ATOMIC STRUCTURE
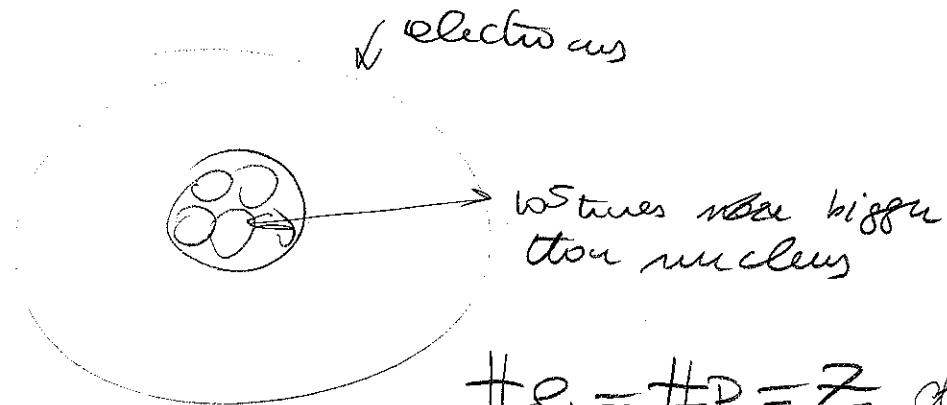
ATOMS = DEMOCRITOS (GREECE!!)

UNITS THAT CANNOT BE SPLIT (WRONG BUT RIGHT)
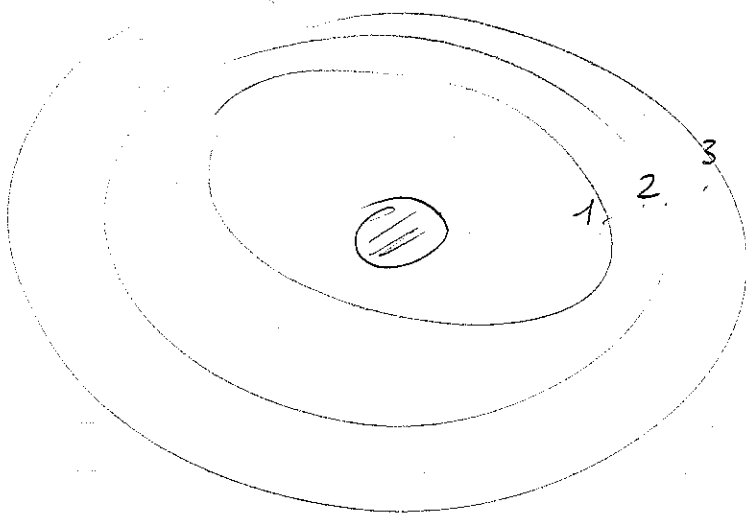
NUCLEUS
PROTONS
, NEUTRONS

electrons

10⁵ times more bigger than nucleus

$\#e = \#p = Z$ atomic number

$\#n =$ variable $\sim Z$

electrons rotate, lost so lost you need QM

$\Rightarrow$ orbitals like planet around the sun

1 2 3 4 misconception

SCHRÖDINGER EQUATION

A1

how to describe orbitals

quantum numbers n, l, m, s

energy ↑   slope ↗   orientation ↗   spin ↑↓

$\psi(r, \theta, \varphi)$
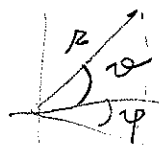
n Boundary for r
l boundary for θ
m boundary for φ

Bohr
2

PAULI $\Rightarrow$ 2e can't have same 4 q. numbers.

$n = 1, 2, 3 \dots \dots$ integer

$l = 0, 1, \dots n-1$

$m = -l, -l+1 \dots 0, \quad l-1, l$

$s = \pm \frac{1}{2}, \frac{1}{2}$

$n = 1$

$1s$ $l = 0$ (s $l=0$ S = spherical)

$m = 0$

$s = +\frac{1}{2}, -\frac{1}{2}$ $\Rightarrow$ 2 electron

A2

$n=2$
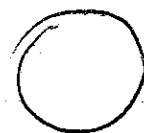
$2s^1, 2s^2$ $l=0$ sperical

$m=0$

$s=\pm\frac{1}{2}$ 2 electrons

$l=1$ $P \longrightarrow$

$m=-1, 0, 1$ $\longleftarrow$ 3 types

P_x, P_y, P_z

$2p^{1\cdots6}$ $s=\pm\frac{1}{2}$ each
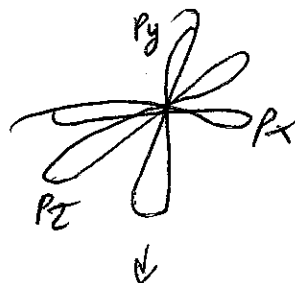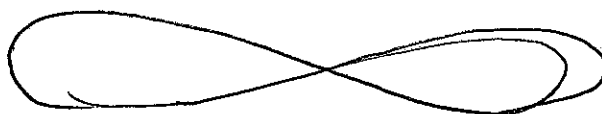
$\Longrightarrow$ 6 electrons
total

SIMMERTRIC
RESPECT THE
CENTER

$n=3$ $l=0$ $3s^{1\cdots2} \Rightarrow 2$
         $l=1$ $3p^{1\cdots6} \longrightarrow 6$ not

$l=2$

$3d^{1\cdots10}$ $m=-2,-1,0,1,2$ d orbitals

$\underbrace{\qquad}_{5}$

A_3 $s=\pm\frac{1}{2}, \downarrow\uparrow$ each   asymetric 5
         $\Rightarrow$ 10 electrons

$n = 4$

$\underset{2}{4s}, \underset{6}{4d}, \underset{10}{4p} , \underset{\text{14 electrons}}{4f}$
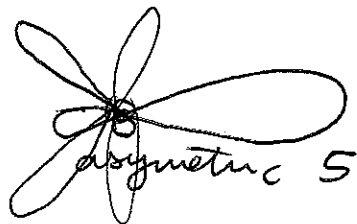
$l = 3$ $m = -3, -2, -1, 0, 1, 2, 3$

$7 \Rightarrow 14$ electrons

Energy

$1s, 2s, 2p, 3s, 3p, 4s, \quad 3d, 4p, 5s, 4d, 5p \cdots$

$\longrightarrow$ increasing energy

HUND RULE

~~in electrons~~ in set of orbitals, ~~too~~ with same energy, is partially occupied the electrons go to maximize total spin

Example $3d^5$

same energy $\Big\{$

$\Rightarrow$ NO   BUT

$\sum s = +\frac{1}{2}$

$\sum s = 2 !!$

Magnetic ~ half filled d & f

Mn, Fe, Co magnetic

Ti, Zn NO   Put AM table

Valence = # e in outer
shell contributing to bond

A#4   BOND = SHARE ELECTRONS

THERMO & KIN

THERMODYNAMICS

Study of relationships
between $p, T,$ Volume, composition @ EQUILIBRIUM
(phases, liquid, solid ...)

KINETIC

study of relationships OUT of EQUILIBRIUM

↳ speed reaction occur

THERMO : increase T — increase Energy

T melting
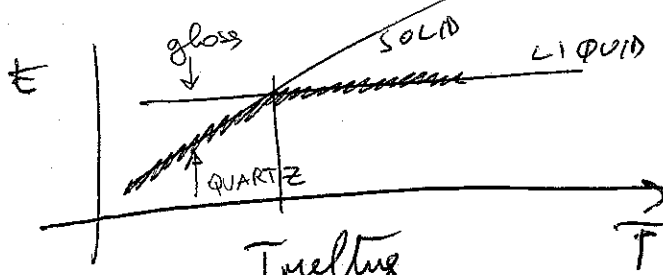
solid   liquid
most favorable   most favorable

low fast?

$$\text{Rate } k(t) = C \, e^{-\frac{Q}{RT}}$$

← kJ/mol
activation
energy

R gas constant $T \uparrow k$ faster

EXAMPLE
Q 2.3-1

ARRHENIOUS LAW
almost always true

phase A $Q =$ energy you need
to apply to see the other side of
the hill

phase B

IRREVE
RSIBILITY

A5
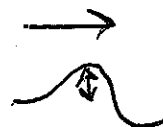
BONDS

Electronegativity = measure how generous
is an atom!
for electrons

EN ↗

give
away e
$E \sim 0$

want e
EN higher
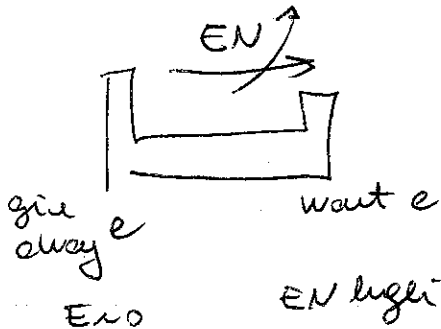
orbitals like
to be as much
as possible full
or empty

