Bondíng ín the solíd state Intermolecular forces Lecture 28

Bondíng ín Solíds



Metallic solids

Extended networks of atoms held together by metallic bonding (Cu, Fe)



Covalent-network solids

Extended networks of atoms held together by covalent bonds (C, Si) © 2012 Pearson Education, Inc.



Ionic solids Extended networks of ions held together by ion–ion interactions (NaCl, MgO)



Molecular solids

Discrete molecules held together by intermolecular forces (HBr, H₂O)

- Solids: 4 types:
 - Metallic solids network of highly delocalized electrons.
- Ionic solids

Metal bonding



Red, nuclei Grey, delocalized Electrons.

Bondíng ín Solíds



Metallic solids Extended networks of atoms held together by metallic bonding (Cu, Fe)



Covalent-network solids Extended networks of atoms held together by covalent bonds (C, Si) © 2012 Pearson Education, Inc.



Ionic solids Extended networks of ions held together by ion-ion interactions (NaCl, MgO)



Molecular solids Discrete molecules held together by intermolecular forces (HBr, H₂O)

- Covalent-network solids are joined by an extensive network of covalent bonds.
- Molecular solids are discrete molecules that are linked to one another only by van der Waals forces.

Bondíng ín Solíds

- In crystalline solids atoms are arranged in a very regular pattern.
- Amorphous solids are characterized by a distinct lack of order in the arrangement of atoms.



Iron pyrite (FeS₂), a crystalline solid



Obsidian (typically KAlSi₃O₈), an amorphous solid © 2012 Pearson Education, Inc.

Crystal Lattices



Oblique lattice ($a \neq b$, γ = arbitrary)



Square lattice (a = b, $\gamma = 90^{\circ}$)



Rectangular lattice ($a \neq b, \gamma = 90^{\circ}$) © 2012 Pearson Education, Inc.

Lattice: repeating pattern.

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Hexagonal lattice ($a = b, \gamma = 120^{\circ}$)

Crystal Lattices



Oblique lattice ($a \neq b$, γ = arbitrary)



Square lattice ($a = b, \gamma = 90^{\circ}$)



Rectangular lattice ($a \neq b, \gamma = 90^{\circ}$)



Hexagonal lattice ($a = b, \gamma = 120^{\circ}$)

Unit cell: The pattern of space that repeats

Crystal Lattices



7. three-dimensional lattices:

- Cubic
- Tetragonal
- Orthorhombic
- Rhombohedral
- Hexagonal
- Monoclinic
- Triclinic

No five fold symmetry.

Crystal Lattices

- For cubic lattice
- 3 types:
- Primitive
- Body centered (lattice pt in center)
- Face centered (lattice pt. in middle of face)



Primitive cubic lattice



Body-centered cubic lattice



Face-centered cubic lattice © 2012 Pearson Education, Inc.

Metallíc Structure



The structures of many metals conform to one of the cubic unit cells.

Cubíc Structures



(a) Primitive cubic metal 1 atom per unit cell







(b) Body-centered cubic metal 2 atoms per unit cell



(b) Body-centered cubic metal 2 atoms per unit cell





Cubic structures

Determine number of atoms per unit cell:

TABLE 12.1 • Fraction of Any Atom as a Function of Location Within the Unit Cell^{*}

Atom Location	Number of Unit Cells Sharing Atom	Fraction of Atom Within Unit Cell
Corner	8	1/8 or 12.5%
Edge	4	1/4 or 25%
Face	2	1/2 or 50%
Anywhere else	1	1 or 100%

*It is only the position of the center of the atom that matters. Atoms that reside near the boundary of the unit cell but not on a corner, edge, or face are counted as residing 100% within the unit cell.

Example problem

- A compound of 2 elements
- Crystal, body centered cubic lattice
- A atoms are on the corners of the cell and in the center
- B atoms on 4 edges and on 2 faces.
- What is the stoichiometry?





Side view



Side view

Atoms touch each other in a crystal.

Pack as tightly as possible.



Unit cell view (a) Hexagonal closepacked metal



Unit cell view (b) Cubic closepacked metal

Intermolecular Forces



Attractions between molecules not nearly as strong as atomic bonds How "sticky" are molecules

Intermolecular Forces



Control important physical properties boiling point melting points, vapor pressures viscosity.

