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The relation between Interatomic bonding and thermal energy

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Abstract: The bonding energy determines many physical and mechanical properties of the materials. Different atomic orbitals will overlap in different ways, so different amounts of energy will be released upon their formation.

Keywords: : *Bonding, thermal energy, cermaics.*

Introduction

An understanding of many of the physical and mechanical properties of materials is enhanced by a knowledge of the interactions that exist among constituent atoms or molecules, and the geometric atomic arrangement.

Electrons in atoms

Atomic models

The atom is the smallest part of any matter. In the center of each atom, a nucleus is present which is composed of positively charged protons and neutral neutrons. The nucleus is encircled by moving negatively charged electrons.

The first successful theory of atomic structure, the **Bohr atomic model** was proposed by Niel Bohr. He used the concept of quantized energy to propose that electrons moved around the nucleus in fixed orbits or shells. Bohr's atomic model represents that each orbit can have a specific number of electrons, which correlates to the energy levels. The shell closer to the nucleus has lower energy while the one farthest away has the highest energy. If an electron jumps to a lower energy orbit, it will give out the extra energy, thereby maintaining the atomic stability (1). (Figure1)

With the establishment of the quantum behavior of entities like electrons, it became quite clear that Bohr's atomic model didn't satisfy the Heisenberg uncertainty principle (2). According to this principle, it is impossible to know the exact position of electrons in an atom, which means they can't exist in fixed orbits, as Bohr hypothesized. In **the quantum mechanical model**, an electron is no longer described as a particle moving in a discrete orbit; rather, the arrangement of electrons could only be described in terms of probability, in other words, there are certain regions where electrons are much more likely to be found. We call these regions “orbital” (1). (Figure2)

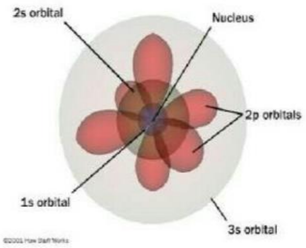

Figure 1: Bohr’s atomic model

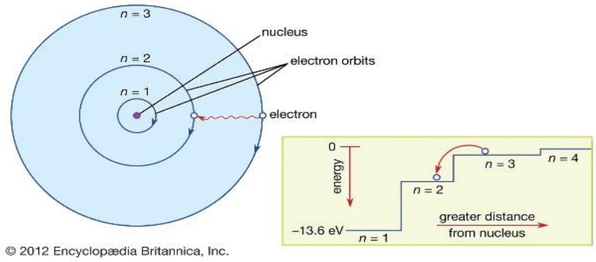

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Figure 2: The quantum mechanical model

Quantum numbers

There are four quantum numbers used to specify each orbital in an atom (1).

- The principal quantum number, n, is the same quantum number that Bohr introduced. n labels the shell of the atom, these shells are sometimes denoted by letters K, L, M, N, O, and so on, which corresponds to n=1, 2, 3, 4, 5, respectively. This quantum number is related to the size of an electron’s orbital. The maximum number of electrons in the shell can be represented by $2n^2$.
- The second quantum number is the angular momentum quantum number, ℓ.

  ℓ represents the subshell. ℓ can have any value from 0 to n-1, for example, if an electron has an n value of 3, it can have an ℓ value of either 0, 1, 2. The subshells are labeled s, p, d, and f.

  ℓ also describes the shape of the orbital. When ℓ=0, we are describing s orbitals which are spherical and centered on the nucleus. When ℓ=1, we are describing p orbitals which are 3 in number oriented perpendicular to each other and each one has a nodal surface in the shape of a dumbbell. When ℓ=2, we are describing d orbitals. (Figure 3)
- The third quantum number, the magnetic quantum number, m_ℓ, represents the number of electron orbitals for each subshell. m_ℓ can have values between - ℓ and ℓ including 0. When ℓ=2, m_ℓ can have a value of -2, -1, 0, 1, 2 which corresponds to the d subshell having 5 orbitals. (Figure 3)
- The fourth quantum number is the spin quantum number, m_s, this one will be either + ½ (spin up) or - ½ (spin down).

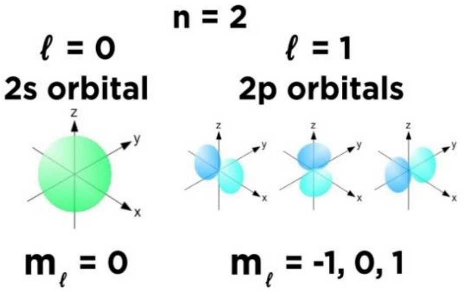


Figure 3: The second and third quantum numbers.

A complete energy level diagram for the different shells, subshells, and orbitals using the wave mechanical model is shown in figure 4.

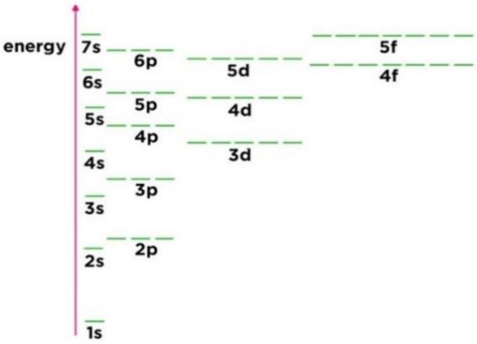


Figure 4: Energy level diagram.

The smaller the principal quantum number, the lower the energy level; for example, the 3p state has higher energy than the 2p state. The energy of the subshell level increases within each shell; for example, the 3d state has higher energy than the 3p state which is higher than 3s. There may be an overlap in electrons of a state in one shell with states in an adjacent shell, this can be found in d and f states as the energy of the 3d state is usually greater than that of a 4s (1).

