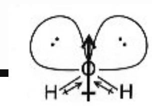
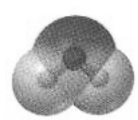
INTERMOLECULAR FORCES: Polarity of Molecules

Seventh Course (General Chemistry)
by Dr. Istadi





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Types of Intermolecular Forces

- The **nature of the phases** and their changes are due primarily to forces among the molecules.
- **Intramolecular and Intermolecular Forces** arise from electrostatic attractions between opposite charges.
- **Bonding forces** are due to the attraction between cations and anions (*ionic bonding*), nuclei and electron pairs (*covalent bonding*), or metal cations and delocalized valence electrons (*metallic bonding*).
- **Intermolecular forces**, on the other hand, are due to the attraction between the molecules as a result of partial charges, or the attraction between ions and molecules

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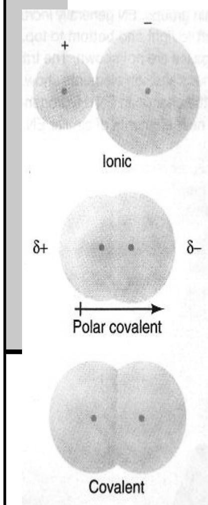
Electronegativity (EN)



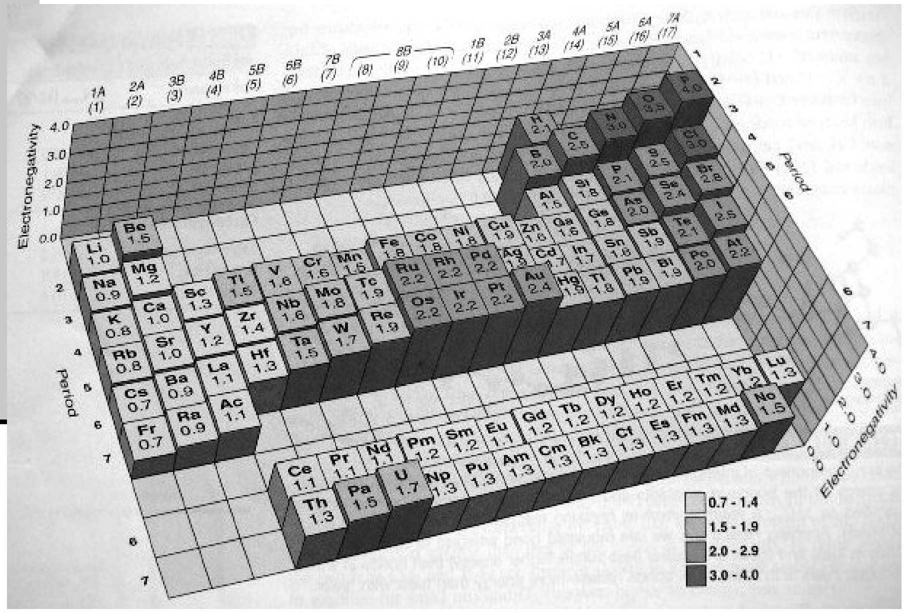
- EN is the relative ability of a bonded atom to attract the shared electrons ==> is not the same as electron affinity (EA)
- H-H bond : 432 kJ/mol; F-F bond : 159 kJ/mol ; Average of HF bond : 296 kJ/mol ==> actually 565 kJ/mol or 269 kJ/mol higher than the average (EN H=2.1; EN F=4.0)
- This difference is due to an electrostatic (charge) contribution to the **H-F** bond energy
- If F attracts the shared electron pair more strongly than H (F is more electronegative than H), the electron will spend more time closer to F
- This unequal sharing of electrons makes the F end of the bond partially negative and the H end partially positive
- The attraction between these partial charges increases the energy required to break the bond

