Materials Science

Lecture 4

Lebanese University - Faculty of Engineering – Branch 3

Fall 2022

Dr. Ali HARKOUS

Contents

Lecture 4:

Chap2: Atomic Structure & Bonding

2.2. The Ionic Bond

Three different types of primary or chemical bond are found in solids:

Primary Bond
- Ionic
- Covalent
- Metallic

Secondary Bond
- Van der Waals

2.2. The Ionic Bond

- For each type of **primary bond**, the bonding necessarily **involves** the **valence electrons**.

- The **nature of the bond depends** on the **electron structures** of the constituent atoms. In general, each of these three types of bonding arises from the **tendency of the atoms to assume stable electron structures**, like those of the **inert gases**, by completely filling the outermost electron shell.

- **Secondary or physical forces** and energies are also found in **many solid materials**; they are **weaker** than the primary ones but **nonetheless influence** the **physical properties** of some materials.

- **Ionic bonding** is perhaps the **easiest to describe and visualize**. It is always found in compounds composed of both **metallic** and **nonmetallic** elements, elements situated at the **horizontal extremities of the periodic table.**

- Atoms of a **metallic element easily give up their valence electrons** to the **nonmetallic atoms**.

- In the process, all the **atoms acquire stable or inert gas configurations** (i.e., completely filled orbital shells) and, **in addition**, an **electrical charge**—that is, they become **ions**.

2.2. The Ionic Bond

◉ **Sodium chloride (NaCl)** is the **classic ionic material**. A sodium atom can assume the electron structure of neon (and a net single positive charge with a reduction in size) by a **transfer** of its one valence **3s electron** to a chlorine atom. After such a transfer, the chlorine ion acquires a net negative charge, an electron configuration identical to that of argon; it is also larger than the chlorine atom.
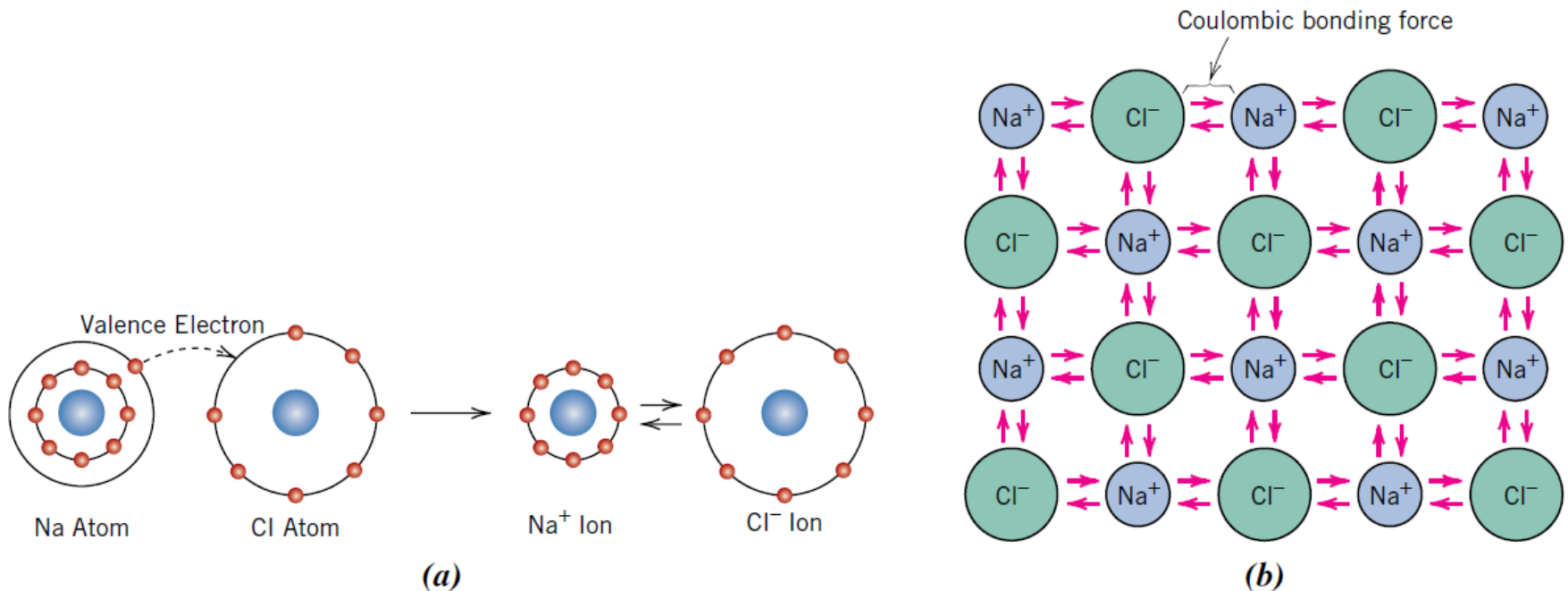
Schematic representations of (*a*) the formation of Na and Cl ions and (*b*) ionic bonding in sodium chloride (NaCl)

2.2. The Ionic Bond

Coulombic force

◉ The **attractive bonding forces are coulombic**—that is, **positive** and **negative ions**, by virtue of their net electrical charge, attract one another.

◉ For **two isolated ions**, the attractive energy E_A is a **function of the interatomic distance** according to:

$$E_A = -\frac{A}{r}$$

◉ **Theoretically**, the constant **A** is equal to:

$$A = \frac{1}{4\pi\epsilon_0}(|Z_1|e)(|Z_2|e)$$

2.2. The Ionic Bond

Coulombic force

$$A = \frac{1}{4\pi\epsilon_0}(|Z_1|e)(|Z_2|e)$$

- Here ϵ_0 is the **permittivity of a vacuum (8.85 X 10^{-12} F/m), $|Z_1|$ and $|Z_2|$** are **absolute values** of the **valences** for the two ion types, and *e* is the **electronic charge** (**1.602 X 10^{-19}C**).

- The value of **A assumes the bond between ions 1 and 2** is <u>totally</u> ionic.

- Inasmuch as bonds in most of these materials are **not 100% ionic**, the value of **A is normally determined from experimental** data rather than computed using the above equation.

2.2. The Ionic Bond

Coulombic force

◉ An **analogous equation** for the **repulsive energy** is:

$$E_R = \frac{B}{r^n}$$

◉ **B and n are constants** whose values **depend** on the **particular ionic system**. The value of **n is approximately 8**.

◉ **Ionic bonding** is termed **nondirectional**—that is, the **magnitude** of the bond is **equal in all directions** around an ion.

◉ It follows that for **ionic materials to be stable**, all **positive ions** must have as **nearest** neighbors **negatively charged** ions **in a three-dimensional scheme**, and vice versa.

2.2. The Ionic Bond

- For ionic bond, **Bonding energies**, which generally range **between 600 and 1500 kJ/mol**, are relatively **large**, as reflected in **high melting temperatures**.

- **Interatomic bonding** is typified by **ceramic materials**, which are characteristically **hard** and **brittle** and, furthermore, **electrically** and **thermally insulative**.

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

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2.3. The Covalent Bond

⊙ A second bonding type, **covalent bonding**, is found in materials whose atoms have **small differences in electronegativity**—that is, that lie **near one another** in the **periodic table**.