Electrons configurations

Pauli exclusion principle states that any orbital can only hold up to 2 electrons and the two electrons in the same exact orbital will have opposite spin values, thus s, p, d, and f subshells may each accommodate respectively 2, 6, 10, and 14 electrons (Figure 5) (Table 1).

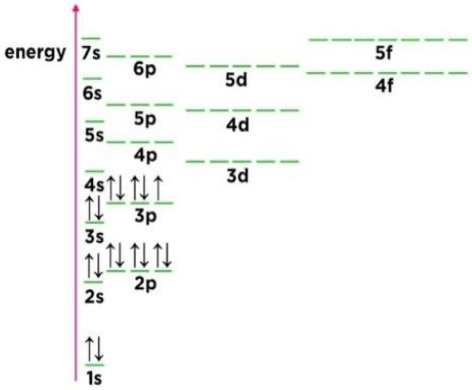
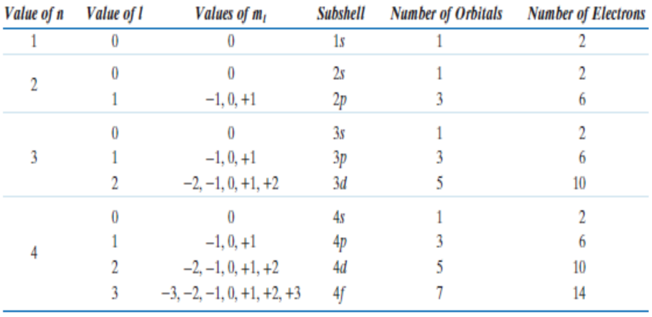


Figure 5: Electrons distribution in Cl.

Table 1: The relationships among the quantum numbers n, ℓ, m_ℓ, numbers of orbitals and electrons.



Value of n	*Value of l*	*Values of m_l*	*Subshell*	*Number of Orbitals*	*Number of Electrons*
1	0	0	1*s*	1	2
2	0	0	2*s*	1	2
	1	−1, 0, +1	2*p*	3	6
3	0	0	3*s*	1	2
	1	−1, 0, +1	3*p*	3	6
	2	−2, −1, 0, +1, +2	3*d*	5	10
4	0	0	4*s*	1	2
	1	−1, 0, +1	4*p*	3	6
	2	−2, −1, 0, +1, +2	4*d*	5	10
	3	−3, −2, −1, 0, +1, +2, +3	4*f*	7	14

At this point, it is important to know what valence electrons are. Valence electrons are those occupying the outermost shell. They determine which type of interatomic bonding will occur between atoms to form a molecule. When the valence shell is filled with 8 electrons except for helium which contains 2 1s electrons, the atom will have what is termed stable electron configuration as in neon and argon, so they are called noble gases or inert, which are unreactive chemically. Some atoms have unfilled valence shells, so they will gain, lose, or share electrons to reach the stable configuration (1).

Interatomic bonds

The process of gaining, losing, or sharing electrons forms strong primary atomic bonds, also called chemical bonds. The formation of primary bonds depends on the atomic structures and their tendency to reach a stable configuration. The molecules are held together by weak forces called secondary bonds.

Primary interatomic bonds

1- Ionic bonds

Ionic bonding is always formed between metals on the left side of the periodic table and non-metals on the right side of the periodic table (Figure 6). Metallic atoms lose their valence electrons to the non-metallic atoms so that all the atoms reach a stable configuration. The metal will acquire a positive charge and the non-metal will acquire a negative charge (Figure 7). The net energy of the formation of positive ions and negative ions is the sum of three terms. First, the energy needed to ionize the metal atoms. Second, the energy released when the metal loses the electrons to the non-metal. Third, the energy released due to attraction between the positive and negative ions (3).

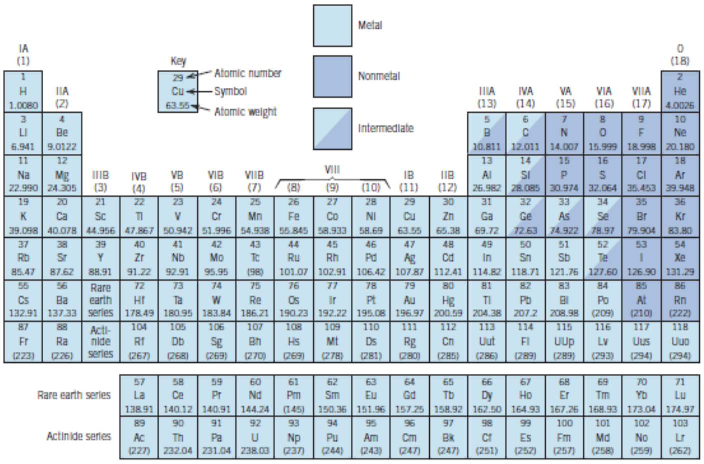


Figure 6: Periodic table of elements.

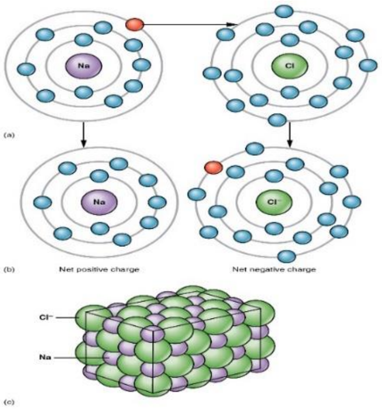


Figure 7: Ionic bonding in sodium chloride and formation of Na+ and Cl− ions.