Polar Covalent Bond and Bond Polarity

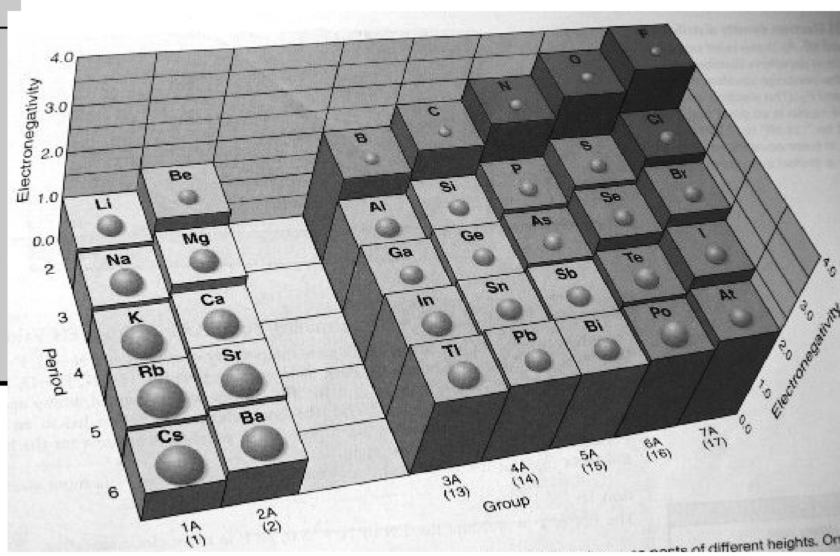
- In HF, the unequal distribution of electron density means the bond has partially negative and positive poles
- polar covalent bond ==> depicted as a polar arrow (+→) pointing toward the negative pole or by δ+ and δ- symbols

- But in H-H and F-F bonds, the atoms are identical, so the bonding pair is shared equally ==> nonpolar covalent bond

The Pauling Electronegativity Scale



Electronegativity and Atomic Size



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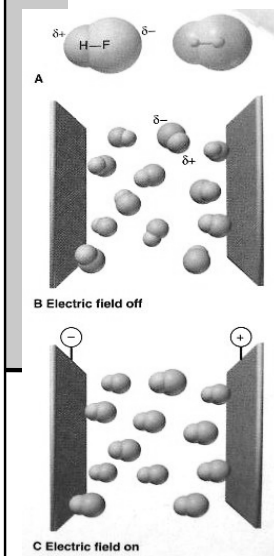
Bond Polarity, Bond Angle, and Dipole Moment



- A covalent bond is polar when it joins atoms of different electronegativity because the atoms share the electrons unequally
- Molecules with a net imbalance of charge have a **Molecular Polarity**.
- In molecules with more than two atoms, both **shape and bond polarity** determine molecular polarity
- **Dipole Moment (*μ*)**: is the product of the partial charges and the distance between them ==> *debye* (D) unit (1 D = 3.34E-30 C.m).
- **Partial Ionic Character**: A greater ΔEN results in larger partial charges and a higher partial ionic character

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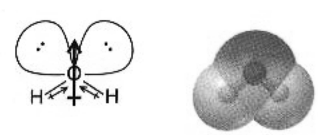
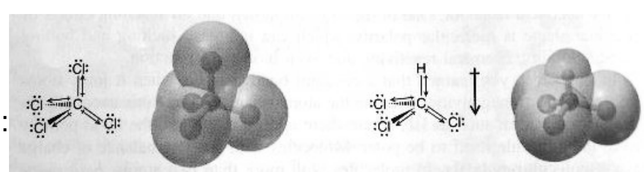
- **Molecular shape** ==> influence the polarity, because the presence of polar bonds does not always lead to a polar molecule
- Example: $\mathbf{CO_2}$: C (EN=2.5), O (EN=3.5) ==> C=O should be quite polar. However, CO_2 is linear shape ==> the two identical bond polarities are counterbalanced ==> no net dipole moment (μ=0 D)

- **Water**:



- **Chloroform**:



Types of Intermolecular Forces

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- **Bonding Forces** are relatively strong because they involve larger charges that are close together
- **Intermolecular Forces** are relatively weak because they typically involve smaller charges that are farther apart