⊙ For these materials, stable electron configurations are assumed by the **sharing of electrons** between **adjacent atoms**. Two covalently bonded atoms will each contribute at least one electron to the bond, and the **shared electrons may be considered to belong to both atoms.**

⊙ Covalent bonding is schematically illustrated in the figure for a molecule of **hydrogen (H_2)**. The hydrogen atom has a single **1s electron**. Each of the atoms can acquire a **helium electron configuration (two 1s valence electrons)** when they share their single electron (right side of the figure).
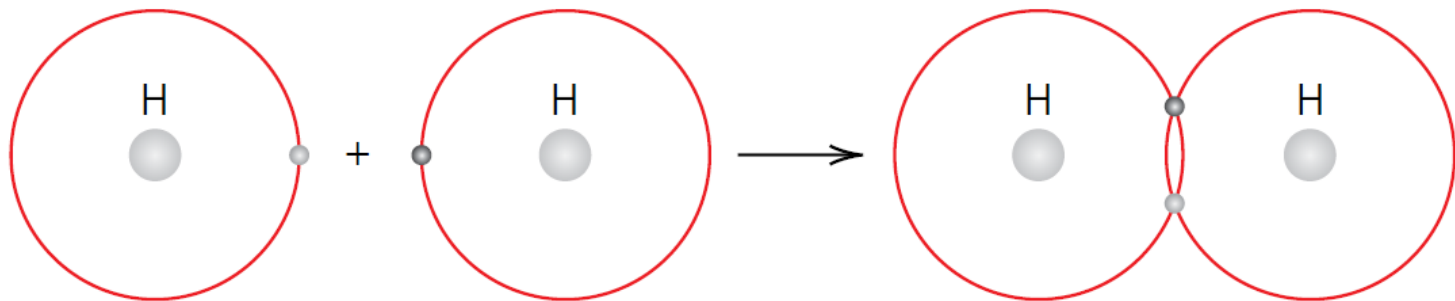
2.3. The Covalent Bond
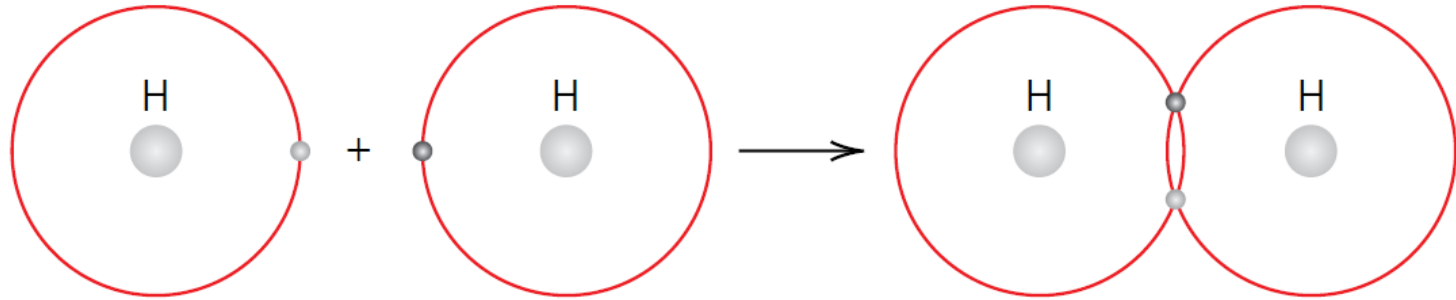
- ☉ Furthermore, there is an **overlapping of electron orbitals** in the region **between the two bonding atoms.**

- ☉ In addition, the **covalent bond** is **directional**—that is, it is **between specific atoms** and may exist only in the direction between one atom and another that participates in the electron sharing.
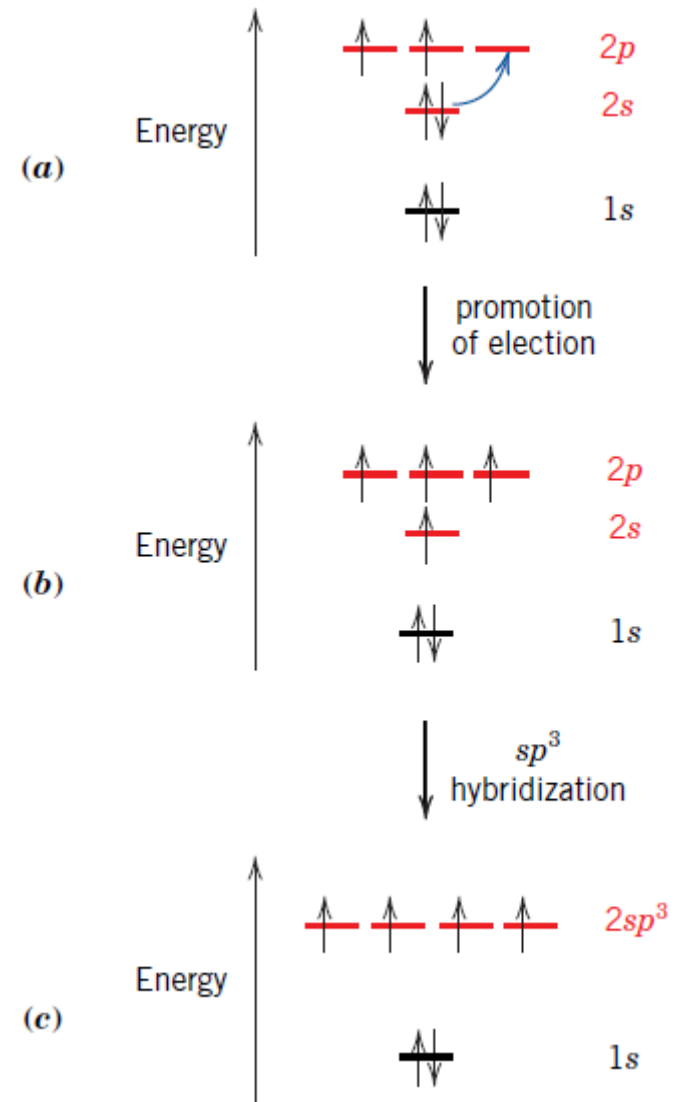
2.3. The Covalent Bond

- **Many nonmetallic elemental molecules** (e.g., Cl_2, F_2), as well as **molecules containing dissimilar atoms**, such as CH_4, H_2O, HNO_3, and HF, are **covalently bonded**.

- Furthermore, this type of bonding is found in **elemental solids** such as **diamond** (**carbon**), **silicon**, and **germanium** and other solid compounds composed of elements that are located on the **right side of the periodic table**, such as **gallium** arsenide (**GaAs**), indium antimonide (**InSb**), and silicon carbide (**SiC**).

- Covalent bonds may be **very strong**, as in **diamond**, which is **very hard** and has a **very high melting temperature**, **3550°C** (6400°F), or they may be **very weak**, as with **bismuth**, which **melts** at about **270°C** (518°F).

- Inasmuch as electrons participating in covalent bonds are **tightly bound** to the bonding atoms, most covalently bonded materials are **electrical insulators**, or, in some cases, **semiconductors.**

- **Mechanical behaviors** of these materials **vary widely**: some are **relatively strong**, others are **weak**; some fail in a **brittle** manner, whereas others experience **significant amounts of deformation** before failure. It is **difficult to predict** the mechanical properties of covalently bonded materials.

2.3. The Covalent Bond

Bond Hybridization in Carbon

- Often associated with the covalent bonding of carbon, the phenomenon of hybridization is the **mixing** (or combining) of **two or more atomic orbitals** with the result that **more orbital overlap during bonding results.**

- **For example:** Consider the electron configuration of **carbon**: $1s^2 2s^2 2p^2$. Under some circumstances, one of the **2s orbitals is promoted to the empty 2p orbital**, which gives rise to a $1s^2 2s^1 2p^3$ configuration.