Na   Cl

$1s^2 2s^2 2p^6 3s^1$

$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$

$Na \rightarrow Na^+$
5.14 eV
IONIZATION
POT

Na^+

$1s^2, 2s^2, 2p^6$

$\Downarrow Cl^-$

$1s^2, 2s^2, 2p^6, 3s^2 3p^6$

$Cl \rightarrow Cl^-$
-4.02 eV
electron affinity
AFFINITY

$Na + Cl \rightarrow Na^+ + Cl^-$
5.14 eV - 4.02 eV
= 1.12 eV > 0
so likely they
form

$Z_1^q = +e$ $Z_2^q = -e$

Na^+ —— r —— Cl^-
coulomb

$V(r)$

attraction

$\longrightarrow r$

attractive
potential
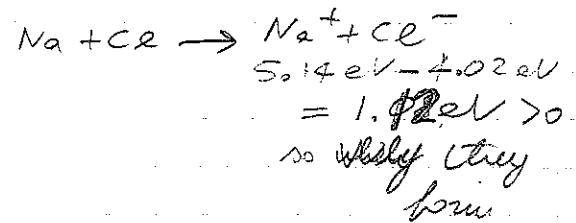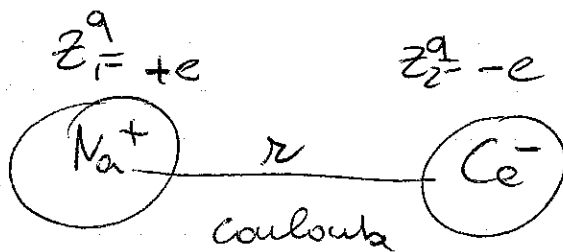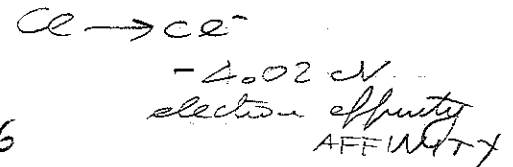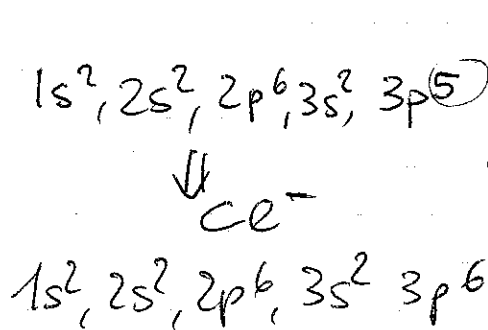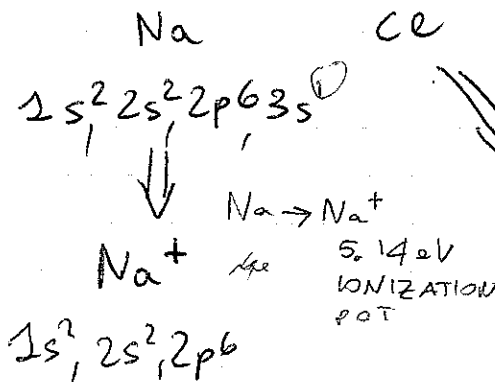
$$F = \frac{|Z_1 Z_2| q^2}{4\pi \varepsilon_0 r^2}$$

$$= \frac{e^2}{4\pi \varepsilon_0 r^2}$$ attractive
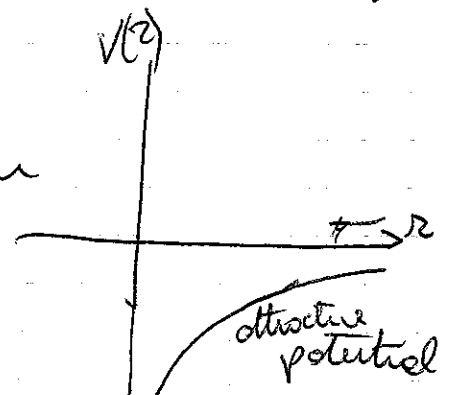
conservative
DYNAMICS
CLASSICAL
MECHANICS

$$F_{(r)} = -\nabla V(r) = \frac{\partial V}{\partial r}$$

grad

Newton

Joules

A6

the ionic force would fuse the
two atoms together

but
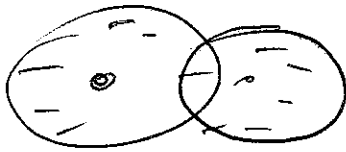
repulsion due by other electrons

$$F \sim \frac{K}{r^m}$$ much stronger than attraction
when r is small m

$m \sim$ ~~~ why 12

$$F = \nabla V \Rightarrow V_{repulsive} \sim \frac{c}{x^{m}}$$ $m = m - 1$

Rep $\frac{\partial}{\partial r}$

$\downarrow$ $\downarrow$
~ 12 ~ 13

$$F_{total} = F_{att} + F_{rep} = \nabla V_{total} = \nabla(V_{REP} + V_{ATT} + V_{FORM})$$

V_{FOR}
to form
$Na^+ Cl^-$
from Na, Cl

V_{tot} repulsion

attraction

V

$\frac{1}{r}$
$\frac{1}{r}$
r 1.12

BOND
LENGTH

BINDING
ENERGY < 0
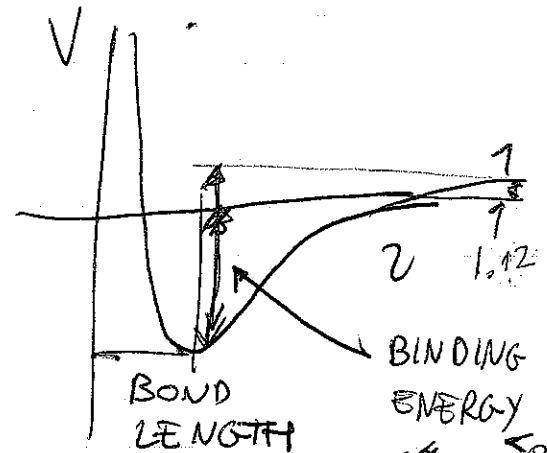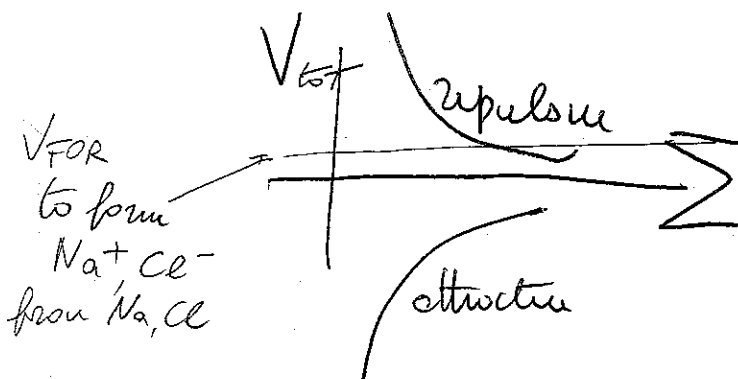
with respect
of pure $NaCl$

Read chap 2 up to 34

A7

$Li_2 O$
$1s^2 2s^2$ $1s^2 2s^2 2p^4$
$\downarrow$ extra time

⊕⊖⊕
⊖⊕⊖
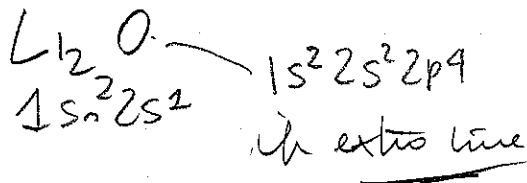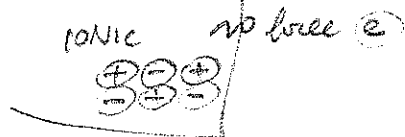
COVALENT   BOND

