate constant!). When the system is not in equilibrium, such as when the system is perturbed or the reactants are first mixed, the ratio of the rate constants is usually represented by a Q.

$$Q=\frac{[C]^c[D]^d}{[A]^a[B]^b}\qquad(\text{use when system is not in equilibrium})$$

By comparing Q and K_{eq}, the progress of the reaction can be determined. The reaction has reached equilibrium when $\mathrm{Q}=\mathrm{K}_{eq}$. If $\mathrm{Q}<\mathrm{K}_{eq}$, the reaction proceeds to produce more products. If $\mathrm{Q}>\mathrm{K}_{eq}$, the reaction proceeds to produce more reactants.

Example: Write an expression for the equilibrium constant for the following reaction:

$$\mathrm{2NO+2H_2\rightarrow N_2+2H_2O}$$

Answer

We can read off the expression for the equilibrium constant from the balanced equation.

$$K_{eq}=\frac{[N_2]\,[H_2O]^2}{[NO]^2[H_2]^2}$$

Solubility product

The *solubility product* is the equilibrium constant for the dissolution of a solid in a solution. The solid that is dissolving is called the *solute*, and the liquid that is doing the dissolving is called the *solvent*. For a solubility product, the solid isn’t included: you can think of the concentration of the solid as being constant throughout the reaction.

Example: Find the solubility product of calcium chloride dissolving in water.

Answer

The equation governing the dissolution of calcium chloride is just the splitting of the compound into constituent ions:

$$\mathrm{CaCl_2}(s)\rightarrow\mathrm{Ca}^{2+}(aq)+2\mathrm{Cl}^-(aq)$$

To write the solubility product, we will ignore the solid part and focus only on the ions in solution, noted (aq) for aqueous. Therefore, the solubility product can be expressed as

$$K_{sp}=\left[Ca^{2+}\right]\left[Cl^-\right]^2$$

Common ion effect

The presence of additional ions in solution can have an impact on the solubility of a solid. In particular, if two solids that share an ion are both dissolved in solution, the equilibrium solubility shifts. The solubility of a salt is usually lower in the presence of another soluble salt which shares a common ion.

Example: What happens if we add silver chloride to an $0.2\mathrm{M}$ solution of calcium chloride? The solubility product if silver chloride is 1.77×10^{-10}.

Answer

First, we need to write a balanced equation for the dissolution of AgCl:

$$AgCl(s) \rightarrow Ag^{+}(aq) + Cl^{-}(aq)$$

Correspondingly, the expression for the solubility product is

$$K_{sp} = \left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]$$

We want to solve for the concentration of AgCl in solution which already contains calcium ions: one handy tool for this process is an ICE table, which stands for initial, change, equilibrium. When setting up an ICE table, we consider the species that is actively dissolving, not the species that already exists in solution.

The initial concentration of ions in solution is determined by the calcium chloride solution: we know it's an $0.2\mathrm{M}$ solution. Let's call the amount of AgCl that dissolves x. From our balanced equation above, we know that there are the same number of moles of Ag and Cl ions in solution. We can set up the ICE table for AgCl as follows:

	$[\mathrm{AgCl}]_s$	$\left[\mathrm{Ag}^{+}\right](\mathrm{aq})$	$\left[\mathrm{Cl}^{-}\right](\mathrm{aq})$
Initial	solid	$0\mathrm{M}$	$0.2\mathrm{M}$
Change	–	$+x\mathrm{M}$	$+x\mathrm{M}$
Final	–	$x\mathrm{M}$	$0.2 + x\mathrm{M}$

At every point as the reaction is proceeding, the equation governing the solubility product must be satisfied. Therefore we can solve for the final concentration of AgCl in solution as follows:

$$K_{sp} = \left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right] = x(0.2 + x) = 1.77 \times 10^{-10}$$
$$x^2 + 0.2x - 1.77 \times 10^{-10} = 0$$

Here, we can either directly solve the quadratic equation and keep only the physical solutions (positive concentration), or we can linearize and solve (since x is small). Either way, we come up with

$$x = 8.85 \times 10^{-10} M$$

Therefore, the concentration of of AgCl that will dissolve in $0.2\mathrm{M}\,\mathrm{CaCl_2}$ is $8.85 \times 10^{-10}\mathrm{M}$.