- Furthermore, the **2s and 2p orbitals can mix** to **produce four sp³ orbitals that are equivalent** to one another, have **parallel spins**, and are **capable** of **covalently bonding with other atoms**.
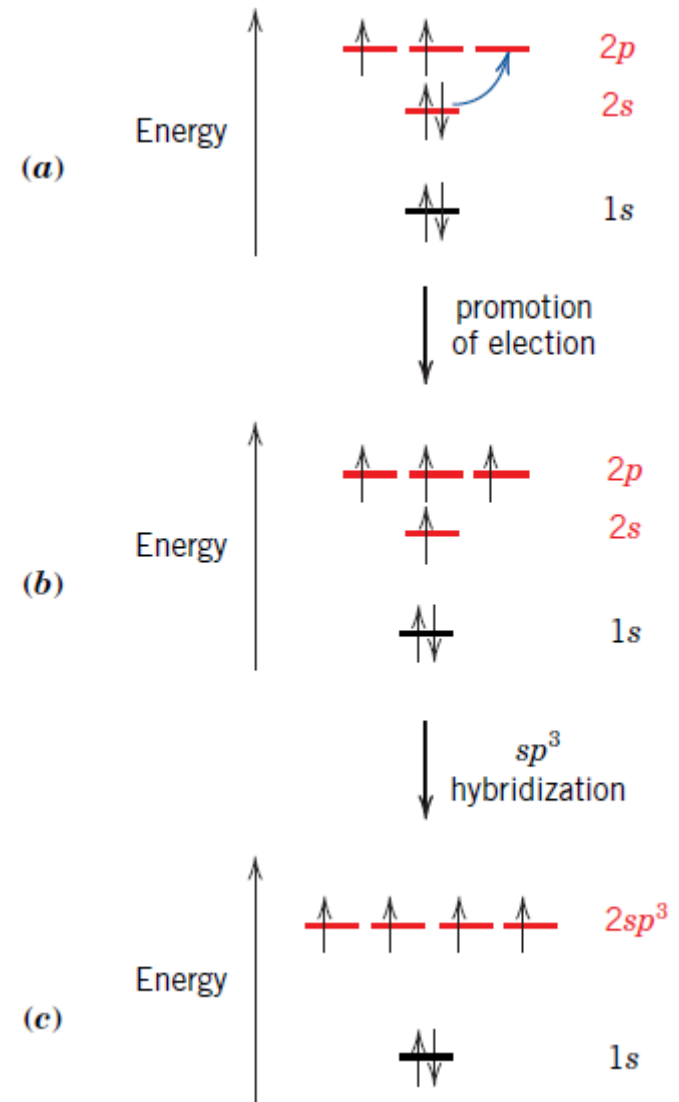
Bond Hybridization in Carbon

⦿ This orbital mixing is termed hybridization, here, **each sp^3 orbital contains one electron**, and, therefore, is **half-filled**.
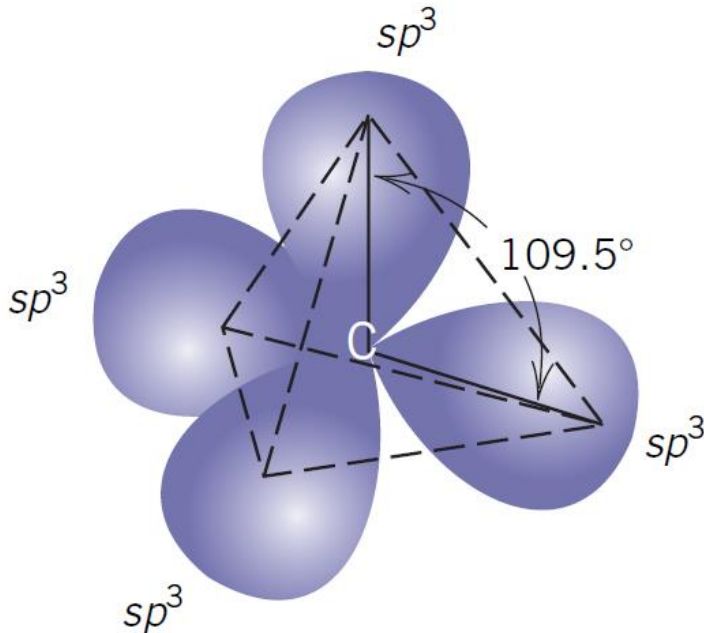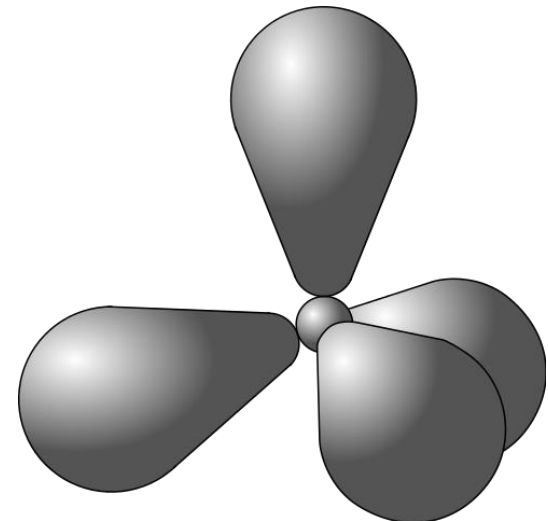
2.3. The Covalent Bond

Bond Hybridization in Carbon

◉ **Bonding hybrid orbitals** are **directional in nature**—that is, <u>**each extends to and overlaps the orbital of an** **adjacent** **bonding atom**</u>.

◉ Furthermore, for **carbon**, **each** of its four **sp³ hybrid orbitals** is **directed symmetrically** from a carbon atom to the vertex of a **tetrahedron**.

◉ The **angle** between each set of **adjacent bonds** is **109.5°**.

Schematic diagram showing four sp³ hybrid orbitals that point to the corners of a tetrahedron