Intermolecular Forces



These intermolecular forces as a group are referred to as **van der Waals forces**.

Van der Waals Forces

- Dipole-dipole interactions
- Hydrogen bonding
- London dispersion forces

London Díspersíon Forces





(a) Two helium atoms, no polariza

Subatomic particle view

Polarization view

While the electrons in the 1s orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.

London Díspersíon Forces Subatomic particle view

At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side.



London Díspersíon Forces



Another helium atom nearby, then, would have a dipole induced in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom 1.

London Díspersíon Forces

Subatomic particle view Electrostatic attraction Atom A Atom B Polarization view δ^+ δ • δ^+ Atom A Atom B (c) Induced dipole on atom A

London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole.

London Díspersíon Forces

- present in all molecules
- polar or nonpolar.
- The tendency of an electron cloud to distort in this way is called polarizability.

Subatomic particle view Electrostatic attraction $e^{e^{-}} e^{-} e^{$

Factors Affecting London Forces

Linear molecule, larger surface area enhances intermolecular contact and increases dispersion force •••••



n-Pentane (C₅H₁₂) bp = 309.4 K

Spherical molecule, smaller surface area diminishes intermolecular contact and decreases dispersion force ••••



• Shape :

- long, skinny molecules (like npentane) tend to have stronger dispersion forces than short, fat ones (like neopentane).
- This is due to the increased surface area in *n*-pentane.

Factors Affectíng London Forces



- increase with increased molecular weight.
- Larger atoms have larger electron clouds that are easier to polarize.

Dípole–Dípole Interactions

- Molecules that have permanent dipoles are attracted to each other.
 - The positive end of one is attracted to the negative end of the other, and vice versa.
 - These forces are only important when the molecules are close to each other.



Dípole-Dípole Interactions



Increasing polarity Increasing strength of dipole–dipole forces

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The more polar the molecule, the higher its boiling point.

Which Have a Greater Effect?

Dípole-Dípole Interactions or Dispersion Forces

- If two molecules are of comparable size and shape, dipole–dipole interactions will likely be the dominating force.
- If one molecule is much larger than another, dispersion forces will likely determine its physical properties.

How Do We Explain This?



- The nonpolar series (SnH₄ to CH₄) follow the expected trend.
- The polar series follow the trend until you get to the smallest molecules in each group.

Hydrogen Bondíng

Covalent bond, Hydrogen bond, intramolecular intermolecular











Special dipole—dipole

• when H is bonded to N, O, or F.

 Much stronger than normal dipole-dipole

hydrogen bonds.

Hydrogen Bondíng

 Arises from high electronegativity of nitrogen, oxygen, and fluorine.



Also, when hydrogen is bonded to one of those very electronegative elements, the hydrogen nucleus is exposed.

Intermolecular Forces Affect Many Physical Properties

Each molecule can form two hydrogen bonds with a neighbor



Acetic acid, CH_3COOH MW = 60 amu bp = 391 K

Each molecule can form one hydrogen bond with a neighbor



1-Propanol, $CH_3CH_2CH_2OH$ MW = 60 amu bp = 370 K© 2012 Pearson Education, Inc. The strength of the attractions between particles can greatly affect the properties of a substance or solution.

Physical properties

- Resistance of a liquid to flow is called viscosity.
- Boiling point/freezing point
- Heat of vaporization



SAE 40 S higher number higher viscosity slower pouring 4

SAE 10 lower number lower viscosity faster pouring

Substance	Formula	Viscosity (kg/m-s)
Hexane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	3.26×10^{-4}
Heptane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	4.09×10^{-4}
Octane	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	5.42×10^{-4}
Nonane	CH ₃ CH ₂ CH ₃	7.11×10^{-4}
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	1.42×10^{-3}

TABLE 11.4 Viscosities of a Series of Hydrocarbons at 20 °C

Surface Tensíon



Surface tension results from the net inward force experienced by the molecules on the surface of a liquid.

Example;

- Arrange in order of increasing melting or boiling pt:
- propane (C3H8), water, hydrogen, sodium