Ionic bonding is considered nondirectional as the magnitude of the bond is equal in all directions around the ion. They have high bonding energies, reflected in their high melting temperature. Bonding energies range between 600 and 1500 KJ/mol (1) (Table 2). Ceramic materials are ionic bonded materials characterized by being hard, electrically, and thermally insulators due to the absence of free electrons or ions. Ceramic materials have high melting temperatures due to the presence of strong electrostatic force so a large amount of thermal energy is required to separate the ions. Ionic solids can conduct electricity in a liquid state.

Examples in dentistry: Ionic bonds exist in some dental materials such as gypsum structures, phosphate-based cement, and ceramics (4).

2- Covalent bonds

Although ionic bond occurs between atoms having a large difference in electronegativity, covalent bonding, is found between atoms having a small difference in electronegativity. For these materials, a stable state is reached by sharing electrons between adjacent atoms. A covalent bond is formed between two non-metallic atoms on the right side of the periodic table (Figure 6) (Figure 8).

A covalent bond is directional as it occurs between specific atoms and electrons are present in the direction between the two adjacent atoms. There is an overlapping of electron orbitals between the two adjacent bonding atoms. Bonding energies and melting temperatures for a few covalent bonded materials are presented in table 2.

Examples in dentistry: Covalent bonds exist in dental resin, where they link to form the backbone of hydrocarbon chains (4). Silica used in ceramics and investment materials is formed from covalent bonds.

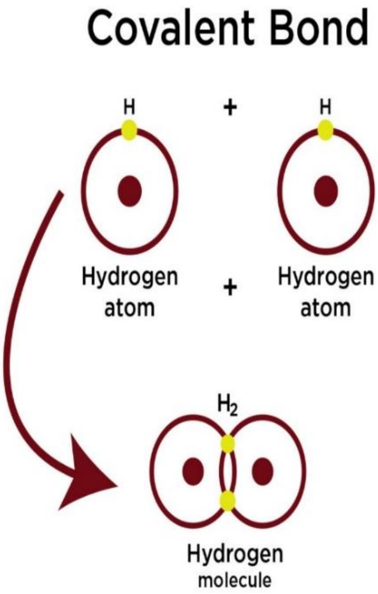
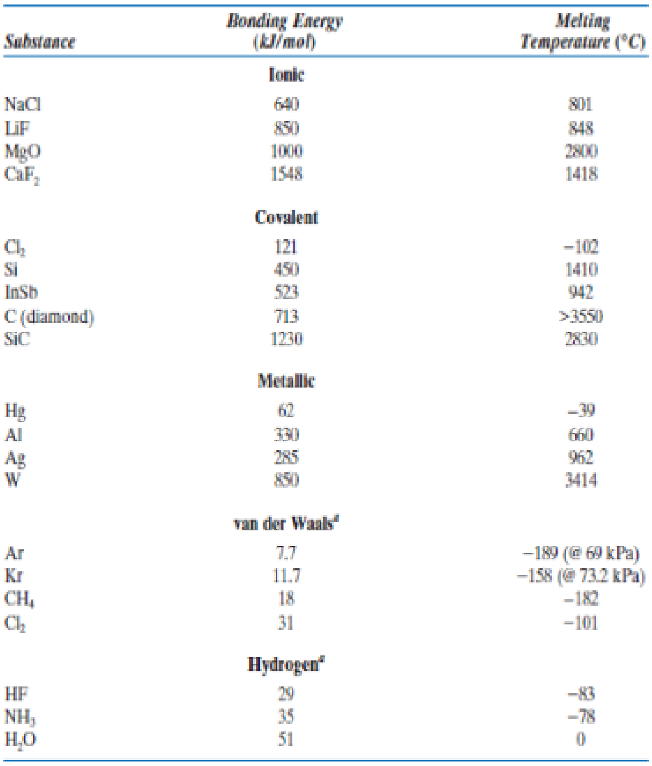


Figure 8: Example of a covalent bond in hydrogen molecule.

Table 2: Bonding Energies and melting temperature for various substances.



Substance	*Bonding Energy (kJ/mol)*	*Melting Temperature (°C)*
	Ionic	
NaCl	640	801
LiF	850	848
MgO	1000	2800
CaF_2	1548	1418
	Covalent	
Cl_2	121	−102
Si	450	1410
InSb	523	942
C (diamond)	713	>3550
SiC	1230	2830
	Metallic	
Hg	62	−39
Al	330	660
Ag	285	962
W	850	3414
	van der Waals[a]	
Ar	7.7	−189 (@ 69 kPa)
Kr	11.7	−158 (@ 73.2 kPa)
CH_4	18	−182
Cl_2	31	−101
	Hydrogen[a]	
HF	29	−83
NH_3	35	−78
H_2O	51	0

Bond hybridization in carbon

The covalent bonding of carbon and other non-metallic substances is associated with hybridization of two or more atomic orbitals so that more overlapping during bonding results.

When a carbon atom finds itself in a bonding situation, its bonding electrons themselves will exist at equivalent energies which requires that they hybridize to an energy that is intermediate between the 2s and 2p energies (Figure 9), and since the energy of these electrons is now changed, the shape of the orbitals they occupy are different as well which is called hybrid orbitals.