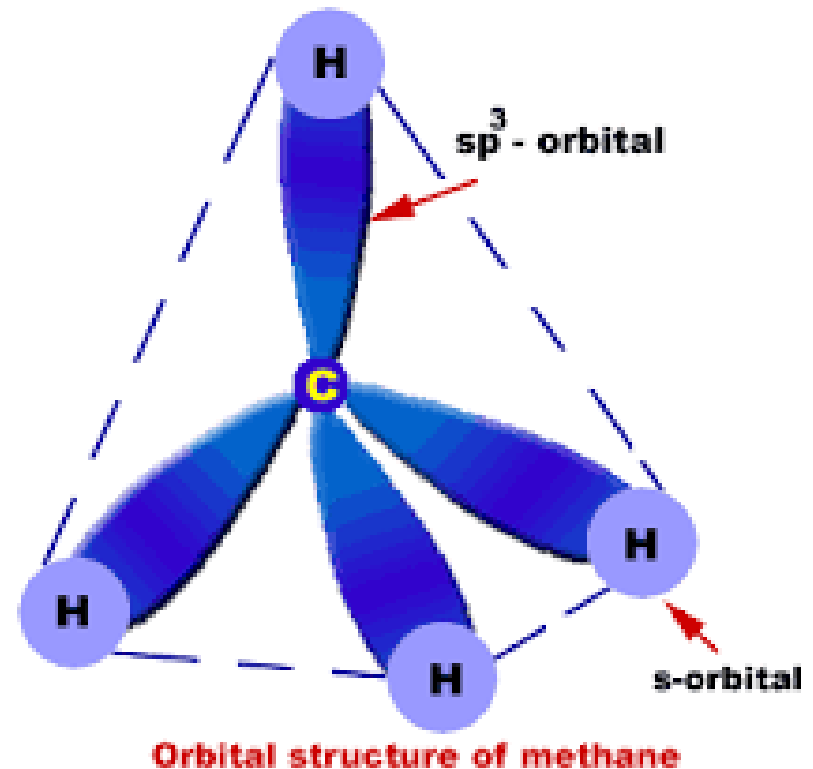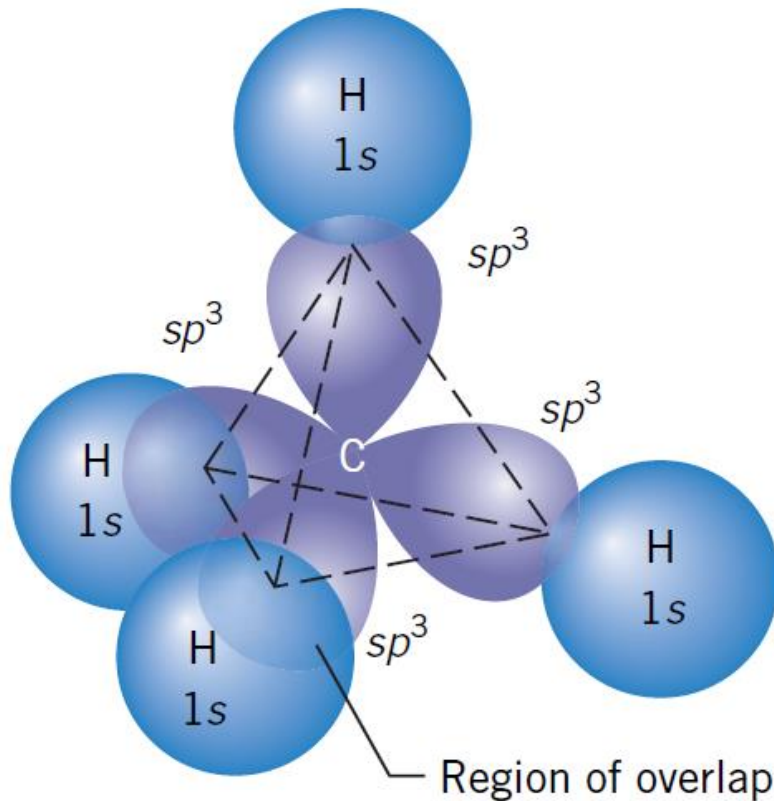## Bond Hybridization in Carbon

◉ The bonding of **sp^3 hybrid orbitals** to the **1s orbitals of four hydrogen atoms**, as in a molecule of **methane (CH_4)**, is presented in the figure.

Orbital structure of methane

2.3. The Covalent Bond

Bond Hybridization in Carbon

◉ For **diamond**, its carbon atoms are bonded to one another with **sp3 covalent hybrids**—**each atom is bonded to four other carbon atoms**.

◉ **The crystal structure for diamond** is shown in the figure. Diamond's carbon–carbon bonds are **extremely strong**, which accounts for its **high melting temperature** and **ultrahigh hardness**.
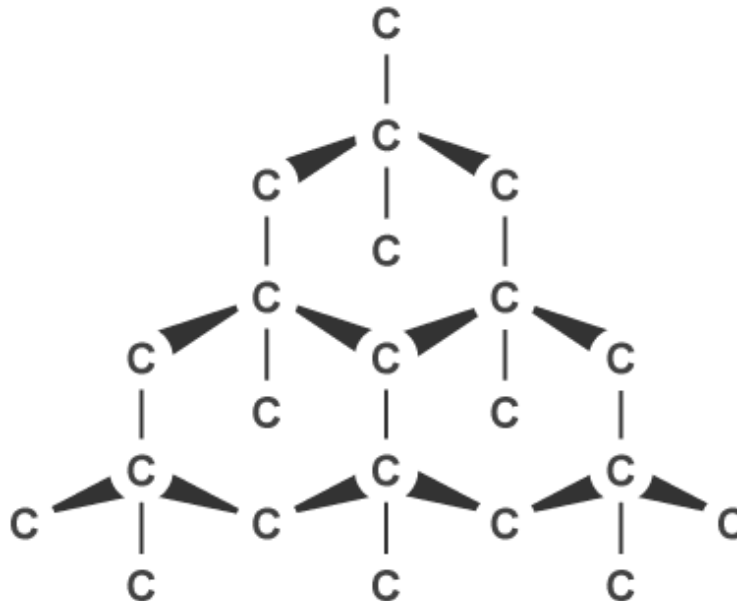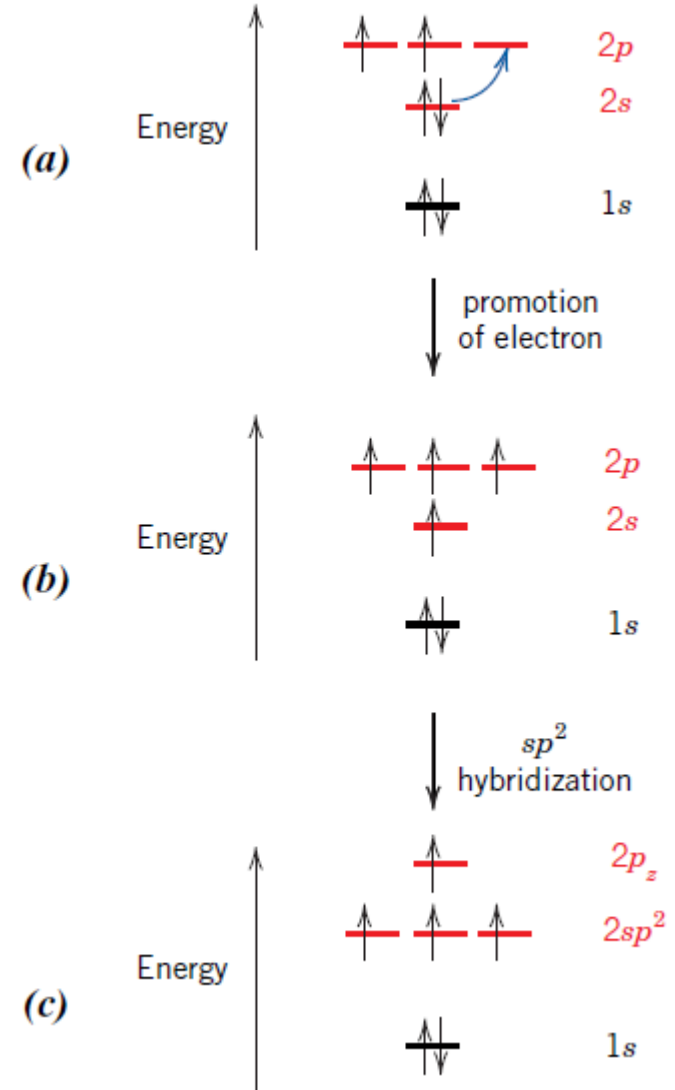
2.3. The Covalent Bond

SP^2 Bond Hybridization in Carbon

- ◉ **Other types** of **hybrid bonds** are possible for **carbon, as well as other substances**. One of these is **sp^2**, in which an **s orbital and two p orbitals are hybridized.**

- ◉ To achieve this configuration, **one 2s** orbital **mixes** with **two of the three 2p orbitals**—the third **p orbital remains unhybridized**;

- ◉ Here, **2p$_z$** denotes the **unhybridized p orbital**.