6.23: Acids, Bases, and Dissociation

Acids and bases

In lecture, we talked about *Brønsted-Lowry* acids and bases as well as Lewis acids and bases. The BrønstedLowry definition of acids and bases is more narrow: a Brønsted-Lowry acid is a *proton donor,* while a Brønsted-Lowry base is a *proton acceptor:* to be clear here, the proton is a hydrogen ion, H^+. More generally, a Lewis acid is an *electron acceptor,* while a Lewis base is an *electron donor.* Water is *amphoteric:* it can be either an acid or a base. Water serves as the solvent for many acid-base reactions. Consider adding a generic acid to water:

$$HA(aq) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)$$

Similarly, consider adding a generic base to water:

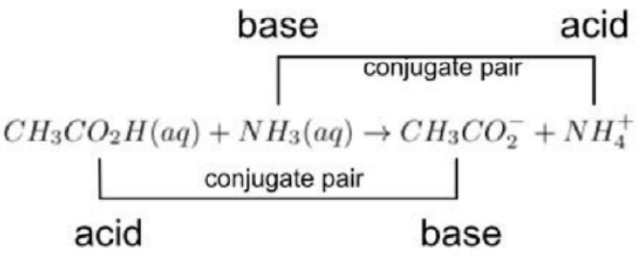
$$B^-(aq) + H_2O(l) \rightarrow HB(aq) + O^-(aq)$$

These serve as prototypical acid-base reactions: we can identify *conjugate acid-base pairs* to relate species that lost/gained a proton (or electron) on either side of the reaction.

Example: Identify the conjugate acid-base pairs in the following reaction:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{NH_3}(aq) \rightarrow \mathrm{CH_3CO_2^-} + \mathrm{NH_4^+}$$

Answer



Dissociation

In the same way we wrote a general equilibrium constant, we can write an acid/base specific equivalent. The equilibrium constant for our acid dissociation reaction above would be

$$K_{eq} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{H_2O}][\mathrm{HA}]}$$

However, since the water is acting as a solvent and is present in excess, it has a constant concentration: we therefore define the acid constant as

$$K_a = K_{eq}[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Similarly, the base dissocation constant is

$$K_b = \frac{[HB][OH^-]}{[B-]}$$

The *stronger* the acid or base, the more readily it dissolves in solution, and the greater the magnitude of K_a or K_b. There are only a few strong acids- acids that fully dissociate into their constituent ions. These include $\mathrm{HCl, HBr, HI, HNO_3, HClO_3, HCLO_4}$, and $\mathrm{H_2SO_4}$. The strong bases are mostly alkali salts, including $\mathrm{LiOH, NaOH, KOH, RbOH, CsOH, Ca(OH)_2, Sr(OH)_2, Ba(OH)_2}$. Of course, the strength of an acid or base is related to its bond energy: polar acids with big differences in electronegativity have a low bond energy rapidly dissociate when placed in water, for example.

Example: Write an expression for the dissociation and for the acid or base dissociation constants for these acids $(\mathrm{HF, CH_3CO_2H})$ and bases $(\mathrm{NH_3, NaOH})$.

Answer

Hydrofluoric acid, HF, is a strong acid. In water, the proton dissociates:

$$HF(aq) + H_2O(l) \rightarrow H_3O^+(aq) + F^-(aq)$$

Its acid dissociation constant is

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{F^-}\right]}{[HF]}$$

We can take a similar approach for acetic acid, a weak acid.