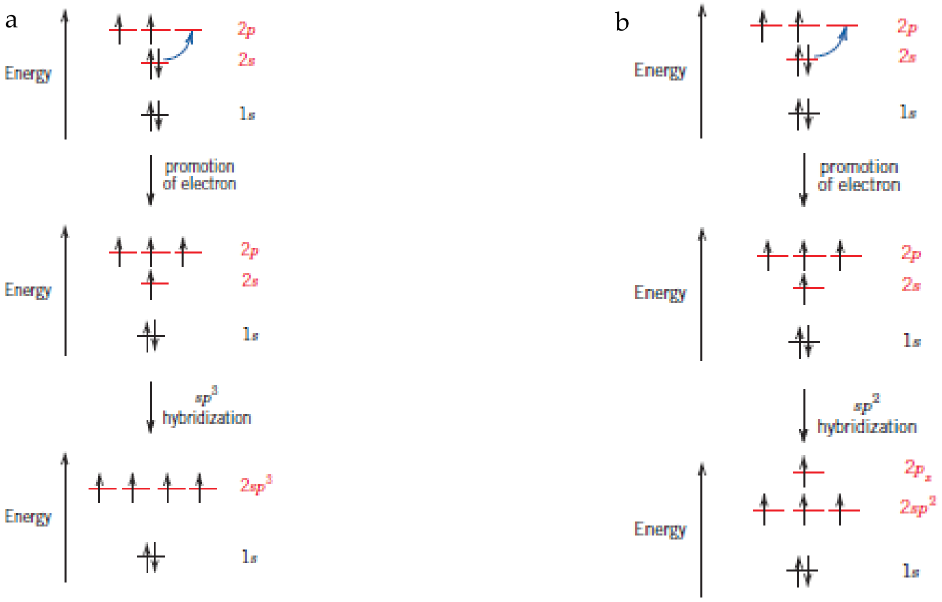


Figure 9: (a)The formation of $2sp^3$ hybrid orbitals and (b) $2sp^2$ hybrid orbitals.

Four $2sp^3$ hybrid orbitals are derived from combining the energies of one 2s orbital and three 2p orbitals (Figure 9 a). When hybridization occurs, the s and p orbitals cease to exist and $2sp^3$ orbitals exist having an entirely different shape, tetrahedral shape since all four $2sp^3$ orbitals are equivalent, each $2sp^3$ orbital repels the other with equal force, resulting in identical bond angles = 109.5° (1) (Figure 10).

In methane CH_4, when hydrogen atoms bind to carbon, each 1s orbital of hydrogen atom binds with carbon hybrid orbitals sp^3 (1) forming a sigma bond which represents the single covalent bond (Figure 11).

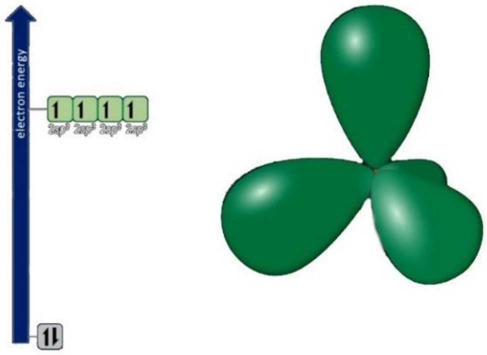


Figure 10: Four *sp*3 hybrid orbitals that point to the corners of a tetrahedron, the angle between orbitals is 109.5°.

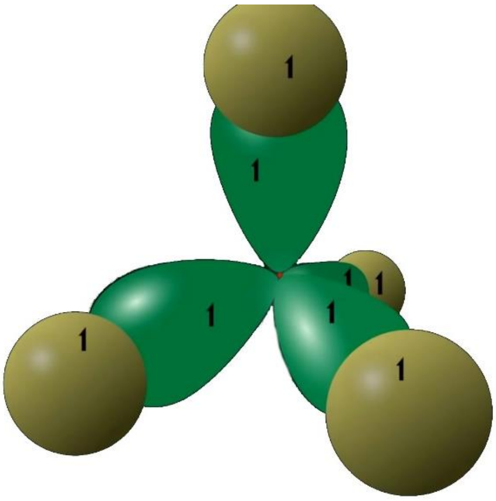


Figure 11: Schematic diagram that shows the bonding of carbon sp3 hybrid orbitals to the 1s orbitals of four hydrogen atoms in a molecule of methane (CH4).

In ethane C_2H_4, the C atom hybridizes one 2s orbital with two 2p orbitals forming 2 sp2 orbitals and one unhybridized 2p orbital. A pi bond will come from the side-to-side overlap of the unhybridized p orbitals, and a sigma bond will come from the head-to-head overlap of the $2sp^2$ hybrid orbitals, so double bonds contain sigma and pi bond ⁽⁵⁾ (Figure 12).

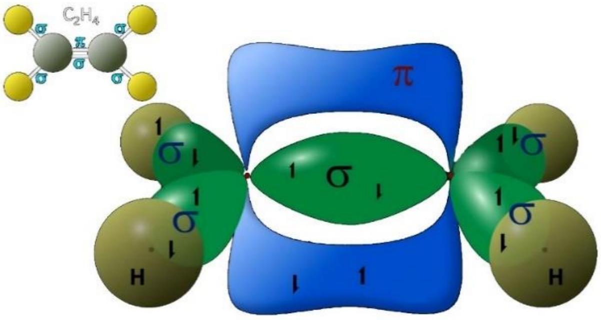


Figure 12: Schematic diagram that shows the bonding of carbon sp^2 hybrid orbitals to the 1s orbitals of four hydrogen atoms in a molecule of ethane (C_2H_4).