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Bonding Force

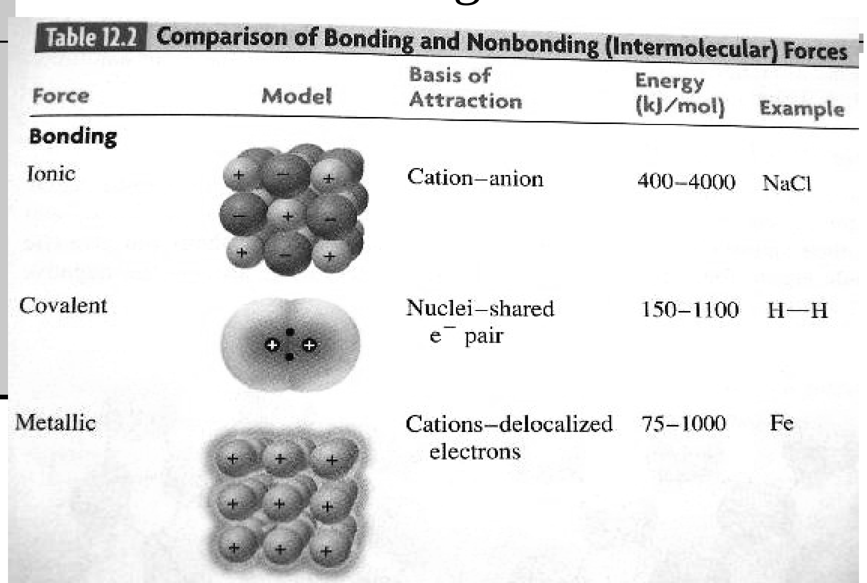
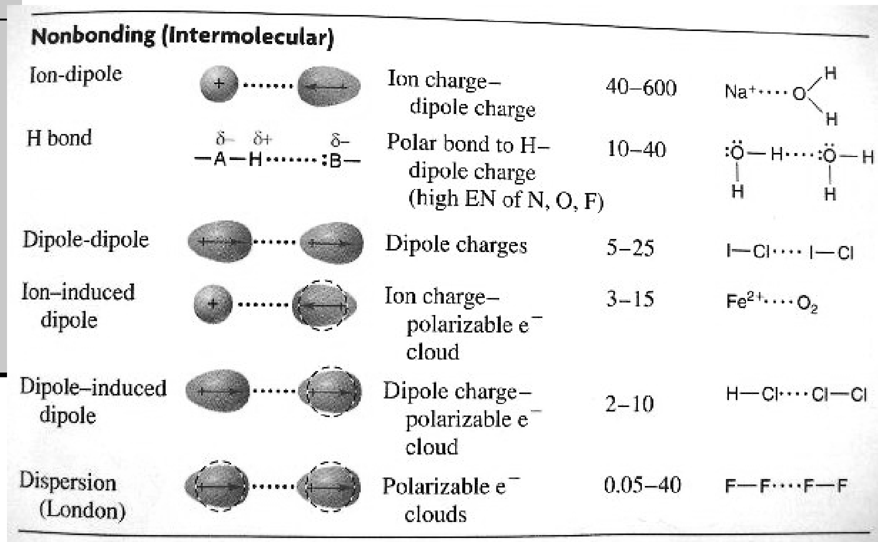


Table 12.2 Comparison of Bonding and Nonbonding (Intermolecular) Forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

Nonbonding (Intermolecular) Force



Nonbonding (Intermolecular)

Ion-dipole	+ ·······	Ion charge–dipole charge	40–600	$Na^+ \cdots O(H)H$
H bond	δ− δ+ δ− —A—H·······:B—	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	:Ö—H····:Ö—H
Dipole-dipole	······	Dipole charges	5–25	I—Cl···· I—Cl
Ion–induced dipole	+ ·······	Ion charge–polarizable e^- cloud	3–15	$Fe^{2+} \cdots O_2$
Dipole–induced dipole	······	Dipole charge–polarizable e^- cloud	2–10	H—Cl····Cl—Cl
Dispersion (London)	······	Polarizable e^- clouds	0.05–40	F—F····F—F