2 atoms   similar electronegativity ⇒ but not positive electro

⇒ no one gives away (+) or steals one electron

then they share

Cl_2, H_2, C_xH_y all hydrocarbons

her

⊕P   P

← LOCALIZED

↑ internal el   ↑   ↑ internal

F_2 $1s^2 2s^2 2p^5$

AMMONIA
NH_3 $1s^2 2s^2 2p^3$

covalent
bonding orbital = guest 2 electrons

COVALENT

NO free e

METALLIC   BOND

$1s^2 2s^2 2p^6, 3s^2$

Mg ⇒

$1s^2 2s^2$ valence

internal
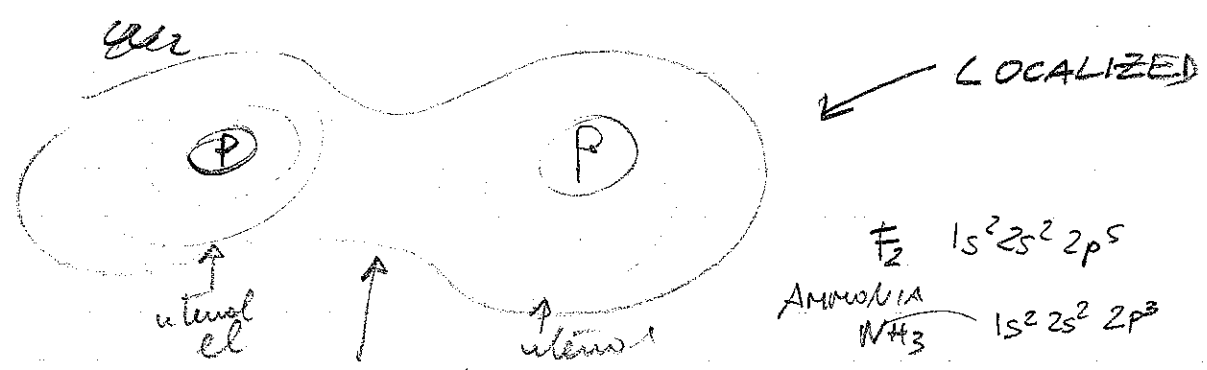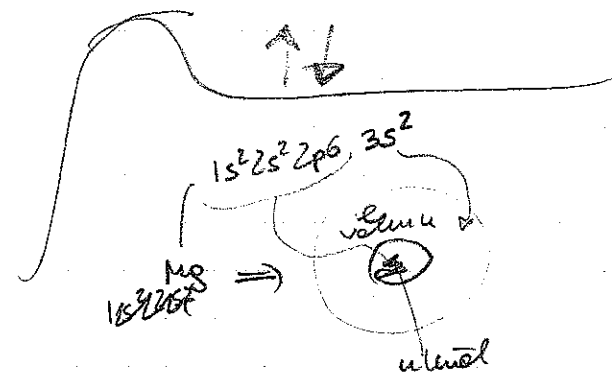
generous atoms give away electrons

⇒ electrons form a SEA 'CLOUD OF ELECTRONS

called FERMI SEA, it's homogeneous
JELLO MODEL

⇒

⇒   ⊕   ⊕   ⊕

plenty of
free
electrons

e⁻   sea of electrons

⊕   ⊕ e⁻ ⊕
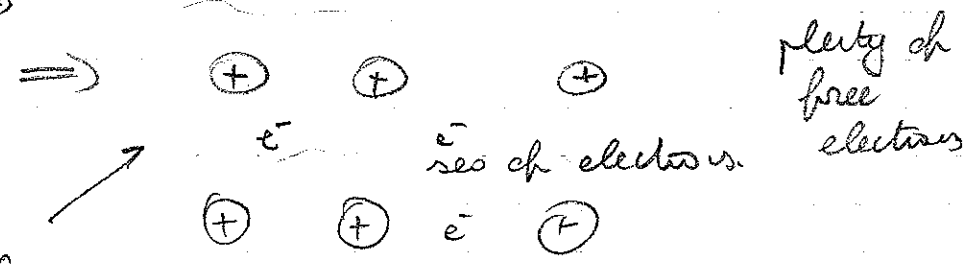
DELOCALIZED
ELECTRONS.

GLOBALLY SHARED ELECTRONS

DUCTILITY — BRTTLE BEHAVIOUR   BOOK PIC

Metals
metallic
Bond

EASY

DUCTILE

CERAMIC
IONIC

HARD

FRACTURE
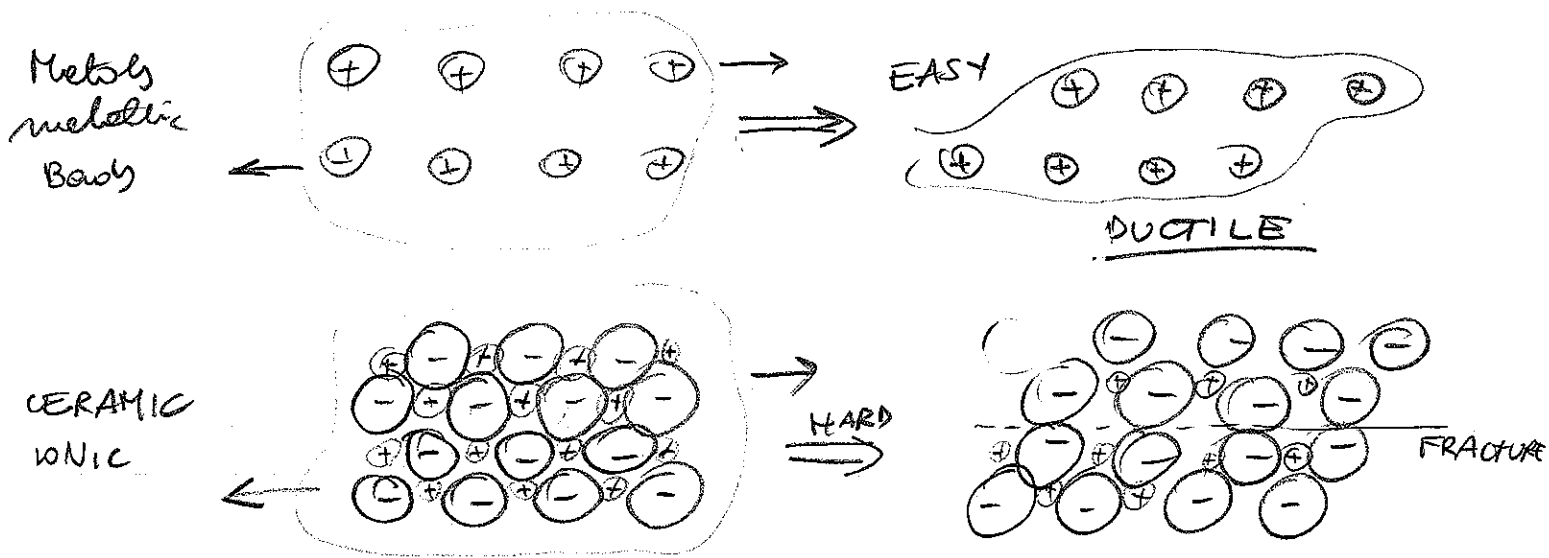
ELECTRICAL CONDUCTIVITY

— type of carrier   (metals, solutions)
— density of carriers (#/Volume)
— mobility (heavy or lighter)

$$V = \mu \bar{E}$$

speed $\uparrow$ $\uparrow$ electric field
       mobility
(ASK ~~LIONS~~ LIONS)

free electrons ⟹ very mobile
bound electrons ⟹ not very mobile

A9

ORIGIN OF YOUNG MODULUS

$V(x)$

interaction
Potential

$\rightarrow$ strength
ch BOND
FRACTURE

$V(x)$ $V(x)$ $V(x)$
$V(x)$

$\varepsilon = \Delta x / \ell$
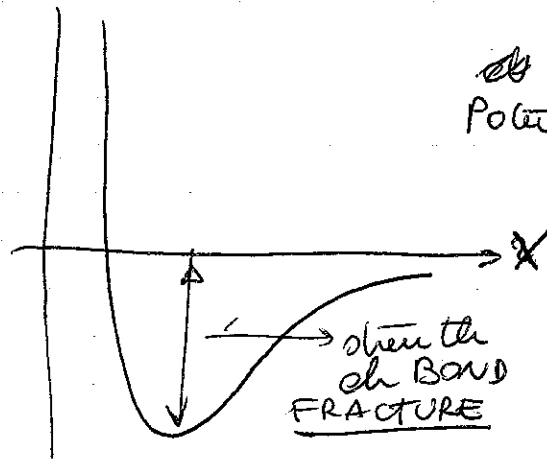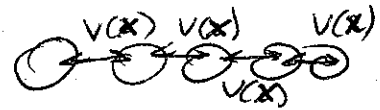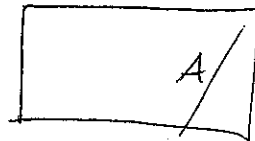
$\bar{\sigma} = E \bar{\varepsilon}$
ELASTICITY