Sigma and pi bonds

A sigma bond is formed by the head-to-head overlap of bonding orbitals along the internuclear axis. This can be formed by any one of the following types of combination of atomic orbitals s-s, s-p, p-p ⁽⁵⁾.

During the formation of pi bonds, atomic orbitals overlap in such a way that their axis remains parallel to each other and perpendicular to the internuclear axis ⁽⁵⁾ (Figure 13).

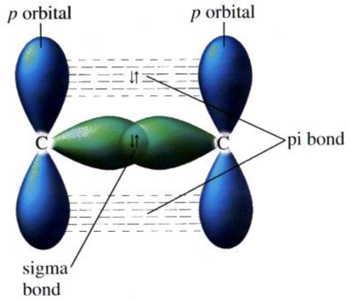


Figure 13: Sigma and pi bonds.

All single bonds are sigma bonds, while multiple bonds contain one sigma and the rest are pi bonds. The strength of a bond depends on the extent of overlapping of orbitals, so sigma bonds are stronger than pi bonds since maximum overlapping is formed along the internuclear axis and this will lead to higher bonding energy (5).

Diamond and graphite are both allotropic forms of carbon and are formed of inter-atomic covalent bonds. Although diamond is one of the hardest-known materials in nature, graphite is relatively soft. In addition, diamond is a poor conductor of electricity, but graphite is a reasonably good conductor. In diamond, each carbon atom has undergone sp^3 hybridization so that it bonds to four other carbon atoms by strong single covalent bonds (sigma bonds) forming a tetrahedral crystal that can be destroyed only by the rupture of many strong bonds. Thus, the extreme hardness, the high melting temperature, and the insulating properties are all consequences of the crystal structure of the diamond (1) (Figure 14).

For the graphite structure, sp^2 hybrid orbitals bond each carbon atom to three other adjacent and coplanar carbon atoms in a hexagonal crystal, inter-layer bonds are perpendicular to these planes and are weak van der Waal forces which give the graphite its slippery property. The unhybridized $2p_z$ orbital is oriented perpendicular to the plane containing sp^2 hybrid orbitals and forms a pi bond with the adjacent $2p_z$ orbital of another carbon atom. The electrons in the pi bond of the un-hybridized orbitals are delocalized (1), they are free to move through the carbon atoms of graphite, thus graphite is considered a semi-conductor material (Figure 15).

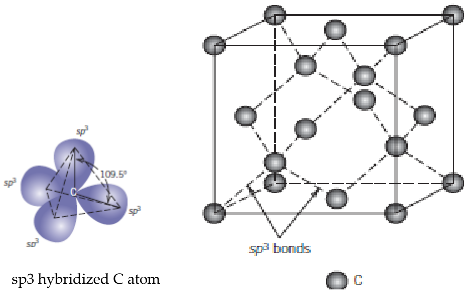


Figure 14: A unit cell for the diamond cubic crystal.

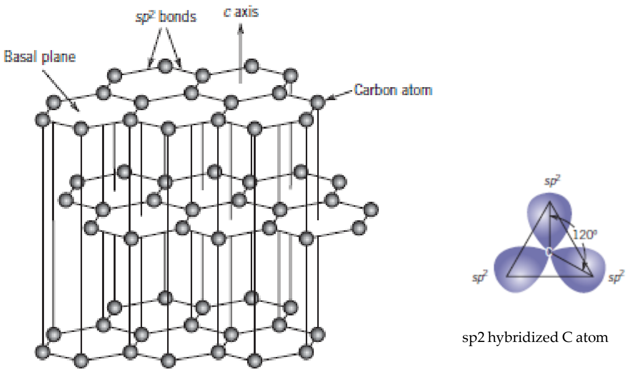


Figure 15: The structure of graphite.

Metallic bonds

The third type of primary atomic bonding is the metallic bond. The valence electrons in metals can be removed easily forming positive ions and the electron cloud. The electrostatic attraction between the electron cloud and positive ions will form the metallic bond (Figure 16).

The properties of metals occur as a consequence of the presence of free electrons. The free electrons make the metal highly thermal and electrically conductive. Metals are opaque and lustrous. The metallic bonds are responsible for the ability of metals to deform plastically. Bonding energies and melting temperatures for several metals are listed in table 2.

Examples in dentistry: Metallic bonds exist in amalgam restorations and dental implants.

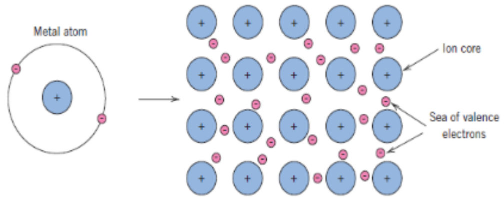


Figure 16: Metallic bonding.

Mixed bonding

The mixed bonds are illustrated in a bonding tetrahedron as shown in figure 17. Actually, for many real materials, more than one type of bond is present.

1- Mixed covalent-ionic bonds show some of the ionic characters to the covalent bond and some of the covalent characters to the ionic bond. The degree of each bond type depends on the difference in their electronegativities, the greater the difference in electronegativity, the more ionic is the bond. The smaller the difference in electronegativity, the greater is the degree of covalent bond. Percent ionic character of a bond between element A and B where A has higher electronegativity may be expressed by the following equation:

$$\%IC= \{1 - \exp[-(0.25)(X_A - X_B)2]\} \times 100 \quad (1)$$

Where X_A and X_B are the electronegativities for the respective elements.

2- Mixed covalent-metallic bond is called metalloids and their properties are intermediate between metals and non-metals.