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2^-}(aq)$$

The acid dissociation constant is

$$K_a = \frac{\left[\mathrm{H_3O^+}\right]\left[\mathrm{CH_3CO_2^-}\right]}{\left[\mathrm{CH_3CO_2H}\right]}$$

For ammonia, the base gains a proton when placed in water:

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

The base dissociation constant for ammonia is

$$K_b = \frac{\left[\mathrm{NH_4^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{NH_3}\right]}$$

Finally, sodium hydroxide fully dissociates:

$$\mathrm{NaOH}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{Na^+}(aq) + \mathrm{OH^-}(aq)$$

The base dissociation constant is

$$K_b = \frac{[Na+]\left[\mathrm{OH^-}\right]}{[NaOH]}$$

Example: Which of these acids is the strongest? sulfurous acid $\left(\mathrm{H_2SO_3}; \mathrm{K}_a = 1.54 \times 10^{-2}\right)$, phosphoric acid $\left(\mathrm{H_2PO_4^-}; \mathrm{K}_a = 6.23 \times 10^{-8}\right)$, citric acid $\left(\mathrm{H_3C_6H_5O_7}; \mathrm{K}_a = 8.4 \times 10^{-4}\right)$

Answer

Stronger acids have larger acid dissociation constants, so sulfurous acid is stronger than citric acid and phosphoric acid.

6.24: pH and pOH, pKa and pKb

pH and pOH

The concentration of ions in solution can be quite high- and can differ from solution to solution by many orders of magnitude. For this reason, it is useful to refer to a logarithmic scale. We will use an operator p defined to be the negative log (base 10) of the value it precedes: for example, $\mathrm{pH} = -\log_{10}\left[\mathrm{H}^+\right]$.

The pH of a solution is a measure of how acidic it is: a pH of 7 indicates the solution is neutral, while lower values are acidic and higher values are basic. The compliment to pH is pOH, a measure of the concentration of hydroxide ions: $\mathrm{pOH} = -\log_{10}\left[\mathrm{OH}^-\right]$. A high pOH corresponds to an acidic solution, while a low pOH indicates a basic solution. pH and pOH are related as

$$pH + pOH = 14$$

Example: The K_a for nitrous acid, $\mathrm{HNO_2}$, is 4.0×10^{-4} . Determine the pH and pOH of $0.1\mathrm{M}$ nitrous acid.

Answer

First, let's write an expression for the dissociation of nitrous acid:

$$\mathrm{HNO_2}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{NO_2^-}(aq) + \mathrm{H_3O^+}(aq)$$

Then, we can write an expression for the acid dissociation constant:

$$K_a = \frac{\left[\mathrm{NO_2^-}\right]\left[\mathrm{H_3O^+}\right]}{\left[\mathrm{HNO_2}\right]}$$

To find the pH, we need to determine the concentration of H^+ ion (equivalently $\mathrm{H_3O^+}$). The initial concentration of nitrous acid is $0.1\mathrm{M}$: we can set up an ICE table to solve for the final concentrations:

	$[\mathrm{HNO_2}]$	$[\mathrm{NO_2^-}]$	$[\mathrm{H_3O^+}]$
Initial	0.1	$0\mathrm{M}$	$0\mathrm{M}$
Change	$-x\mathrm{M}$	$+x\mathrm{M}$	$+x\mathrm{M}$
Final	$0.1 - x\mathrm{M}$	$x\mathrm{M}$	$x\mathrm{M}$

Plugging in the final values to the expression for K_a, we can solve for x to find the concentration of hydrogen ions:

$$\begin{gathered} K_a = \frac{\left[\mathrm{NO_2^-}\right]\left[\mathrm{H_3O^+}\right]}{\left[\mathrm{HNO_2}\right]} = \frac{x^2}{0.1 - x} = 4.0 \times 10^{-4} \\ x^2 = 4.0 \times 10^{-5} - x\left(4.0 \times 10^{-4}\right) \\ x^2 + x\left(4.0 \times 10^{-4}\right) - 4.0 \times 10^{-5} = 0 \\ \left[\mathrm{H_3O^+}\right] = x \approx 0.006 \end{gathered}$$