Ion-Dipole Forces

- an ion and a nearby polar molecule (dipole) ==> attract each other ==> **ion-dipole force**
- Example: *ionic compound dissolves in water*.
- The ions become separated because the attractions between the ions and the oppositely charged poles of the H_2O molecules overcome the attraction between the ions themselves

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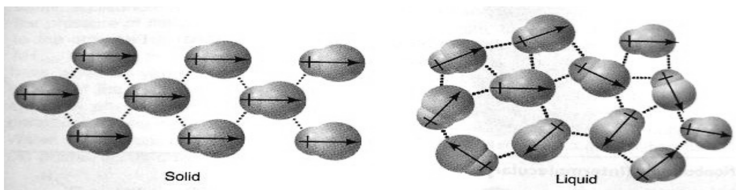
Dipole-Dipole Force

- From the orientation of polar molecules in an electric field, when polar molecules lie near one another, as in liquid and solid, their partial charges act as tiny electric fields that orient them and give rise to dipole-dipole forces (the positive pole of one molecule attracts the negative pole of another



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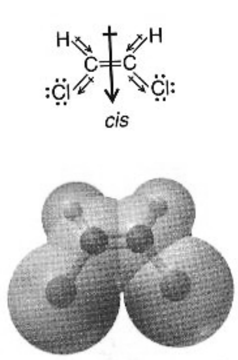
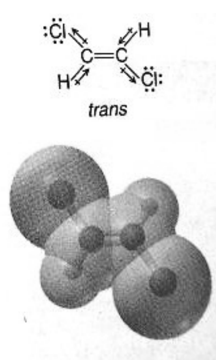
- The forces give polar cis-1,2-dichloroethylene a higher boiling point than the nonpolar trans compound





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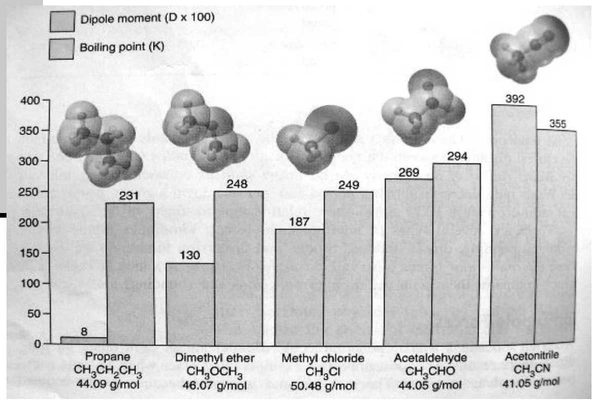
Dipole Moment and Boiling Point

- For the molecular compounds of approximately the same size and molar mass, the greater the dipole moment, the greater the dipole-dipole forces between the molecules are, and so the more energy to separate them



Example: Methyl Chloride has a smaller dipole moment than acetaldehyde ==> less energy is needed to overcome the dipole-dipole forces between its molecules ==> and it boils at a lower temperatures

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Polarizability and Charge-Induced Dipole Forces

- A nearby electric field can distort a cloud of negative charge, therefore pulling electron density toward a positive charge or pushing it away from a negative charge
- In effect, the field induces a distortion in the electron cloud
- For a nonpolar molecule, this distortion creates a temporary induced dipole moment
- For a polar molecule, it enhances the dipole moment already present.
- The ease with which the electron cloud of a particle can be distorted ==> **POLARIZABILITY**
- Smaller atoms (or ions) are less polarizable than larger ones, because their electrons are closer to the nucleus and therefore are held more tightly