3- Mixed metallic-ionic bonds present in compounds composed of metals having a large difference in electronegativity. The larger the difference in electronegativity, the greater the degree of ionic characters.

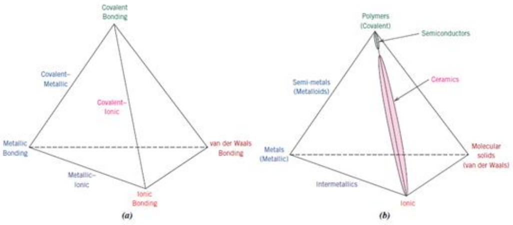
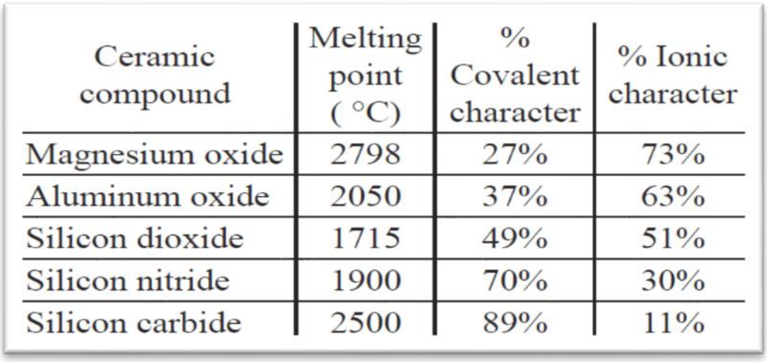


Figure 17: Bonding tetrahedron, each bond is located at one corner and three mixed bonding types are located along tetrahedron edges.

Examples in dentistry:

- Dental ceramics is a mixed ionic and covalent bond. The degree of presence of each bond depends on ionic character %. If there is an increase in ionic character %, the bond will be more ionic and if there is a decrease in ionic character %, the bond will be more covalent (6) (Table 3).
- Calcium sulfate, present in gypsum products is a mixture of both ionic and covalent bonds. The sulfur and oxygen atoms in sulfate ion(SO_4^{2-}) bonded covalently but they need two electrons to be stable, so they react with calcium which contains two electrons that can be easily removed, so an ionic bond is formed between Ca^{+2} ion and SO_4^{2-} ion (4).

Table 3: ionic character % of dental ceramic material.



Ceramic compound	Melting point (°C)	% Covalent character	% Ionic character
Magnesium oxide	2798	27%	73%
Aluminum oxide	2050	37%	63%
Silicon dioxide	1715	49%	51%
Silicon nitride	1900	70%	30%
Silicon carbide	2500	89%	11%

Secondary bonds

There are two types of molecules according to the difference in electronegativity of the constituent atoms; polar molecules where the unequal sharing of electrons induces permanent dipoles as in HCl and nonpolar molecules where there is an equal sharing of electrons as in methane. The random movement of electrons within the nonpolar molecule creates fluctuating dipoles.

Secondary bonds are intermolecular physical bonds. They arise from atomic or molecular dipoles either fluctuating induced dipole bonds (Van der Waals forces) or polar molecule-induced dipole bonds, permanent dipole bonds, and hydrogen bonds.

Secondary bonds are weak bonds in comparison to primary bonds but influence the physical properties of some materials. Bonding energies range between 4 & 30 KJ/mole (1). The magnitude of the hydrogen bond is generally greater than that of the other types of secondary bonds and may be as high as 51 kJ/mol. Bonding energies and melting temperatures of various molecular solids are present in table 2.

In dentistry, all polymer-based materials contain secondary bonds such as acrylic resin denture bases, artificial teeth, endodontic fillings, and resin composite restorative materials.

Interatomic bond distance and thermal energy

Bonding Force

Between any two atoms, two types of forces exist; forces of attraction drawing the two atoms together and forces of repulsion pushing them apart. Attraction forces (F_A) depend on the particular type of bonding that exists between the two atoms. Repulsive forces (F_R) occur due to interaction between negatively charged electron clouds for the two atoms when their orbitals begin to overlap.

At large distances, the atoms are too far apart to have an influence on each other, so interactions are negligible. However, at small separation distances, both attraction and repulsive forces increase. The sum of both attraction and repulsive forces will give the net force (F_N) acting on the two atoms.

$$F_N = F_A + F_R \tag{1}$$

When the two atoms are far apart, F_A will exceed F_R so the net force will be an attraction force. However, when the two atoms are much closer, F_R will exceed F_A and the net force will be a repulsion force (4).

Interatomic bond distance

When F_A and F_R are equal in magnitude and opposite in sign, the net force will be zero and a state of equilibrium will exist. The interatomic distance at equilibrium (r_0) represents the distance between the centers of two adjacent atoms (Figure 18). For many atoms, r_0 is approximately 0.3nm (1). consequently, as atomic bonds are stretched, atoms tend to attract each other, and as the bonds are compressed, atoms tend to repel each other (7).

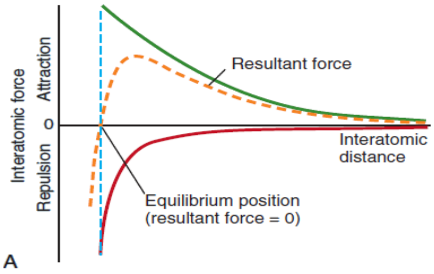


Figure 18: Relation of interatomic forces to interatomic bond distance.

<u>The correlation between the shape of the force-interatomic distance curve and the modulus of elasticity</u>:

The slope for a relatively stiff material at the $r = r_0$ position on the curve will be quite steep; however, the slopes are shallower for more flexible materials (1) (Figure 19).