Finally, we can solve for pH :

$$pH = -\log\left[H^+\right] = -\log\left[H_3O^+\right] = -\log(0.006) = 2.21$$

The value of pOH follows using the relation that $\mathrm{pH} + \mathrm{pOH} = 14$:

$$pOH = 14 - pH = 11.79$$

Example: What is the pH of $0.04\mathrm{MHI}$, which is a strong acid?

Answer

The key phrase to solving this problem is 'strong acid.' When we have a strong acid, we don't need an acid dissociation constant because we know it fully dissociates! Here, the concentration of hydrogen ion simply equals the initial concentration of acid:

$$pH = -\log\left[H^+\right] = -\log(0.04) = 1.4$$

$\mathbf{pK}_a$ and $\mathbf{pK}_b$

In the same way that it is convenient to express the concentration of hydronium or hydroxide ions as a logarithmic value, it can be useful to express the acid and base dissociation constants as pK_a and pK_b, since they can again differ by many orders of magnitude between species. The definition of p as an operator remains the same, so $\mathrm{pK}_a = -\log_{10}(\mathrm{K}_a)$ and $\mathrm{pK}_b = -\log_{10}(\mathrm{K}_b)$.

Example: For an $0.2\mathrm{M}$ solution of pyridine $(\mathrm{C_5H_5\,N})$, a base with a pH of 9.28, determine the pK_b.

Answer

First, let's write a dissociation equation for pyridine:

$$C_5H_5N(aq) + H_2O(l) \rightarrow C_5H_5N^+(aq) + OH^-$$

Then, we can convert the pH to a pOH, since pyridine is a base:

$$pOH = 14 - pH = 14 - 9.28 = 4.72$$

Next, we can convert the pOH into a concentration of hydroxide ions:

$$pOH = -\log_{10}\left[OH^-\right]$$
$$\left[OH^-\right] = 10^{-pOH} = 10^{-4.72} = 1.89 \times 10^{-5}$$

Then, we can write an expression for the base dissociation constant:

$$K_b = \frac{\left[C_5H_5\mathrm{NH}^+\right]\left[\mathrm{OH}^-\right]}{\left[C_5\mathrm{H}_5\,\mathrm{N}\right]}$$

And write our ICE table: Plugging these final values into the expression from above for K_b:

	$[\mathrm{C_5H_5\,N}]$	$[\mathrm{C_5H_5NH^+}]$	$[\mathrm{OH^-}]$
Initial	0.2	$0\mathrm{M}$	$0\mathrm{M}$
Change	$-x\mathrm{M}$	$+x\mathrm{M}$	$+x\mathrm{M}$
Final	$0.2 - x\mathrm{M}$	$x\mathrm{M}$	$x\mathrm{M}$

$$K_b = \frac{x^2}{0.2 - x}$$

Above, we determined the value of $x = \left[\mathrm{OH}^-\right] = 1.89 \times 10^{-5}$, so we can simply plug in to solve for K_b:

$$K_b = \frac{\left(1.89 \times 10^{-5}\right)^2}{0.2 - 1.89 \times 10^{-5}} = 1.8 \times 10^{-9}$$

Finally,

$$pK_b = -\log(K_b) = 8.74$$

6.24: pH and pOH, pKa and pKb is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