YOUNG

$F = E a \Delta x$

geometrical
factor

$F(x) = \dfrac{\partial V}{\partial x}$

$E = \dfrac{\sigma}{\varepsilon}$ but $E(\varepsilon) = \dfrac{\partial \sigma}{\partial \varepsilon}$
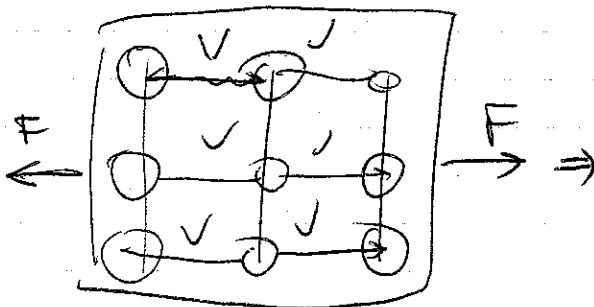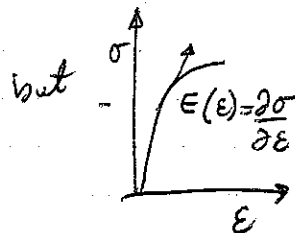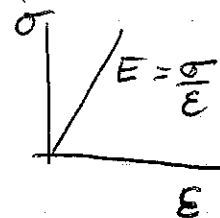
$E = a \dfrac{\partial F}{\partial x} = a \dfrac{\partial}{\partial x} \dfrac{\partial V}{\partial x}$

elastic
modulus $= a \dfrac{\partial^2 V}{\partial x^2}$ CURVATURE

$E(\varepsilon) = \dfrac{\partial \sigma}{\partial \varepsilon} \sim \dfrac{\partial F/A}{\partial \Delta x / x_0} \sim \dfrac{\partial F}{\partial x}$

$= a \dfrac{\partial F}{\partial x}$

constant

V

x_0

F

x

F

$\rightarrow$

F

x_0

E

E

elasticity

E

constant

x_0

elasticity

A10

parabola
$$V(x) \sim V(x_0) + \frac{1}{2} \in \left(x - x_0\right)^2 a$$
↑
imp
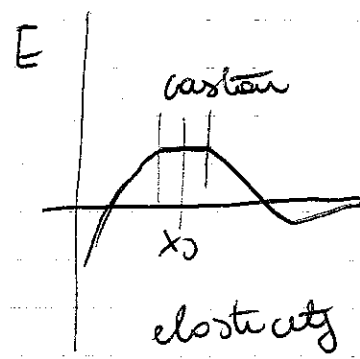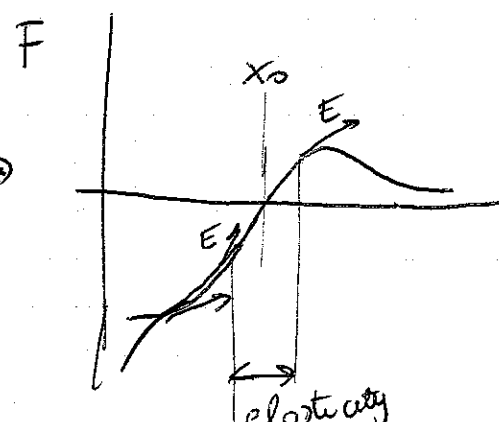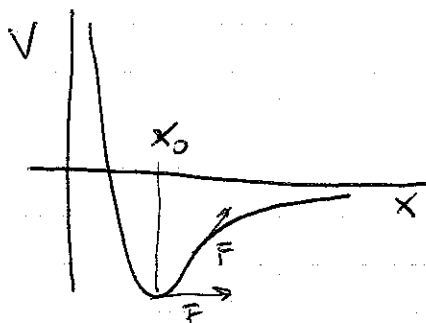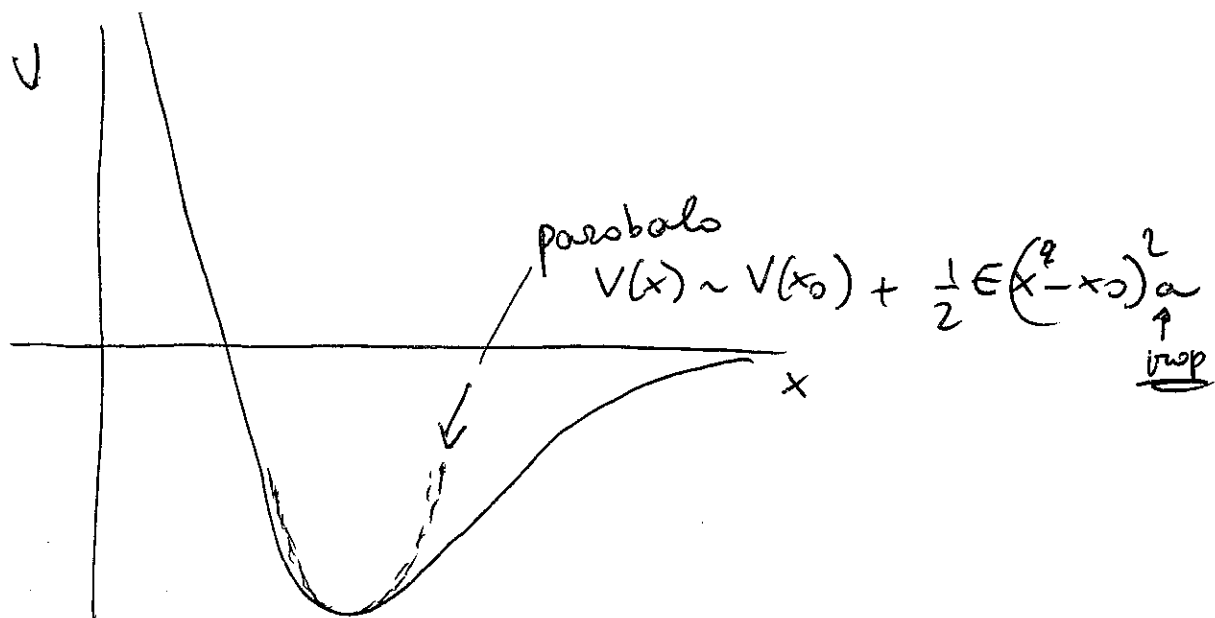
THERMAL EXPANSION

$V(t)$ not symmetric
$\Rightarrow$ expansion

V(x)

rattling in the middle

equal compd

Energy + Temperature energy
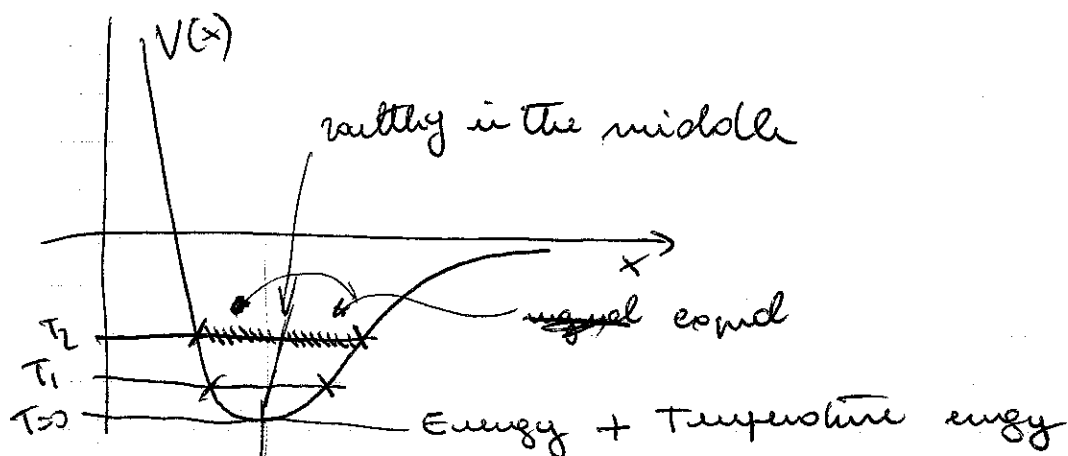
$\frac{1}{2} kT$ per degree of freedom (3 ax)
↳ kT