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Polarizability Trends

- **Polarizability increases down a group**, because size increases so the larger electron clouds are farther from the nucleus, and thus more easily distorted
- **Polarizability decreases from left to right across a period**, because the increasing Zeff shrinks atomic size and holds the electrons more tightly
- **Cations** are less polarizable than their parent atoms because they are smaller
- **Anions** are more polarizable because they are larger
- Ion-induced dipole and dipole-induced dipole forces are the two types of charge-induced dipole forces ==> most important in solution

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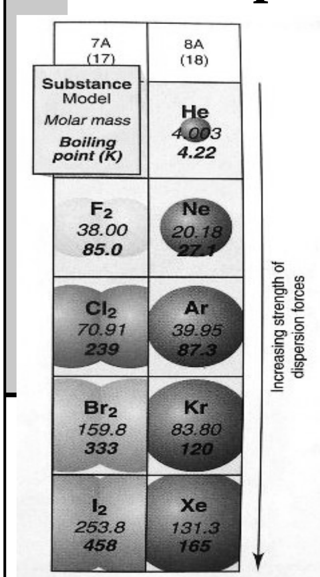
Dispersion (London) Forces



- What forces cause nonpolar substances like octane, chlorine, and argon to condense and solidify?
- ==> The intermolecular force primarily responsible for the condensed states of nonpolar substances ==> is dispersion force or London force.
- Dispersion forces are caused by momentary oscillations of electron charge in atoms and therefore are present between all particles
- The strength of dispersion forces increases with number of electrons
- which usually correlates with molar mass
- As a result, boiling point increase down the halogens and the noble gases

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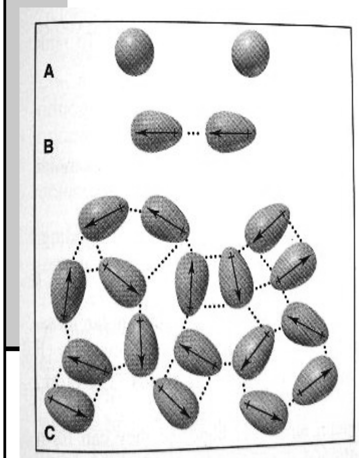
Dispersion Forces Among Ar Atoms



- Dispersion force is responsible for the condensed states of noble gases and nonpolar molecules
- **A** : Separated Ar atoms are nonpolar
- **B** : An instantaneous dipole in one atom induces a dipole in its neighbor. These partial charges attract the atoms together
- **C** : This process takes place among atoms throughout the sample

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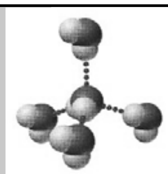

The Uniqueness of Water

- Water molecule is composed of H and O atoms. Each atom attains a filled outer level by sharing electrons in single covalent bonds
- With two bonding pairs and two lone pairs around the O atom and a large electronegativity difference in each O-H bond, the H_2O molecule is bent and **highly polar**
- Because it has two O-H bonds and two lone pairs, one H_2O molecule can engage in as many as four H bonds to surrounding H_2O molecules, which are arranged **tetrahedrally**
- **Solvent Properties**: The **great solvent power** of water is due to its polarity and exceptional H-bonding ability
- It dissolves ionic compounds through ion-dipole forces that separate the ions from the solid and keep them in solutions

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- Water dissolves many polar nonionic substances, such as ethanol (CH_3CH_2OH) and glucose ($C_6H_{12}O_6$), by forming H bonds to them
- It even dissolves nonpolar gases, such as those in the atmosphere, to a limited extent, through dipole-induced dipole and dispersion forces.
- **Thermal properties**: Water has an exceptionally high specific heat capacity, higher than almost any other liquid
- When a substance is heated, some of the energy increases the average molecular speed, some increases molecular vibration and rotation, and some is used to overcome intermolecular forces
- Because water has so many strong H bonds, it has a high specific heat capacity

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- **Surface Properties**: The H bonds that give water its remarkable thermal properties are also responsible for its high surface tension and high capillarity
- Water's high capillarity, as a result of its high surface tension, is crucial to land plants and animal life
- Water expands on freezing because of its H bonds, which lead to an open crystal structure of ice

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Macroscopic Properties of water