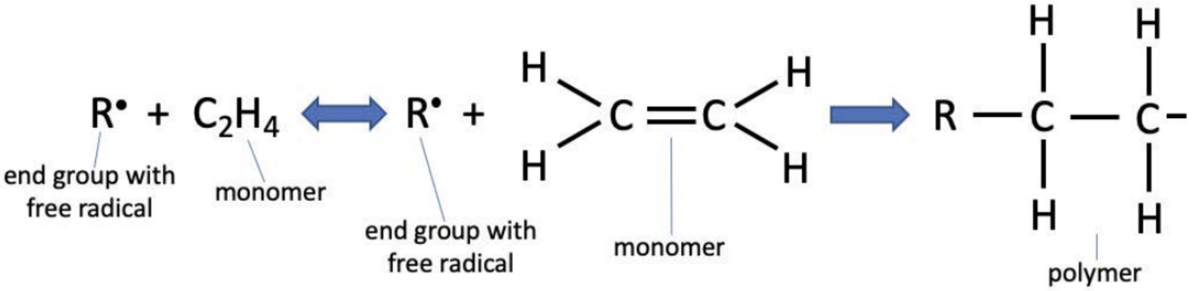
6.25: Polymers, Radical Polymerization, Condensation Polymerization, and Polymer Properties

Polymers

A *polymer* is a long molecule comprised of many (poly) iterations of a molecular unit cell (mer). There are many knobs available to turn to design a polymer with just the right properties. In 3.091, we'll focus on two types of polymerization reaction: radical and condensation.

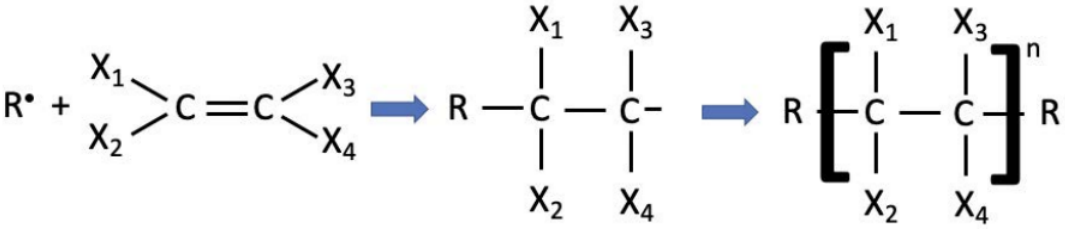
Radical polymerization

One mechanism to achieve polymerization is *radical polymerization*, a chain reaction that is started with the introduction of an initiator with a free radical. The initiator is shown below as R; more important than its chemistry is the *free radical*, a highly reactive single electron. The radical polymerization of polyethylene is shown below:



The free radical introduces an extra electron to the monomer, breaking the double bond between the carbon atoms and propagating through to react with another nearby monomer (shown as a half-bond in the polymer above). As long as there is monomer near the end of the chain, the reaction will proceed. Of course, as with any reaction, it is critical that mass is conserved. We can double check that this is the case by counting electrons. The polyethylene monomer has 12 electrons, and with the radical, the system has 13 electrons. In the polymerized picture, there are still 13 electrons.

Radical polymerization works for all sorts of *steric* groups, where steric refers to the spatial arrangement of atoms in a molecule or side group. For polyethylene, the steric side groups are simply hydrogen atoms; in general, there are limitless options for side groups. Below, the generic reaction shows that what is really important for a radical polymerization to take place is the presence of a carbon=carbon double bond. The



leftmost part of the figure shows a generalized representation of a polymer: there are groups on the end (symbolized as R, but they don't necessarily need to be the same), and n repeat units that make up the backbone of the polymer.

Condensation polymerization

Condensation polymerization is a type of step-growth reaction that occurs between monomer units with end groups that react to form water as a by-product. The monomers that react could all be the same, or they could be different: this distinction impacts the size of the repeat unit in the polymer that results.