$x_e = x_0(T=0) + \partial x_0 (T - T_0)$

$\partial \equiv \frac{1}{x_0} \frac{\partial x}{\partial T}$ $\sim 10^{-5} k^{-1}$
thermal expansion

$E_{BOND} \uparrow \Rightarrow T_{melting} \uparrow \Rightarrow \partial_{th} \downarrow$

more symetric and $\partial \downarrow$

All

COORDINATION NUMBER & PACKING

ionic material (spherical, all dimensional consideration)

     cation (the one that he gets the $(+)$)

     anion (the one that gets the $(-)$)

"usually" $r(cation) < r(anion)$

    go right left   go length   then $r \leqslant R$
    in TABLE   in TABLE

    $\dfrac{r}{R}$ defines structure   CN= coordination number
                           # of first neighbours

    $CN = \frac{4}{4}$ staggered   Show PIC Book 45

covalent
    CN depends on the electron valence shells

SECONDARY BONDS

vdW (temporary dipoles)   (weakest possible bonds ⇒ spherical   He crystals)

electrons while rotating produce a momentary
electric dipole (TEMPORARY DIPOLE)
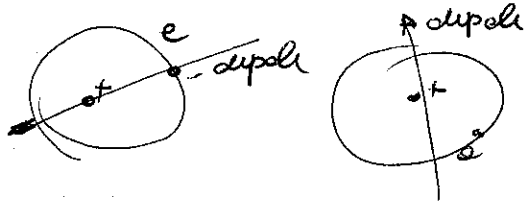
$$\overline{dipole} = \bar{\ell} \, e$$

coulomb ↓ distance vector

⇒ attraction between
dipoles , also id
the net charge is ~~zero~~ !!

⇒ van der Waals   weak ~ $V_{vdW} \sim -\dfrac{1}{z^6}$

PERMANENT DIPOLES

when they have a permanent asymmetric distribution

$H_2O \Rightarrow$ O $1s^2 \; 2s^2 \; 2p^4$

6 electrons in Sp^3 hybridisation

tetrahedron

ℓ ~~dey~~ dipole

hydrogen
bond
⇒ liquid
water

Same for ⓢ . ~~SO4~~ H_2S & NH_3

$\underbrace{2s^2 2p^3}$
Sp^3 with S
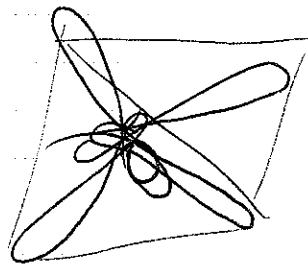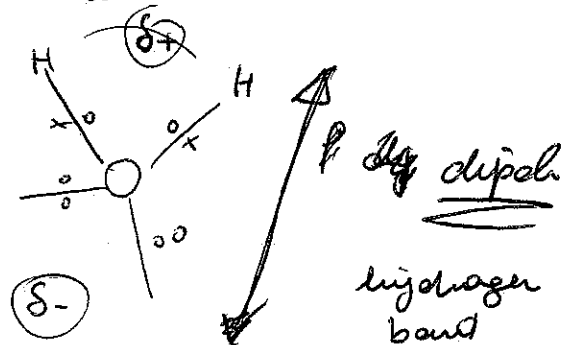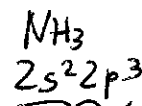
Permanent Bonds > VdW

√A13

POLYMERS : MACROMOLECULES

— SATURATED

$$-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}-$$

NO ~~free~~ electrons to share ⟹
saturated ⟹ bonds between molecules
are secondary (vdW & dipole permanent)
⟹ [Thermoplastic] : they melt and
can be reused many times (ABS+)

NO $C=C$
to break
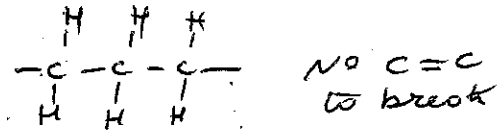
— UNSATURATED

they have free electrons to ~~share~~ ⟹

$$A-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle A}{|}}{C}}=\overset{\overset{\displaystyle H}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle}{|}}{C}\ldots$$
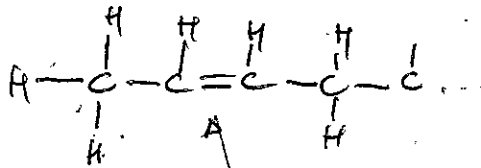
⟹ have unsaturated
double bonds

⟹

upon heating up, these
bonds breate and join

with other chains
making "cross links"

[Thermoset polymers]

Rubber comes from LATTICE (natural)
with sulphurisation
GOOD YEAR

A14

determined by the value of the quantum number l and is given by $2(2l + 1)$. Thus, the maximum numbers of electrons in an s, p, d, and f subshell are respectively 2, 6, 10, and 14.

The **electron configuration** represents the distribution of electrons within the permissible energy levels. In the **ground state,** an atom's electrons occupy the lowest-energy subshells consistent with the Pauli exclusion principle. The subshells can be arranged in order of increasing energy as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d . . .

In this notation, the number of electrons in each subshell is indicated using an integer superscript on the corresponding letter. For example, a half-filled subshell with quantum numbers $n = 3$ and $l = 2$ would be designated as $3d^5$.

How can we use this notation to describe the ground-state electron configuration for an oxygen atom that contains eight electrons? In the ground state the subshells will "fill" in the order 1s, 2s, 2p . . . and the maximum number of electrons in s and p subshells will be two and six, respectively. Thus, the ground-state electron configuration for oxygen is $1s^2 2s^2 2p^4$, indicating two electrons in each of the (filled) 1s and 2s subshells and four electrons in the (partially filled) 2p subshell.

In addition to the quantization of energy, another key result of the wave model is that the exact position of an electron within an atom can never be known. Instead, probability density functions (PDFs) are used to describe the spatial location of electrons. As shown in Figure 2.2–2, the shape of the PDF depends on the value of the quantum number l. Note that not all the distribution functions are radially symmetric. The consequence of a nonsymmetric PDF is that definite bond angles can be found in structures such as diamond, organic molecules, and polymeric chains. We will see that these specific bond angles influence the macroscopic engineering properties of the corresponding materials.

FIGURE 2.2–2

A highly schematic illustration of the probability density functions for electrons in certain subshells of an atom. Note that the s subshells are radially symmetric while the p subshells (and all other subshells) are highly directional.

s orbitals are spherically symmetric

p orbitals have a dumbbell shape

(a)   (b)   (c)   (d)
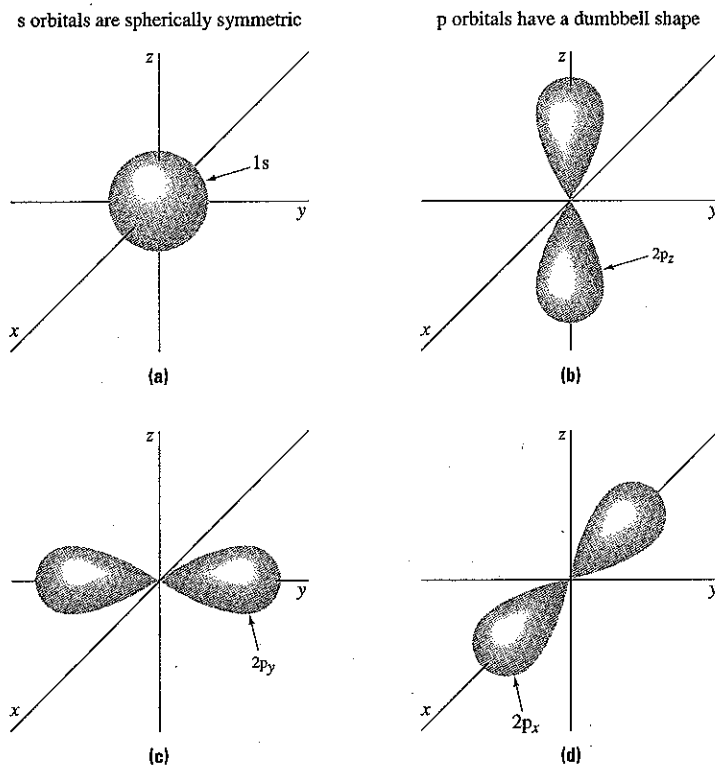
d. For CdTe, $\Delta EN = 2.1 - 1.9 = 0.2$. Using the table in Appendix B, this corresponds to a bond that is ~1% ionic. Therefore, the bonding in CdTe is either metallic or covalent. Since the average number of valence electrons in CdTe is $(2 + 6)/2 = 4$, we predict the bonding in CdTe is likely to be covalent.