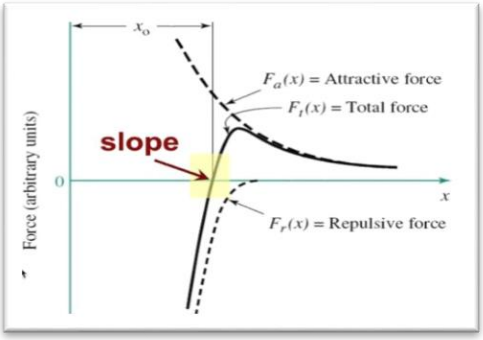


Figure 19: The slope at r = r_0 indicates the material’s modulus of elasticity.

Bonding energy

The conditions of equilibrium are more related to energy factor than to interatomic distance. Mathematically, energy (E) and force (F) are related where the integration of the interatomic force over the interatomic distance yield the interatomic energy.

$$E = \int F\, dr \qquad (1)$$

And, for atomic systems,

$$\begin{aligned} E_N &= \int_r^{\infty} F_N\, dr \\ &= \int_r^{\infty} F_A\, dr + \int_r^{\infty} F_R\, dr \\ &= E_A + E_R \end{aligned} \qquad (1)$$

in which E_N, E_A, and E_R are, respectively, the net, attractive, and repulsive energies for two isolated and adjacent atoms.

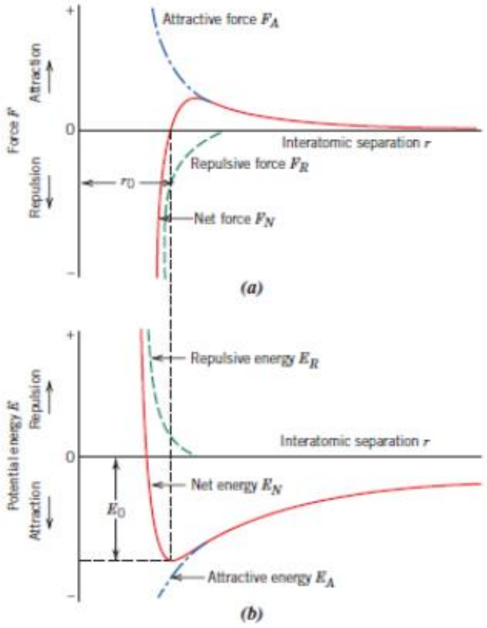


Figure 20: (*a*) The dependence of forces on interatomic separation for two isolated atoms.

(*b*) The dependence of potential energies on interatomic separation for two isolated atoms.

Figure(20 b) describes the attractive, repulsive, and net potential energies in relation to the atomic distance between two atoms. The net curve is the sum of attractive and repulsive curves. Beginning at the right edge of the curve, the atoms are far apart, the interactions are negligible, so potential energy = 0. As they move closer to each other, their 1s orbitals begin to overlap allowing each electron to interact with the proton of the other atom, and energy decreases until an ideal inter-nuclear distance is reached. This decrease in potential energy occurs because each electron is interacting with the protons of the two nuclei. As the potential energy decreases, the stability increases. Bonding energy at E_0 corresponds to energy at r_0, this is a stabilizing and energetically favorable situation. E_0 represents the energy required to separate these two atoms to an infinite separation, E_0 also shows why bond formation is an exothermic reaction because there will always be a decrease in potential energy as a result of orbital overlap and that difference in energy must be released to the environment, so the energy is absorbed to break the bond, and energy is evolved as bonds are made (8).

If we continue to push the protons together, the situation becomes less favorable due to cumulative proton-proton repulsion and electron-electron repulsion which will quickly begin to outweigh any attraction and the curve will rise steeply to the left.

Thermal energy

The atoms at a temperature above zero are in a constant state of vibration. The vibration of the atoms occurs between two positions and the mean interatomic distance is calculated (Figure 21).

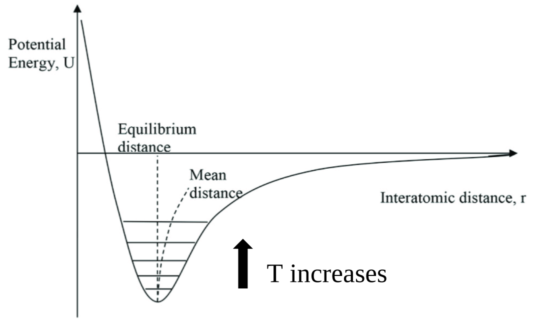


Figure 21: The mean interatomic distance.

As the temperature increases, the mean interatomic distance increases due to the asymmetry of the energy-interatomic distance curve, if the curve was symmetrical, there would be no change in the mean interatomic distance and this increase in mean interatomic distance is less with deeper energy trough than that in shallower energy trough (4) (Figure 23).

The correlation between the energy-interatomic distance curve and the melting temperature of the materials:

The magnitude of the bonding energy and the shape of the energy-interatomic separation curve varies from material to material. Many material properties depend on the curve shape and bonding type.

For example, materials having large bonding energy will have a high melting temperature (1) (table 2) (Figure 22). A greater slope of the force curve implies a narrower and deeper trough in the energy curve; Hence, a high melting point is usually associated with greater stiffness (4).