Here, the polymerization reaction mechanism is that the hydroxyl group on the end of one monomer reacts with the hydrogen that terminates the other monomer. Each time this reaction happens, the resulting polymer grows. The polymerization can be halted in many ways; of course, when all of the monomer is consumed or there aren't monomers near the end of the chain to react, it stops growing. In this case, the hydroxyl group on one end of the monomer comes from the hydroxyl-terminated monomer. The other end could end up being either an OH group or a H group, depending on what the terminal monomer is- here, it's drawn assuming an even number of monomers reacted. For each of $2n$ monomers that add on to the chain, one water molecule is formed as a by-product: this lends the name *condensation* reaction. Alternatively, a similar process could take place if all of the monomer units are terminated with hydroxyl groups:

The same caveats apply here: there is nothing special about having two different monomers; it could just as easily be a single monomer or many more. The key difference in this case is that there is an extra oxygen on the end of one of the monomers when the water condenses off: this integrates into the backbone as shown, and results in a polymer that is terminated by a hydroxyl group at both ends.

These examples are simply meant as illustrations. With so much flexibility as to the choice of monomer groups, mixtures, and reaction conditions, there is really a whole world of properties that can be engineered.

Polymer properties

The thesis of many efforts in materials science is that structure dictates properties, and polymers are no exception. We have to look at both the chemistry of the monomers and the specific polymerization and processing conditions to understand the electronic and molecular structure, which in turn provide insights as to the micro- and macroscopic properties of the material that results.

Monomer composition: the size and composition of the side groups can play a big role in how tightly a polymer packs. If there are big groups (with a lot of *steric bulk*), the backbones of the polymer chains can't sit very close together, resulting in a lower degree of crystallinity.

IMFs: just as the size of the side groups plays a role, the composition can affect how tightly bound neighboring chains are to each other. For example, chains of polyethylene, with just H for side groups, slide across each other much easier than chains with side groups that are polar or can form hydrogen bonds.

Backbone structure: depending on how the specific reaction is run, the resulting polymer chains can end up being either linear or branched. Branched polymers pack less densely: you can think of branched polymers as a tangled mess of tree branches, while linear polymers are branches that have been cut into straight pieces and stacked.

Chain length: shorter chains can more easily slide past each other and move around, while long chains get tangled. It's harder to pull apart a polymer comprised of long chains. If long polymer chains are a tangled mess of cooked spaghetti, short chains are like macaroni. The chain length that results from a given polymerization reaction is called the *degree of polymerization*, and it is often advantageous to try and engineer the resulting distribution of chain lengths to be as narrow as possible.

Tacticity: the tacticity of a polymer refers to how the side groups are arranged: if all on the same side, it is *isotactic*. If the groups alternate positions, the polymer is *syndiotactic*, and if they are randomly arranged, it is *atactic*.

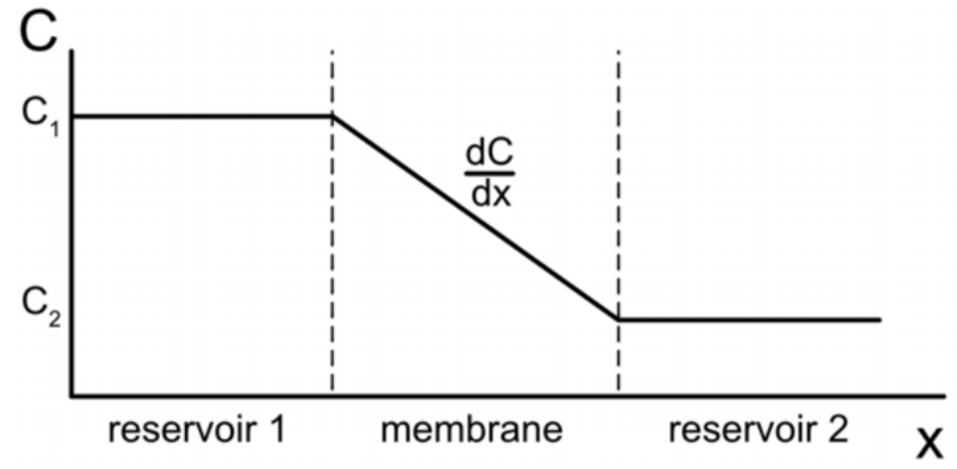
6.26: Steady State Diffusion, Diffusion Coefficient, Fick’s Second Law