2.4.4 Influence of Bond Type on Engineering Properties

At this point we can make a few preliminary observations concerning some of the mechanical and electrical properties of solids as a function of bond type.

Consider the difference in the response of a metal and an ionic solid (ceramics and oxide glasses are examples of solids with considerable ionic character) when each material is struck with a blow from a hammer. Atoms in the metal can slip and slide past one another without regard to electrical-charge constraints in response to the applied force and thus absorb the impact without breaking. This phenomenon is called **ductile** behavior of metals. On the other hand, as illustrated in Figure 2.4–5a, in an ionic solid, each ion is surrounded by oppositely charged ions. Thus, ionic slip may lead to like charges moving into adjacent positions, causing coulombic repulsion (see Figure 2.4–5b). This makes slipping much more difficult to achieve, and the material responds by breaking. This is one of the reasons why ceramics and oxide glasses fracture easily. Such behavior is known as **brittle** behavior.
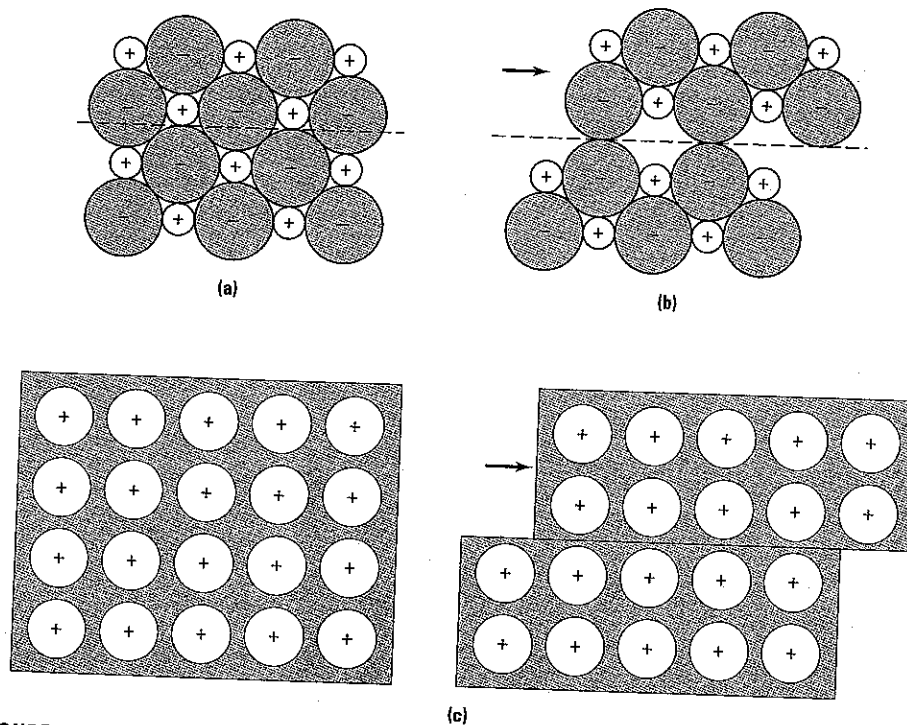
FIGURE 2.4–5 A comparison of the difference in the atomic scale response of a metal and an ionic solid to a hammer blow. **(a)** In an ionic solid before the hammer blow each ion is surrounded by oppositely charged ions. **(b)** When the ions attempt to slip past one another in response to the applied force, strong repulsive forces develop and lead to cracking. **(c)** In contrast, in a metal the electron cloud shields the positively charged atomic cores from each other so that the repulsive forces do not develop.

TABLE 2.5–1   Latent heat of fusion, melting temperatures, and coefficients of thermal expansion for some metallic elements.

Material	Latent heat of fusion (J/g)*	Melting temperature (K)	Coefficient of thermal expansion ($\times 10^{-6}$ °C)*
Row III metals			
Na	113	371	70
Mg	368	922	25
Al	397	933	25
Si†	1800	1685	3
Row IV metals			
K	63	336	83
Se	67	494	37
Zn	113	693	35
Cu	205	1358	17
Mn	268	1517	22
Fe	272	1809	12
Co	276	1768	12
Ni	297	1726	13
Cr	331	2130	6
V	410	2175	8
Ti	418	1943	9

*Adapted from the *CRC Handbook of Tables for Applied Engineering Science*, copyright CRC Press, Boca Raton, FL, 1979.

† Although silicon is not usually considered a metal, it is included here for comparison.

sufficient accuracy to facilitate calculation of the absolute values of bond length, bond energy, modulus of elasticity, and coefficient of thermal expansion. The values of these properties for engineering materials are usually directly measured in the laboratory.

DESIGN EXAMPLE 2.5–2

The bond-energy curves for two engineering materials are shown in Figure 2.5–3. Your task is to select the better material for use in each application described below.

FIGURE 2.5–3

A comparison of the bond-energy curves for two hypothetical materials, A and B.
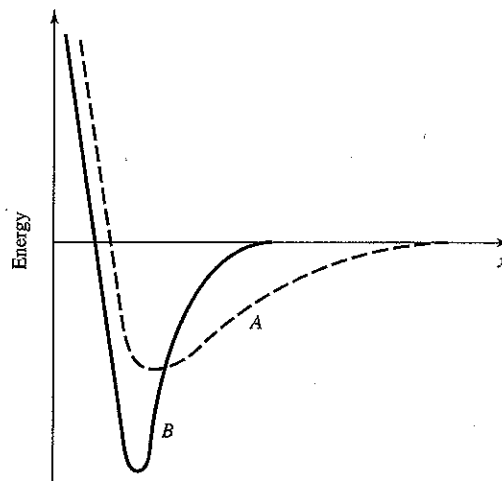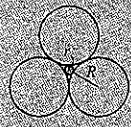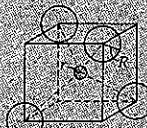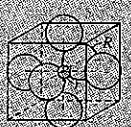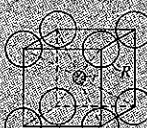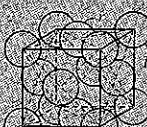
TABLE 2.6-1   The critical (r/R) ratio for each coordination number. (Note that the drawings are not to scale.)

Coordination number	Critical (r/R) value	(r/R) Stability range	Geometry
2	0	$0 < r/R < 0.155$	Always possible
3	0.155	$0.155 \leq r/R < 0.225$	
4	0.225	$0.225 \leq r/R < 0.414$	
6	0.414	$0.414 \leq r/R < 0.732$	
8	0.732	$0.732 \leq r/R < 1$	
12	1	$r/R = 1$	

(handwritten margin notes: "DUNNO!", "LAYERED", "TETRAGONAL", "OCTAHEDRA", "BCC", "FCC")

estimate the CN of the anion. Once the CN of the smaller ion is known, the CN of the larger ion can be determined based on the cation : anion ratio, or the stoichiometry of the compound.

EXAMPLE 2.6-1

Table 2.6-1 gives the ionic radius ratio range for CN = 6 as $0.414 \leq (r/R) < 0.732$. Derive these limiting values by investigating the critical geometry for CNs of 6 and 8.