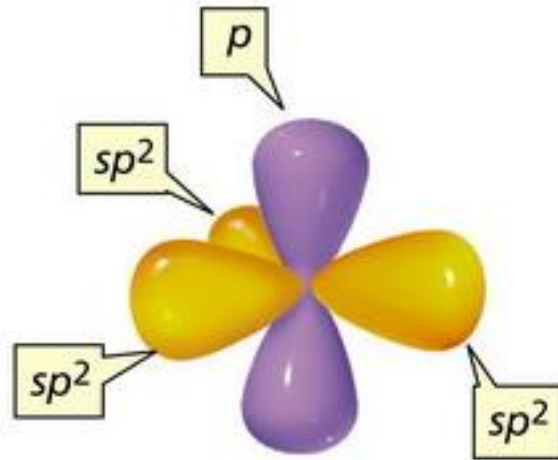# 2.3. The Covalent Bond

SP² Bond Hybridization in Carbon

- **Three sp² hybrids belong to each carbon atom**, which lie in the same plane such that the angle between adjacent orbitals is **120°**; lines drawn from one orbital to another form a **triangle**.

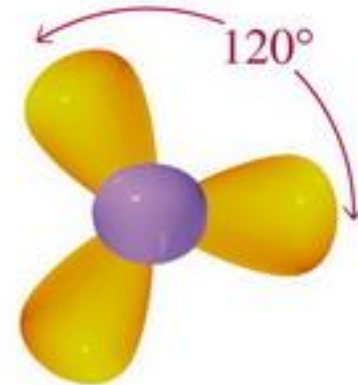- Furthermore, the **unhybridized 2p$_z$ orbital is oriented perpendicular to the plane containing the sp² hybrids.**
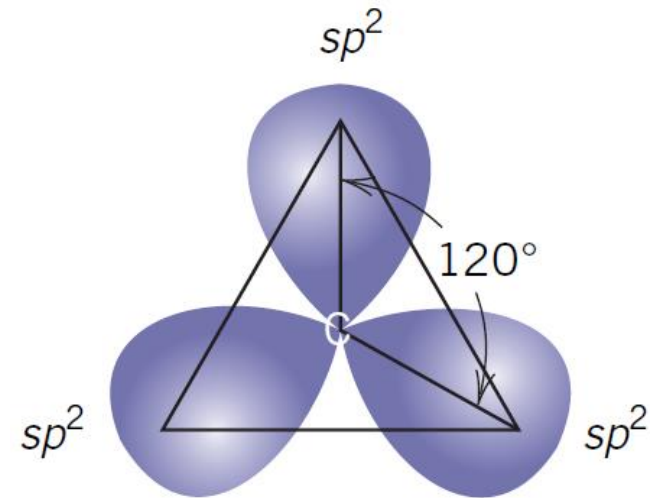
2.3. The Covalent Bond
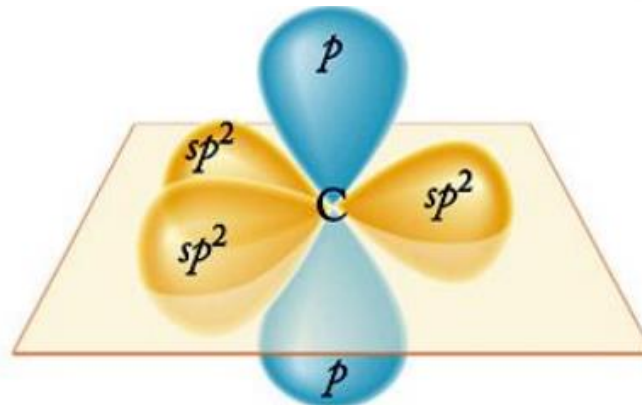
SP² Bond Hybridization in Carbon

side view
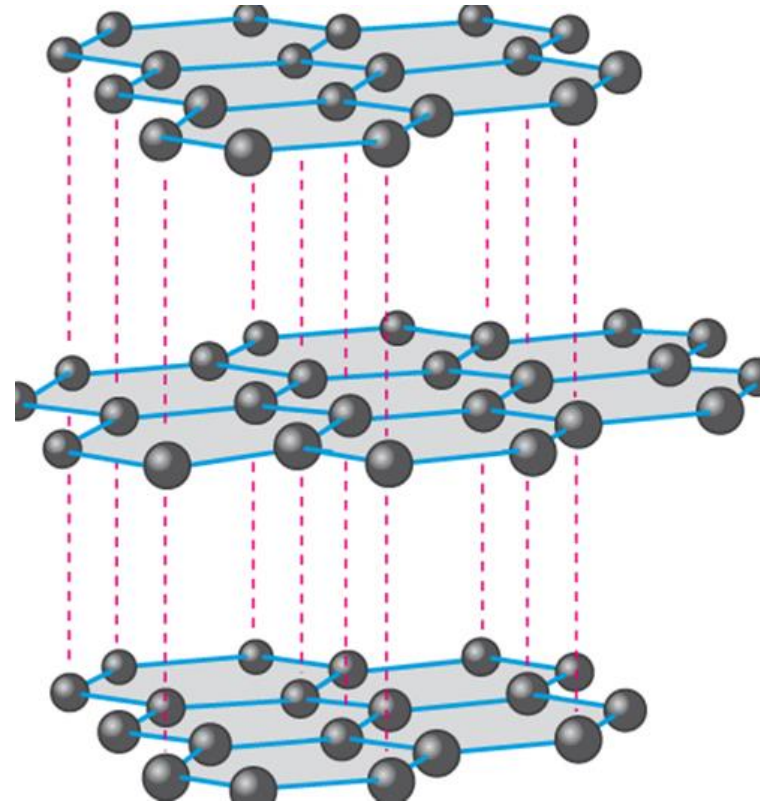
top view

SP² Bond Hybridization in Carbon

- These **sp² bonds** are found in **graphite**, **another form of carbon,** which has a structure and **properties distinctly different** from those of diamond.

- Graphite is composed of **parallel layers** of **interconnecting hexagons**.

Graphite

2.3. The Covalent Bond

SP² Bond Hybridization in Carbon

⊙ **Hexagons** form **planar sp² triangles** that bond to one another in the manner presented in the figure —a **carbon atom is located at each vertex**.

⊙ In-plane **sp² bonds are strong**; by way of **contrast**, **weak interplanar bonding results from van der Waals forces** that **involve electrons originating from the unhybridized 2pᶻ orbitals**.
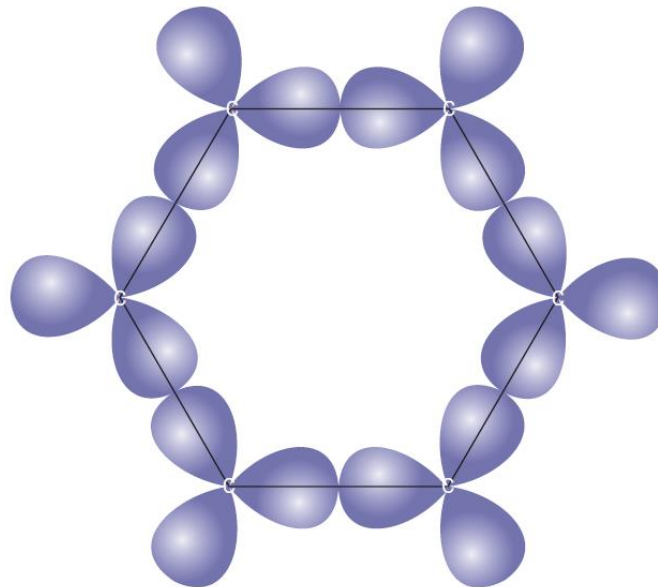
Graphite

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2.4. The Metallic Bond

- **Metallic bonding**, the final primary bonding type, is found in **metals** and **their alloys**.