Steady state diffusion

Diffusion refers to the net movement of a species down a concentration gradient, from an area of *high concentration* to an area of *low concentration*. Importantly, diffusion can take place in any phase of matter, including in solids! Steady state (time independent) diffusion is described by *Fick’s first law:*

$$J = -D\frac{dC}{dx}$$

Here, J is the *diffusion flux:* the rate at which an amount of a substance passes through a surface area. The diffusion flux has units of $\frac{\text{amount}}{\text{areaxtime}}$, or $\frac{\text{mol}}{\text{m}^2 s}$. D is the *diffusion coefficient*, which is sometimes called *diffusivity*. It depends on the specific circumstances the diffusion is occurring in, including what materials are involved and the state of the surrounding environment. It has units of $\frac{m^2}{s}$. Finally, here C is concentration (M or $\frac{\text{mol}}{\text{volume}}$, so $\frac{dC}{dx}$ is the change in concentration with respect to change in position. Therefore, Fick's first law tells us how concentration change flows over the region between two different concentrations.



Example: If you heat steel in a carbon rich atmosphere, carbon atoms will diffuse into the steel, hardening it. Calculate the diffusivity of a steel plate if the flux of carbon atoms through the plate is $2 \times 10^{-6}\frac{g}{m^2 s}$, the concentration 2 mm under the surface is $300\frac{g}{m^3}$, and the concentration 5 mm under the surface is $100\frac{g^3}{m^3}$.

Answer

We can rearrange Fick’s First law and plug in:

$$D = -J\left(\frac{dC}{dx}\right)^{-1} = -J\left(\frac{x_2 - x_1}{C_2 - C_1}\right) = -2 \times 10^{-6}\frac{g}{m^2 s}\left(\frac{\left(2 \times 10^{-3} - 5 \times 10^{-3}\right)m}{\left(3 \times 10^2 - 1 \times 10^2\right)\frac{g}{m^3}}\right)$$

$$D = 3 \times 10^{-11}\frac{m^2}{\text{s}}$$

Where we have approximated the concentration gradient as being linear.

Diffusion coefficient

Diffusion is a thermally-activated process, and the temperature dependence is reflected in the diffusion coefficient. The diffusion coefficient (diffusivity) is also described by an Arrhenius relationship! Picture an atom diffusing through a crystalline solid: it has to move through the lattice. One way this can happen is, if the atom is sufficiently small, it can travel hop from interstitial site to interstitial site. Larger atoms can diffuse, too, but it’s a more energy-consuming process. One mechanism for this to happen is if a vacancy is first created in the lattice, and then the diffusing atom moves into the now-vacant lattice site. As vacancies diffuse through the lattice, other species can follow. Of course, there are more moving parts with this process, and more energy is required.

The energy required for diffusion to occur can be thought of as an *activation energy*. The diffusion coefficient is

$$D = D_0 e^{-\frac{E_a}{k_B T}}$$

Here, D_0 is the maximum value of diffusivity, E_a is the activation energy, k_B is the Boltzmann constant, and T is temperature. By describing the diffusion coefficient with an Arrhenius relation, recall that we are saying that at a given temperature, T, the ratio of the thermal energy given by $k_B T$ to the activation energy E_a sets the value of the diffusion coefficient, and it is maximized at infinite temperature.

Fick's second law

If the concentration profile varies with respect to time, the steady-state assumption no longer holds, and instead *Fick's second law* is used instead:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Solutions to Fick's second law are of the form

$$\frac{C(x,t) - C_0}{C_s - C_0} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Here, C_s is the concentration of the source, C_0 is the initial concentration, $C(x,t)$ is the expression for concentration as a function of position and time, D is the diffusion coefficient, and erf is the error function.

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