Solution

The geometry for the critical (minimum) r/R ratio for CN = 6 is shown in Table 2.6-1. If a represents the length of the edge of the cube, then when all of the ions are just touching each other

$$r + R = \frac{a}{2} \quad \text{and} \quad R + R = \frac{a}{\sqrt{2}}$$

Dividing the first equation by the second equation yields

$$\frac{r + R}{2R} = \frac{1}{\sqrt{2}}$$

(left margin fragments)
$/(r + R)$
0.155

e mini-

nts this
results

e anion
see Fig-
become
2.6-1.
etrically
energet-
hus, the

ger than
smaller
basis of
the elec-
ge in the
r^0. Using

y bonded
r (cation)
used to

b. In the C_2H_6 molecule each H atom is bonded to one of the C atoms. Since each C atom must form four covalent bonds, there is a single covalent bond bridging the two C atoms (see Figure 2.6–3b).

c. In the compound C_2H_3Cl each H and Cl atom forms a single covalent bond with one of the C atoms. Each C atom must form four covalent bonds, so that there will be a *double* bond between the two C atoms (see Figure 2.6–3c).

d. In silicon, each atom must be bonded to four other Si atoms, and the resulting structure is similar to the diamond structure described previously (see Figure 2.6–2b).

Covalent bonds are directional and are characterized by specific **bond angles.** The bond angles can be determined by the geometry of the structure or vice versa. Shared electrons, or bond pairs, and lone electron pairs constitute mutually repulsive negative-charge centers that tend to separate as much as possible. As shown in Figure 2.6–4a, the bond angle in a tetrahedral structure such as diamond is 109.5°, which places nearest-neighbor C atoms (and their associated shared electron pairs) as far apart as possible in space while satisfying the valency requirements. In contrast, when carbon is bonded to only three other atoms (one of which involves a double bond), the resulting structure is planar with a bond angle of about 120°, as shown in Figure 2.6–4b. The existence of specific bond angles in covalent molecules is important in understanding the properties of polymers.

3-D structure, with
all angles = 109.5°

(a)

2-D (planar) structure,
with all angles = 120°

(b)
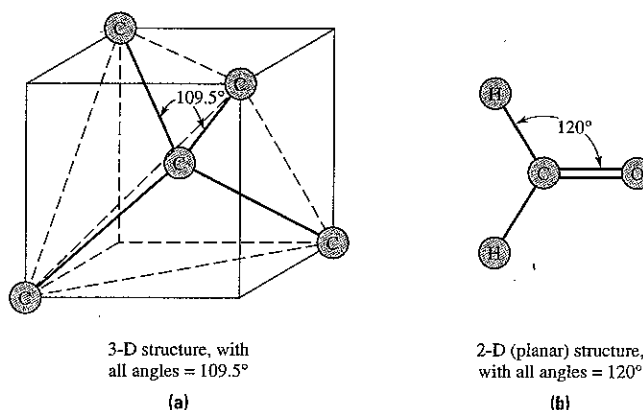
FIGURE 2.6–4   A schematic illustration of covalent bond angles in two compounds: **(a)** the bond angle in a tetrahedral structure such as diamond is 109.5°; **(b)** when the C is bonded to only three other atoms (one of which involves a double bond), the resulting structure is planar with a bond angle of ~120°.

EXAMPLE 2.6–4

Sketch the three-dimensional arrangement of covalent bonds in the H_2O molecule.

Solution

The geometry of the H_2O molecule can be envisioned by placing the O atom at the center of an imaginary cube and noting that its four pairs of electrons, two bonding and two nonbonding electron pairs, must be spatially separated as much as possible. This separation, shown in Figure 2.6–5, is obtained by placing the electron pairs along directions pointing to an alternating set of four corners of the imaginary cube. The H atoms are positioned at two of the cube corners associated with the
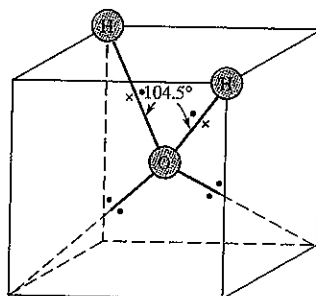
FIGURE 2.6–5   A schematic illustration of covalent bond angles in water. Note that the bond angle is 104.5°, which is slightly less than the tetrahedral angle of 109.5°.

bonding electron pairs. The structure of H_2O deviates slightly from this model, since nonbonding electron pairs repel each other slightly more than bonding electron pairs. The result is that the H—O—H bond angle is 104.5°—slightly less than the predicted 109.5°.

The shared electrons in a metallic bond are delocalized. Thus, the CN of an atom in a metallic solid is determined primarily by geometrical considerations. Indeed, many pure metals (e.g., Al, Cu, and Ni), for which $r/R = 1$, have structures with a CN of 12; however, several common pure metals such as Fe, Cr, and W have CNs of only 8, even in their purest forms.

Coordination numbers are useful because they describe the **short-range order,** defined as the number and type of nearest neighbors, associated with a particular solid structure. All solids exhibit short-range order. As we expand the consideration to include second- and higher-order neighbors, we find that there are two distinct types of solids. Those that exhibit both short-range order (SRO) and **long-range order** are called **crystalline materials** while those with SRO only are termed **amorphous,** or **noncrystalline, materials.**

2.7 SECONDARY BONDS

Secondary bonds are fundamentally different from primary bonds in that they involve neither electron transfer nor electron sharing. Instead, attractive forces are produced when the center of positive charge is different from the location of the center of negative charge. The resulting electric dipole can be either temporary, induced, or permanent and can occur in atoms or molecules. As shown in Figure 2.7–1 for Ar, a **temporary dipole** is formed when the electrons, which are constantly in motion, are momentarily arranged so as to produce an asymmetric charge distribution. The temporary dipole can then induce another dipole in an adjacent Ar atom. The two dipoles then experience a coulombic force of attraction. This type of bonding is responsible for the condensation of noble gases at low temperatures and is known as **van der Waals** (or van der Waals–London) bonding. Van der Waals bonds can also occur between symmetric molecules such as CH_4 and CCl_4. The total attractive force between molecules due to the van der Waals bond generally increases as the number of atoms in the compound increases. Hence, large molecules can have a large net attractive force. This phenomenon explains why the melting temperatures of the hydrocarbons with chemical formulas C_nH_{2n+2} increase as n increases.

Isolated Ar atom
(center of positive charge
same as center of negative charge)

Due to statistical nature of electron motion, occasionally
the center of negative charge is spatially different than
the center of positive charge (i.e., a temporary dipole)

Secondary
bond

Temporary dipole at left can induce a dipole in
a neighboring Ar atom; result is a van der
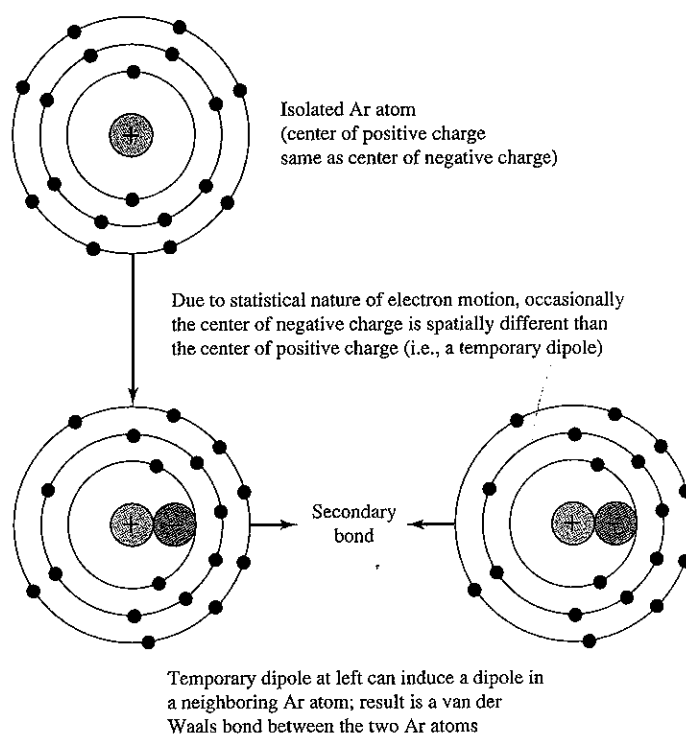Waals bond between the two Ar atoms

FIGURE 2.7–1   Formation of a temporary dipole in an Ar atom can induce a dipole in an adjacent Ar atom. This type of secondary bond is known as a van der Waals bond.