- A relatively **simple model has been proposed** that very nearly approximates the bonding scheme. With this model, these **valence electrons are not bound** to **any particular atom** in the solid and are more or less **free to drift** throughout the entire metal.

- They may be thought of as belonging to the metal as a whole, or forming a "**sea of electrons**" or an "**electron cloud**."

- The **remaining nonvalence electrons** and **atomic nuclei** form what are called **ion cores**, which possess a **net positive charge equal** in magnitude to the **total valence electron charge per atom**.

2.4. The Metallic Bond

- The figure illustrates metallic bonding.
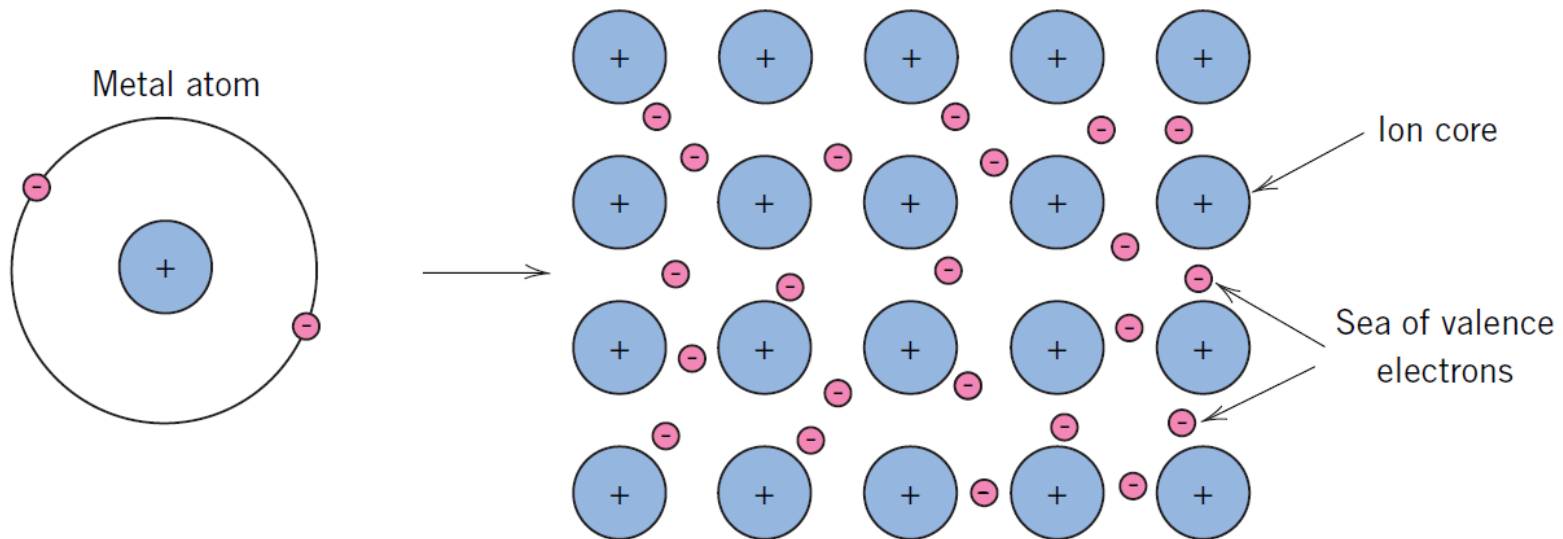
- The **free electrons shield the positively charged ion cores** from the mutually **repulsive** electrostatic forces that they would otherwise exert upon one another; consequently, the metallic bond is **<u>nondirectional</u>** in character.

- In addition, these **free electrons** act as a "**glue**" to **hold the ion cores together**.

2.4. The Metallic Bond

- Bonding may be **weak or strong**; **energies range** from **62 kJ/mol for mercury to 850 kJ/mol for tungsten**.

- Their respective **melting temperatures** are **-39°C** and **3414°C**.

- Metallic bonding is **found** in the periodic table for **Group IA and IIA** elements and, in fact, for **all elemental metals**.

- **Metals** are **good conductors** of both **electricity** and **heat** as a consequence of **their free electrons**.

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2.5. The Secondary, or Van der Waals, Bond

⊙ **Van der Waals** (**physical**) bonds, are **weak** in comparison to the primary or chemical bonds; **bonding energies** range between about **4 and 30 kJ/mol**.

⊙ Secondary bonding exists **between virtually all atoms or molecules**, but its presence may be **obscured if any of the three primary bonding types is present.**

⊙ Secondary bonding is evidenced for the **inert gases**, which have stable electron structures.

⊙ In addition, secondary (or intermolecular) bonds are **possible between atoms or groups of atoms**, **which themselves are joined together by primary (or intramolecular) ionic or covalent bonds**.

2.5. The Secondary, or Van der Waals, Bond

⊙ Secondary bonding forces arise from **atomic or molecular dipoles**. In essence, an **electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule.** The bonding **results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one** (figure).

⊙ **Dipole interactions occur between:**

1. Induced dipoles.

2. Induced dipoles and polar molecules (which have permanent dipoles).

3. Polar molecules.

Atomic or molecular dipoles
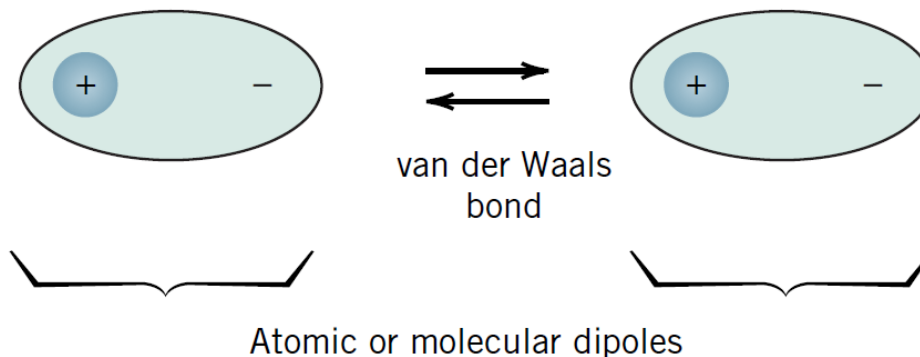
⦿ **Hydrogen bonding, a special type of secondary bonding**, is found to exist between some molecules that have hydrogen as one of the constituents (detailed later).

1. Induced dipoles: Fluctuating Induced Dipole Bonds

⦿ A dipole may be created or induced in an atom or molecule that is normally electrically symmetric—that is, the **overall spatial distribution of the electrons is symmetric with respect to the positively charged nucleus.**

⦿ All **atoms experience constant vibrational motion that can cause instantaneous and short-lived distortions of this electrical symmetry for some of the atoms or molecules and the creation of small electric dipoles.**

⦿ One of these dipoles can **in turn produce a displacement of the electron distribution of an adjacent molecule or atom**, which induces the second one also to become a dipole that is then weakly attracted or bonded to the first, this is one type of van der Waals bonding.