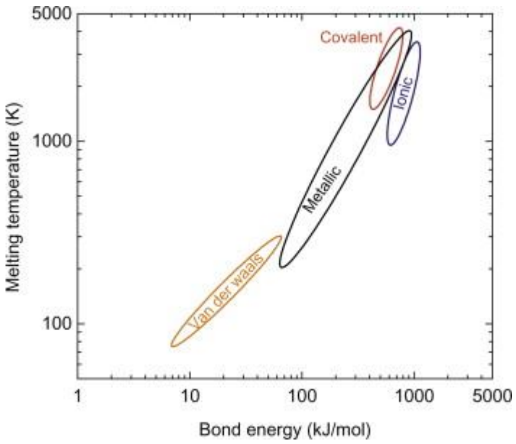


Figure 22: Melting temperature plotted against interatomic bond energy showing the ranges of different interatomic bonds.

The correlation between the energy-interatomic distance curve and coefficient of thermal expansion:

A deep and narrow trough which typically occurs for materials having large bonding energies normally correlates with less change in mean interatomic distance upon temperature changes than the shallow curve. The change in the interatomic distance will lead to thermal expansion. This means that the coefficient of thermal expansion in a deep and narrow trough is less than in a shallow trough, and the linear coefficient of thermal expansion for materials having similar atomic structures is inversely proportional to the melting temperature (4) (Figure 23).

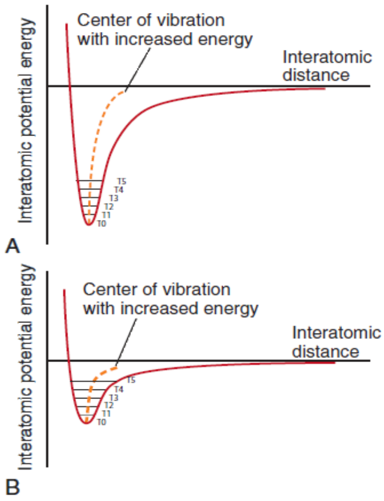


Figure 23: A represents a deep energy trough. B represents a shallow energy trough.

If the temperature continues to increase, the increase of interatomic distance will result in a change in the state of the material from solid to liquid and then to gas. There is a correlation between the magnitude of bonding energy and the state of materials; solids have large bonding energy (deeper trough depth) which corresponds to higher melting and boiling temperatures, while gases have small energies, and liquids tend to have intermediate energies (4) (7).

Conclusion

The bonding energy determines many physical and mechanical properties of the materials. Different atomic orbitals will overlap in different ways, so different amounts of energy will be released upon their formation. The greater the orbitals overlap, the stronger the bond between the two atoms, and the greater is the minimum potential energy (E_0).

A deep and narrow energy trough occurs in materials having large bonding energies, high melting temperatures, high stiffness, and a low coefficient of thermal expansion (Figure 24).

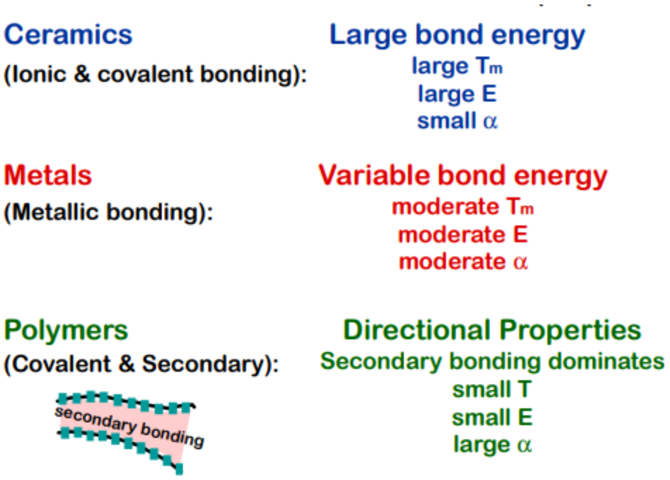


Figure 24: Interatomic bonding and materials properties where Tm is melting temperature, E is the modulus of elasticity, and α is coefficient of thermal expansion.

References:

(1) Callister Jr WD, Rethwisch DG. Callister's materials science and engineering (10th ed.). John Wiley & Sons; 2020 Feb 5; chapter 2, page 19.

(2) Is the Bohr model consistent with the Heisenberg Uncertainty Principle? – MassInitiative. (2020d, January 20). Retrieved 21 October 2022, from https://massinitiative.org/is-the-bohr-model-consistent-with-the-heisenberg-uncertainty-principle/

(3) Atkins, P. W. (2022, September 29). chemical bonding | Definition, Types, & Examples. Encyclopedia Britannica. Retrieved 21 October 2022, from https://www.britannica.com/science/chemical-bonding

(4) Anusavice KJ, Shen C, Rawls HR, editors. Phillips' science of dental materials (12th ed.). Elsevier Health Sciences; 2012 Sep 27; Chapter 2, page 17.

(5) General Data Protection Regulation (GDPR) Guidelines BYJU'S. (2021b, March 22). BYJUS. Retrieved 21 October 2022, from https://byjus.com/jee/sigma-and-pi-bond/

(6) Subedi, M. M. (2013, December 23). Ceramics and its Importance | Himalayan Physics. Retrieved 21 October 2022, from https://www.nepjol.info/index.php/HP/article/view/9433

(7) Chapter 2. Atomic Structure and Interatomic Bonding. (n.d.).Retrieved 21 October 2022,from https://web.eng.fiu.edu/wangc/EGN3365-2b.pdf

(8) chemical reaction | Definition, Equations, Examples, & Types. (2020, November 4). Encyclopedia Britannica. Retrieved 21 October 2022, from https://www.britannica.com/science/chemical-reaction/The-conservation-of-matter