Figure 2.7–2 shows the charge distribution in H_2O, H_2S, and NH_3. These molecules are **permanent dipoles,** because their center of positive charge (indicated by the symbol δ^+) is always different from their center of negative charge (δ^-). Permanent dipole bonds are generally stronger than van der Waals bonds. One especially important type of permanent dipole bond is the **hydrogen bond,** which occurs whenever a hydrogen atom can be shared between two strongly electronegative atoms such as N, O, F, or Cl. The hydrogen bond is the strongest type of secondary bond, but it is still significantly weaker than a primary bond. Hydrogen bonds hold the wood fibers in a sheet of paper together.
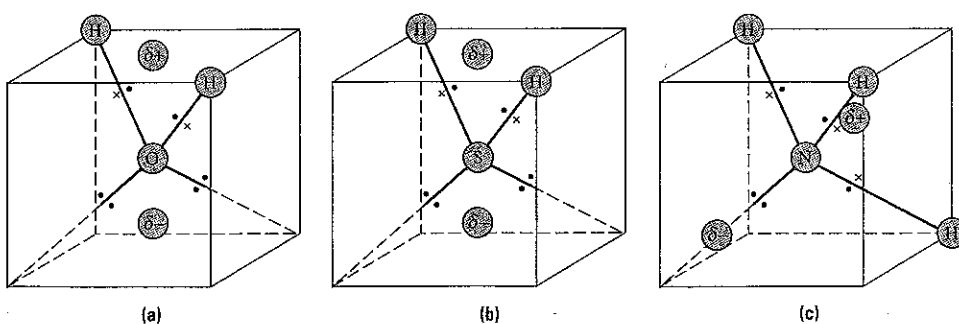

(a)   (b)   (c)

FIGURE 2.7–2   A schematic illustration of three permanent dipole molecules: **(a)** H_2O, **(b)** H_2S, and **(c)** NH_3. The x's represent the valence electrons from the H atoms and the •'s represent those from either O, S, or N. The δ^+ and δ^- symbols represent the spatial centers of positive and negative charge for the molecule. Note that nonbonding electron pairs are local regions of negative charge and the isolated nucleus of an H atom is a local region of positive charge.
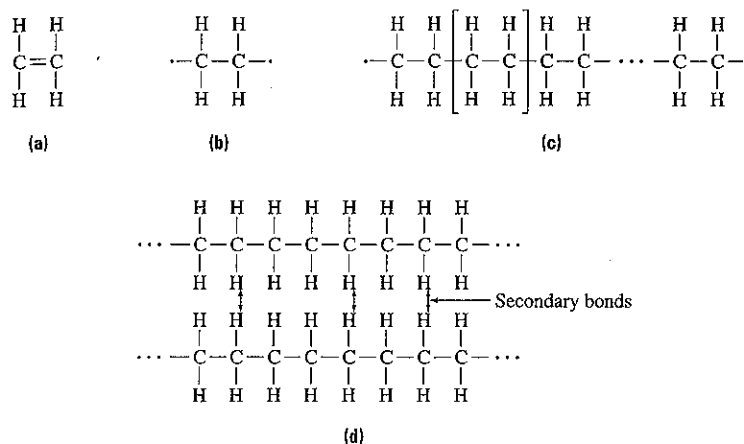
(a)   (b)   (c)

(d)

FIGURE 2.9–1   The structure of polyethylene, PE: **(a)** the basic building block for PE is the C_2H_4 monomer; **(b)** the double bond in the monomer is "opened" so that **(c)** many monomers can be linked together to form the PE polymer chain; **(d)** since the polymer chains are saturated, the only type of bond that can form between PE chains is the secondary bonds.

energy of the system. Thus, the formation of a PE polymer chain from a collection of identical monomers is a thermodynamically favored reaction. Note that in contrast to the monomer, the PE polymer chain is saturated, so there are no additional sites for primary bond formation. Thus, the only mechanism that remains for bond formation between PE chains is secondary bond formation. Linear polymers that form melts upon heating, such as PE, are called **thermoplastic polymers.**

The structure of rubber is fundamentally different from that of the thermoplastic polymers. Careful examination of the generic hydrocarbon rubber structure in Figure 2.9–2a shows that the polymer chains contain an unsaturated double bond. The existence of this double bond within the macromolecule permits the formation of additional primary bonds between chains (Figure 2.9–2b). The primary bonds between rubber chains formed by the opening of the unsaturated double bonds are known as **crosslinks.** When the crosslink density is low, only a small fraction of the double bonds have been opened, and the individual polymer chains retain their identity. There are only a "few" primary bonds between chains. As the crosslink density increases, the individual chains lose their identity and the structure begins to resemble a three-dimensional network of primary bonds. This 3-D primary bond structure is characteristic of many polymers that do not form a melt, or **thermoset polymers.**
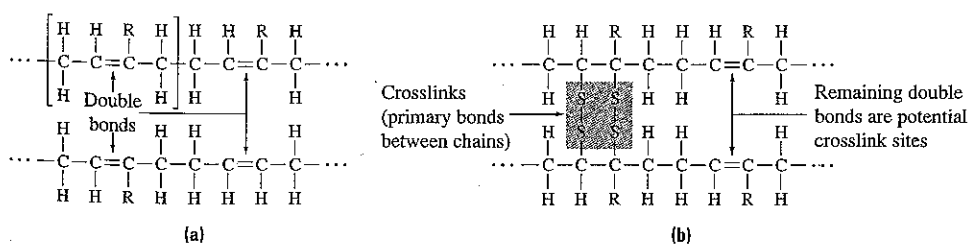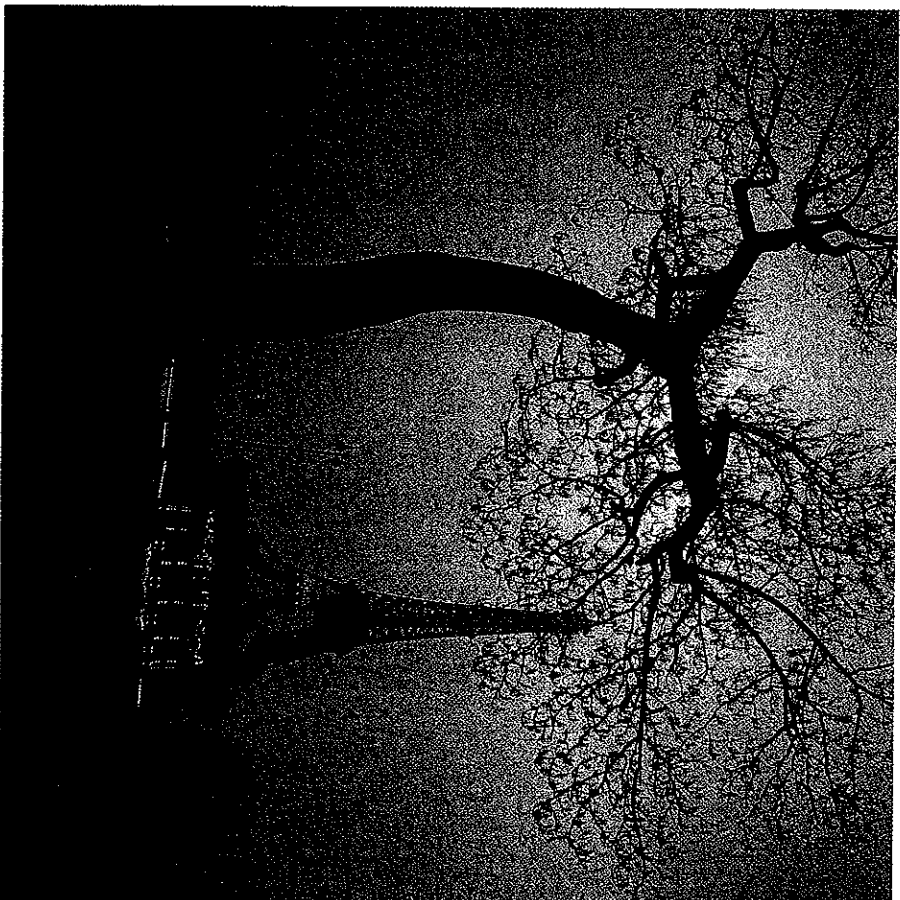
(a)   (b)

FIGURE 2.9–2   The structure of crosslinked rubber. The existence of double bonds along the length of the polymer chains shown in part **(a)** permits the formation of crosslinks between chains, as shown in part **(b)**. Note that in this case the crosslinks are composed of short chains of sulfur atoms.

Il moto é causa d'ogni vita

(Movement is the cause of all life)

Leonardo da Vinci

Design .... Is the fount and body of painting and sculpture
and architecture ... and the root of all sciences.

Michelangelo Buonarroti