2.5. The Secondary, or Van der Waals, Bond

1. Induced dipoles: Fluctuating Induced Dipole Bonds
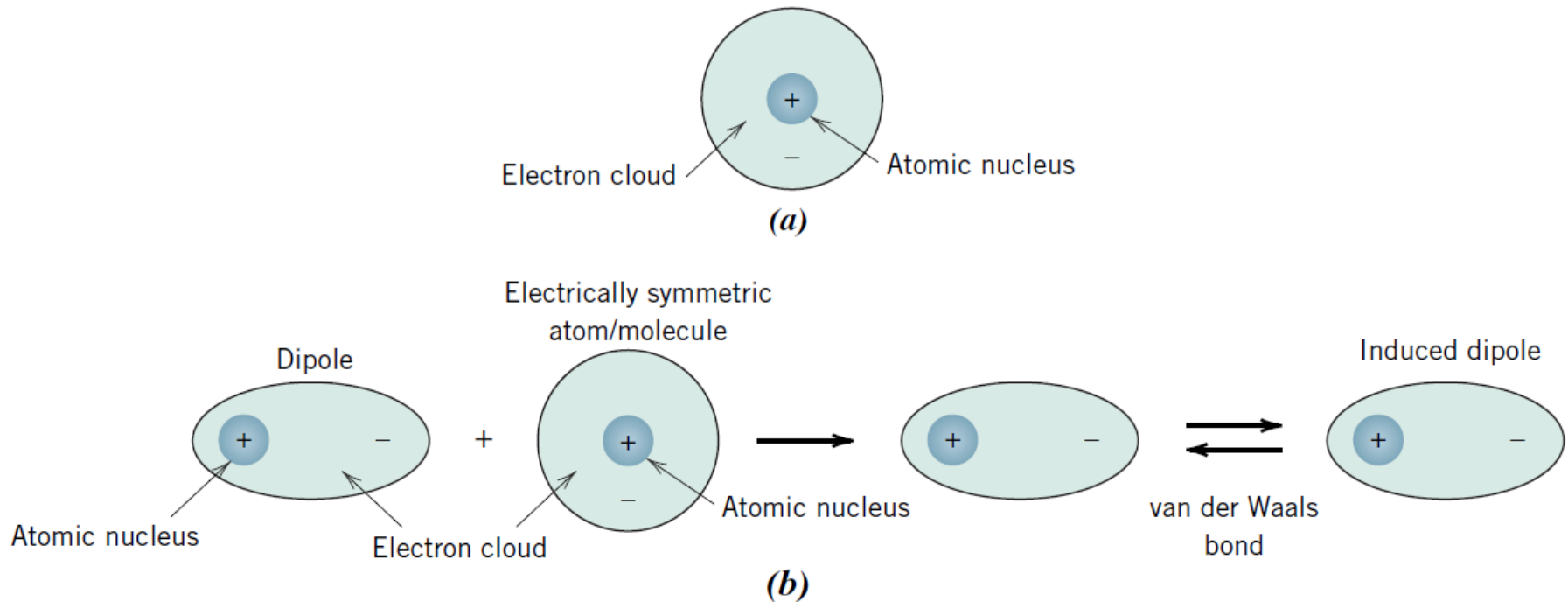
- These attractive forces, which **forces are temporary and fluctuate with time**, may exist between large numbers of atoms or molecules.

- The liquefaction and, in some cases, the solidification of the inert gases and other electrically neutral and symmetric molecules such as H_2 and Cl_2 are realized because of this type of bonding.

2.5. The Secondary, or Van der Waals, Bond

2. Polar Molecule–Induced Dipole Bonds

◉ **Permanent dipole moments exist in some molecules** by virtue of an **asymmetrical arrangement** of positively and negatively charged regions; such molecules are termed **polar molecules**.

◉ The magnitude of this bond is **greater than for fluctuating induced dipoles**.

(a)

(b)
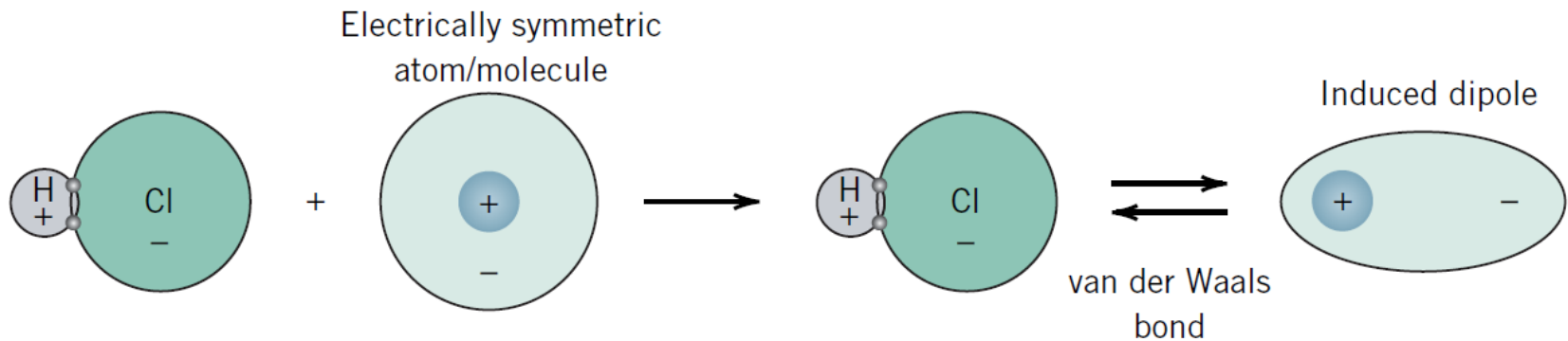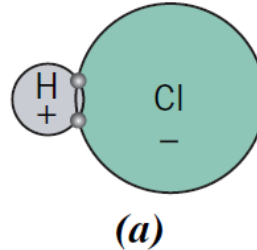
(a) A hydrogen chloride molecule (dipole)
(b) how an HCl molecule induces an electrically symmetric atom/molecule to become a dipole.

3. Polar molecules: Permanent Dipole Bonds

◉ **Coulombic forces also exist between adjacent polar molecules**. The associated bonding energies are significantly **greater than for bonds involving induced dipoles**.

◉ **Example:** The strongest secondary bonding type, the **hydrogen bond**, is a special case of polar molecule bonding. It occurs between **molecules in which hydrogen is covalently bonded** to fluorine (as in HF), oxygen (as in H_2O), or nitrogen (as in NH_3). For each H-F, H-O, or H-N bond, the **single hydrogen electron is shared** with the other atom. Thus, the hydrogen end of the bond is essentially a **positively charged** bare proton unscreened by any electrons. This highly positively charged end of the molecule is capable of a strong attractive force with the negative end of an adjacent molecule. This **single proton forms a bridge between two negatively charged atoms**. 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**.

Hydrogen bond
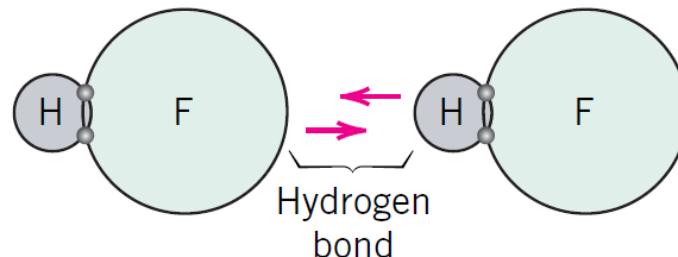
2.5. The Secondary, or Van der Waals, Bond

3. Polar molecules: Permanent Dipole Bonds

◉ **Melting and boiling temperatures** for **hydrogen fluoride, ammonia, and water** are abnormally high in light of their low molecular weights, as a consequence of hydrogen bonding.

Example of secondary bonds in natural phenomena and many products :

◉ **Solubility** of one substance in another, **surface tension** and **capillary action**, **vapor pressure**, **volatility**, and **viscosity**.

◉ Common applications that make use of these phenomena include **adhesives**—van der Waals bonds form between two surfaces so that they adhere to one another.

◉ **Surfactants**—compounds that lower the surface tension of a liquid, and are found in soaps, detergents, and foaming agents.

◉ **Emulsifiers**—substances that, when added to two immiscible materials (usually liquids), allow particles of one material to be suspended in another (common emulsions include sunscreens, salad dressings, milk, and mayonnaise).

◉ The strengths, stiffnesses, and softening temperatures of **polymers**, to some degree, depend on secondary bonds that form between chain molecules.

2.5. The Secondary, or Van der Waals, Bond

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

a: Values for van der Waals and hydrogen bonds are energies *between* molecules or atoms (*inter*molecular), not between atoms within a molecule (*intra*molecular).

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⊙ Sometimes it is illustrative to represent the **four bonding types**—ionic, covalent, metallic, and van der Waals—on what is called a **bonding tetrahedron**—a three-dimensional tetrahedron with one of these **"extreme" types located at each vertex**.
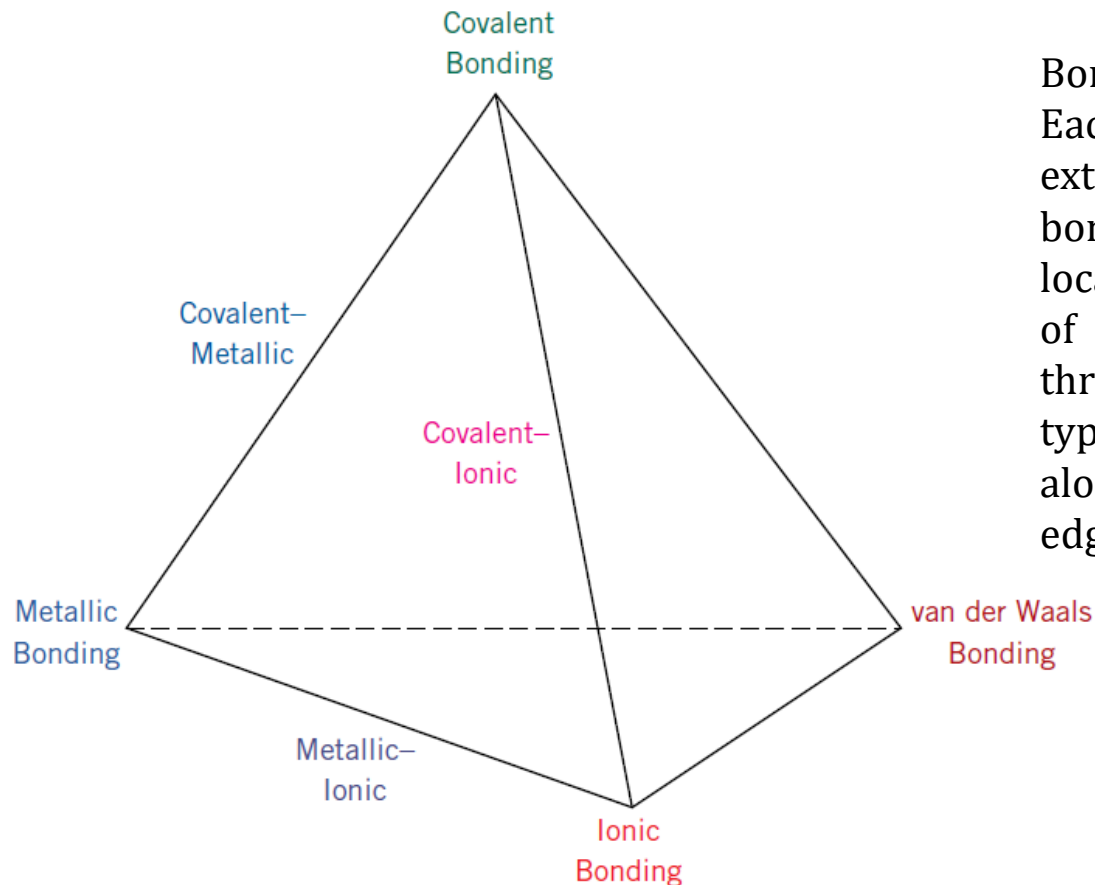
Bonding tetrahedron: Each of the four extreme (or pure) bonding types is located at one corner of the tetrahedron; three mixed bonding types are included along tetrahedron edges.

2.6. Materials: The Bonding Classification

◉ For many real materials, the **atomic bonds are mixtures of two or more of these extremes** (i.e., mixed bonds).

◉ **Three mixed-bond types**: **covalent–ionic**, **covalent–metallic**, and **metallic–ionic** are also included on edges of this tetrahedron; we now discuss each of them.

1. Covalent–ionic bonds

◉ For mixed covalent–ionic bonds, there is some ionic character to most covalent bonds and some covalent character to ionic ones.

◉ The degree of either bond type **depends on the relative positions of the constituent atoms in the periodic table or the difference in their electronegativities**. The **wider the separation** (both horizontally & vertically) from the lower left to the upper right corner (i.e., the greater the difference in electronegativity), the **more ionic is the bond**.

◉ Conversely, the **closer the atoms** are together (i.e., the smaller the difference in electronegativity), the **greater is the degree of covalency.**

2.6. Materials: The Bonding Classification

◎ **Percent ionic character (%IC)** of a bond between elements A and B (A being the most electronegative) may be approximated by the expression:

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

where X_A and X_B are the **electronegativities** for the respective elements.

2. Covalent–metallic bonds

◎ Are found for some elements in **Groups IIIA, IVA, and VA of the periodic table** (viz., B, Si, Ge, As, Sb, Te, Po, and At). Interatomic bonds for these elements are mixtures of metallic and covalent.

◎ These materials are called the **metalloids or semi-metals**, and their properties are intermediate between the metals and nonmetals.

◎ In addition, for **Group IV elements**, there is a gradual **transition from covalent to metallic bonding as one moves vertically down this column.**

◎ **For example**, bonding in **carbon (diamond) is purely covalent**, whereas **for tin and lead, bonding is predominantly metallic.**

2.6. Materials: The Bonding Classification

3. Metallic-Ionic bonds

- Mixed metallic–ionic bonds are observed for compounds composed of **two metals** when there is a **significant difference between their electronegativities.**

- This means that **some electron transfer is associated with the bond inasmuch as it has an ionic component.**

- Furthermore, the **larger this electronegativity difference**, the **greater the degree of ionicity.**

- **For example,** there is little ionic character to the titanium–aluminum bond for the intermetallic compound $TiAl_3$ because electronegativities of both Al and Ti are the same.

2.6. Materials: The Bonding Classification

⊙ Some correlations have been drawn between bonding type and material classification—namely, ionic bonding (ceramics), covalent bonding (polymers), metallic bonding (metals), and van der Waals bonding (molecular solids). We summarized these correlations in the material-type tetrahedron: