# Chapter 12

# Liquids, Solids, and Intermolecular Forces Dr. Arno Papazyan<br>Dr. Arno Papazyan<br>Includes material from the slides provided with Introductory Chemistry, Fifth Edition<br>By Dr. Sylvia Esjornson<br>Southwestern Oklahoma State University<br>Weatherford, OK

Dr. Arno Papazyan

Includes material from the slides provided with Introductory Chemistry, Fifth Edition

By Dr. Sylvia Esjornson Southwestern Oklahoma State University Weatherford, OK

# Example of Intermolecular forces in life: Climbing Geckos

- Geckos can adhere to almost any surface
- Recent studies indicate that this amazing ability is related to intermolecular attractive forces
- Geckos have millions of tiny hairs on their feet that branch out and flatten out on the end Franks can adhere to almost any surface<br>
Franks and the set are almost an analy ability<br>
Franks and the setae forces<br>
Franks have millions of tiny hairs on their feet<br>
hat branch out and flatten out on the end<br>
— setae = h

• This structure allows the gecko to have unusually related to intermolecular attractive forces<br>Geckos have millions of tiny hairs on their feet<br>that branch out and flatten out on the end<br>— setae = hairs, spatulae = flat ends<br>This structure allows the gecko to have unusuall intermolecular attractive forces to act strongly

The state of a sample of matter—solid, liquid, or gas depends on how strong intermolecular attractive forces The state of a sample of matter—solid, liquid, or gas—<br>depends on how strong intermolecular attractive forces<br>are — compared to forces needed to keep the molecules<br>from flying apart from one another<br>The molecules and atoms from flying apart from one another

- The molecules and atoms that compose matter are in constant random motion that increases with increasing temperature. The energy associated with this motion is called thermal energy.
- The weaker the intermolecular forces (and corresponding energies) relative to thermal energy, the more likely the sample will be gaseous.
- The stronger the intermolecular forces (and corresponding energies) relative to thermal energy, the more likely the sample will be liquid or solid.

#### Relative strength of inter-particle forces





Liquid

#### Large

Enough to keep particles together, but can't pin them down



Solid

## Large

Enough to keep particles together & to pin them down

# Intermolecular Forces

- 
- **Intermolecular Forces**<br>• Occur <u>between</u> (rather than within) molecules<br>• For any pair of molecules, much weaker than chemical<br>bonding • For any pair of molecules, much weaker than chemical bonding
- 1. Forces created by permanent polarization
	- Between the molecular dipoles: **dipole-dipole**
	- Between N-H, O-H, F-H bonds and N, O, F atoms in molecules: hydrogen bonding
- 1. Forces created by <u>permanent polarization</u><br>
 Between the molecular dipoles: **dipole-dipole**<br>
 Between N-H, O-H, F-H bonds and N, O, F atoms in<br>
molecules: **hydrogen bonding**<br>
2. Forces created by <u>temporary polarizati</u> fluctuations in electron density: dispersion (London)

# Forces created by permanent polarization Case 1: dipole-dipole forces

Between the molecular dipoles: dipole ...... dipole



Exists between polar molecules (molecules with a permanent dipole)

# Forces created by permanent polarization

# Case 2: "hydrogen bonding" forces

Between N-H, O-H, F-H bonds and N, O, F atoms in molecules



H is "electron-poor" ( $\delta^+$ ) when bonded to N, O, F

(especially their lone pair electrons)

A "hydrogen bond" has some tiny amount of "chemical bond" character but is not a chemical bond

Intermolecular forces: "hydrogen bonding"



## More on Hydrogen Bonding

- It is a strong intermolecular force
- It is an interaction between specific parts of two molecules
- It is not a generic dipole-dipole interaction
- Therefore, it can exist even if the overall molecule is nonpolar
- If we could make a molecule with symmetrically placed bond dipoles that cancel out for the total molecular dipole, it would still have hydrogen bonding interactions with other molecules

# London (dispersion) forces

**Condon (dispersion) forces**<br>Forces created by <u>temporary polarization due to fluctuations</u><br>in electron density<br>All atoms randomly create temporary dipoles (a quantum in electron density

All atoms randomly create temporary dipoles (a quantum mechanical effect).

A randomly created dipole on one particle induces a smaller, parallel dipole on nearby particles.

 $\delta$  would push away electrons on other particles, creating a  $\delta^*$ 

Then these dipoles attract, before they pop out of existence.



## More on London (dispersion) forces

- All atoms and molecules create this kind of force – Because electron clouds always fluctuate
- Dispersion forces exist in all materials
- Dispersion force between any pair of atoms is relatively weak; but can be very strong between molecules with many atoms
- The more electrons there are, the larger the potential fluctuations, and the stronger it gets
- It doesn't take a lot of atoms to give a molecule enough electrons to create stronger dispersion forces than dipoledipole forces
	- Even for a polar molecule

# Molar mass and London (dispersion) forces

- An often-used proxy for the number of electrons on an atom or a molecule is the molar mass.
	- Larger molar mass goes with more electrons per molecule
- London forces have nothing to do with how An often-used proxy for the number of electrons<br>on an atom or a molecule is the molar mass.<br>— Larger molar mass goes with more electrons per<br>molecule<br>London forces have nothing to do with how<br>heavy a molecule is. As long a become a misconception, using molar mass as a quick-and-dirty measure of London forces is acceptable.

#### Ion–Dipole Forces

Ion–dipole forces are the strongest intermolecular forces by far

Much larger than dipole-dipole or dispersion (London) forces

For example, ion-dipole forces exist between Na<sup>+</sup> and the negative ends of  $H_2O$  molecules and between Cl<sup>-</sup> and the positive ends of  $H<sub>2</sub>O$  molecules.



#### Different Types of Intermolecular Forces



# How is the strength of intermolecular forces revealed?

One very common property we use to judge the<br>strength of intermolecular forces:<br>Boiling point<br>Stronger intermolecular forces  $\rightarrow$  <u>higher</u> boiling point One very common property we use to judge the strength of intermolecular forces: How is the strength of intermole<br>One very common property we us<br>strength of intermolecular forces:<br>Boiling point<br>Stronger intermolecular forces

 $\begin{array}{r|l|l} \text{Domain} & \text{non}^{\prime\prime} \text{left the often-quoted "dispersion forces are weak" statement mis \textbf{dispression forces} & \textbf{can easily be stronger than dipco \textbf{cores}}, & \textbf{given enough electrons} \ \textbf{HCI} & & \text{Has polar molecules} \ \text{Has dipole-dipole forces} & & \text{Has nonpolar mole} \ \text{Has dispersion forces} & & \text{Has only dispersion forces} \ \text{If} & \text{new} & \text{class} & \text{class} \ \text{if} & \text{new} & \text{class} \ \text{if} & \text{new} & \text{class} \ \text{if} & \text{new} & \text{class} \ \text$  $\begin{aligned} \n\text{S are weak}^{\prime\prime} \text{ statement missing} & \text{the probability that} \n\end{aligned}$ <br> **Cl<sub>2</sub>**<br>
Has nonpolar molecules<br>  $\Rightarrow$  <u>No dipole-dipole</u> forces<br>
Has <u>only</u> dispersion forces stronger than dipole-dipole<br>  $Cl_2$ <br>
Has nonpolar molecules<br>  $\Rightarrow$  <u>No dipole-dipole</u> forces<br>
Has <u>only</u> dispersion forces<br>
(from 17 + 17 = 34 e<sup>-</sup>)<br>  $\rightarrow$  ... Dispersion forces can easily be stronger than dipole-dipole forces, given enough electrons Intermolecular forces – London (dispersion) forces<br>
Weak" statement misguide you<br>
nger than dinolo-dinolo Don't let the often-quoted "dispersion forces are weak" statement misguide you

# **HCl**

Has polar molecules

 $(from 1 + 17 = 18 e^-)$ )  $\|$ 

# $Cl<sub>2</sub>$

Has nonpolar molecules

Has dispersion forces **Helpersion** forces  $(from 17 + 17 = 34 e^-)$ )  $\|$ 

HCl<br>
Has polar molecules<br>  $\Rightarrow$  Has dipole-dipole forces<br>
Has dispersion forces<br>
(from 1+17 = 18 e<sup>-</sup>)<br> **Boiling point = 188 K**<br>
Stronger intermolecular forces<br>  $\Rightarrow$  higher boiling point<br>
Boiling point = 238 K<br>
Boiling poi Stronger intermolecular forces  $\rightarrow$  higher boiling point CI<sub>2</sub> has stronger intermolecular forces than the polar HCl molecule, even if it only has dispersion forces.

# But hydrogen-bonding forces are harder to compete with

#### Example:

Predict which molecule has stronger intermolecular forces, and explain:

 $N_2$  H<sub>2</sub>O

- $H<sub>2</sub>O$  has hydrogen bonding (in addition to some London dispersion).
- $N_2$  exhibits London dispersion forces only, and with more electrons than  $H_2O$ , they are stronger than for  $H_2O$ , but it would take many more electrons to compete with H-bonding between  $H_2O$  molecules.

Predict which gas would behave more ideally at the **SET AT SET ASSEM SET ASSEMUST A THE SAME PREDICT Which gas would behave more ideally at the same pressure and temperature, and explain.**<br>HCN or  $N_2$ Intermolecular forces<br>
build behave more ideally at the<br>
Elemperature, and explain.<br>
HCN or  $N_2$ <br>
a the same number of electrons Predict which gas would behave more ideally<br>same pressure and temperature, and explain.<br> $HCN$  or  $N_2$ <br>Both molecules have the same number of elec<br>So their London forces are very similar.<br>HCN is a polar molecule, so it has

Both molecules have the same number of electrons.

HCN is a polar molecule, so it has dipole-dipole forces.

N<sub>2</sub> is nonpolar (lacks a dipole), so it has no dipole-dipole forces.

Since  $N<sub>2</sub>$  has weaker intermolecular forces, it would behave more like an ideal gas.

# Boiling point, an excellent measure of intermolecular forces, shows, for example, when hydrogen bonding happens



# Some other properties that get larger with stronger intermolecular forces: Intermolecular forces

- Enthalpy of vaporization
	- Energy required to vaporize molecules into gas phase
- Melting point
	- Less reliable; molecules with unwieldy shapes don't fit into a crystal lattice and have lower melting points
- Viscosity
	- Resistance to flow
	- Also higher for molecules that can get "tangled up"
- Surface tension
	- How hard it is to create more liquid surface

Intermolecular Forces in Action: Surface Tension and Viscosity

- The most important manifestation of intermolecular forces is the very existence of liquids and solids.
- Without intermolecular forces, solids and liquids would not exist and all matter would be gaseous.
- In liquids, we can observe several other manifestations of intermolecular forces, including surface tension and viscosity.

#### Surface Tension

- A paper clip will float on water if it is carefully placed on the surface of the water. It is held up by surface tension.
- You can't float a paper clip on gasoline because the intermolecular forces among the molecules composing gasoline are weaker than the intermolecular forces among water molecules.



Dr. P's note: The liquid also should not "wet" the object.

#### Surface Tension

Molecules at the surface have fewer neighbors to stabilize them (so they are at higher energy)



To minimize the number of molecules with missing neighbors, the "surface tension" force minimizes the surface area of the liquid.

## Water droplet in the space station



A sphere has the minimum area for a given volume Surface tension favors a spherical shape

If there are no other forces, droplets are spherical

# Bubbles also tend to be spherical unless distorted by other forces (like gravity)

For the same reason.



# **Viscosity**

- Viscosity is the resistance of a liquid to flow.
- Liquids that are viscous flow more slowly than liquids that are not viscous.
- Motor oil is more viscous than gasoline.
- Maple syrup is more viscous than water.
- Viscosity is greater in substances with stronger intermolecular forces because molecules cannot move around each other as freely, hindering flow.
- Long molecules, such as the hydrocarbons in motor oil, tend to form viscous liquids because of molecular entanglement. Viscosity is greater in substances with stronger<br>ntermolecular forces because molecules cannot move<br>rround each other as freely, hindering flow.<br>ong molecules, such as the hydrocarbons in motor oil,<br>end to form viscous liq
	- dispersion forces that contribute to viscosity as well

#### **Viscosity**

• Maple syrup is more viscous than water because its molecules interact strongly, so they cannot flow past one another easily.



## Evaporation, Condensation, and Thermal Energy

The rate of vaporization increases with the following: Evaporation, Condensation, and Therma<br>
The rate of vaporization increases with<br>
• Increasing surface area<br>
• Increasing temperature

- 
- 
- Evaporation, Condensation, and Thermal<br>
The rate of vaporization increases with<br>
 Increasing surface area<br>
 Increasing temperature<br>
 Decreasing strength of intermolecul
- The rate of vaporization increases with the following:<br>
 Increasing surface area<br>
 Increasing temperature<br>
 Decreasing strength of intermolecular forces<br>
 Liquids that evaporate easily are termed volatile,<br>
while those • Liquids that evaporate easily are termed volatile, while those that do not vaporize easily are termed nonvolatile.

## Evaporation

Not all molecules in a liquid have the same kinetic energy.

**Evaporation**<br>Not all molecules in a liquid have the<br>same kinetic energy.<br>They constantly bump around,<br>exchange energy, and some<br>molecules end up with more kinetic exchange energy, and some molecules end up with more kinetic energy than others.

The most energetic molecules can break away into the gas state in the process called evaporation.

In evaporation or vaporization, a substance is converted from its liquid state into its gaseous state.



#### Evaporation, Condensation, and Thermal Energy

- At a given temperature, a sample of molecules or atoms will have a distribution of kinetic energies.
- Only a small fraction of molecules has enough energy to escape.

At a higher temperature,<br>the fraction of<br>molecules with enough<br>energy to escape<br>increases. the fraction of molecules with enough energy to escape increases.



## Evaporation and Condensation

- Condensation is a physical change in which a substance is converted from its gaseous state to its liquid state.
- Evaporation and condensation are opposites: Evaporation is a liquid turning into a gas, and condensation is a gas turning into a liquid.
- At the point where the rates of condensation and evaporation become equal, dynamic equilibrium is reached and the number of gaseous water molecules above the liquid remains constant.
- The vapor pressure of a liquid is the partial pressure of its vapor in dynamic equilibrium with its liquid.

#### Evaporation and Condensation



# Vapor Pressure

Vapor pressure increases with the following:

- Increasing temperature
- Decreasing strength of intermolecular forces
	- Can't change it for a given substance at a given T
	- Only useful for comparing different substances

Vapor pressure is independent of surface area because an increase in surface area at equilibrium equally affects the rate of evaporation and the rate of condensation.

Boiling During boiling, thermal energy is enough to cause water molecules in the interior of the liquid to become gaseous, forming bubbles containing gaseous water molecules.



Nature of phase transitions for pure substances: Nature of phase transitions for pure substances:<br>They occur at a <u>constant temperature</u> (at a given<br>pressure), characteristic to the pure substance pressure), characteristic to the pure substance

- Once the boiling point of a liquid is reached, additional heating only causes more rapid boiling; it does not raise the temperature of the liquid above its boiling point.
- A mixture of boiling water and steam will always have a temperature of 100 °C (at 1 atm pressure).
- Only after all the water has been converted to steam can the temperature of the steam rise beyond 100 °C.
### The temperature of water as it is heated from room temperature to the boiling point. A "Heating Curve" for Water<br>The temperature of water as it is heate<br>temperature to the boiling point.



During boiling, the temperature remains at 100 °C until all the liquid is evaporated.

### Energetics of Evaporation

- Evaporation is endothermic—when a liquid is converted into a gas, it absorbs heat because energy is required to break molecules away from the rest of the liquid.
- Our bodies use the endothermic nature of evaporation for cooling.
- When we overheat, we sweat, causing our skin to be covered with liquid water.
- As this water evaporates, it absorbs heat from our bodies, cooling us down.
- High humidity slows down evaporation, preventing cooling. When the air already contains high amounts of water vapor, sweat does not evaporate as easily, making our cooling system less efficient.

### Energetics of Condensation

- Condensation, the opposite of evaporation, is exothermic Energetics of Condensation<br>
sondensation, the opposite of evaporation, is exothermic<br>
— heat is released when a gas condenses to a liquid.<br>
S steam condenses to a liquid on your skin, it releases<br>
eat, causing a severe bur
- As steam condenses to a liquid on your skin, it releases heat, causing a severe burn.
- The exothermic nature of condensation is also the reason that winter overnight temperatures in coastal cities, which tend to have water vapor in the air, do not get as low as those in deserts, which tend to have dry air.
- As the air temperature in a coastal city drops, water condenses out of the air, releasing heat and preventing the temperature from dropping further.
- In deserts, there is little moisture in the air to condense, so the temperature drop is greater.

### Heat of Vaporization

- **Heat of Vaporization**<br>• The amount of heat required to vaporize 1 mol of liquid is<br>the **heat of vaporization**  $(\Delta H_{vap})$ . the heat of vaporization  $(\Delta H_{\text{vap}})$ .
- The heat of vaporization of water at its normal boiling point (100 °C) is 40.7 kJ/mol. the heat of vaporization  $(\Delta H_{vap})$ .<br>
• The heat of vaporization of water at its normal boiling point<br>  $(100 °C)$  is 40.7 kJ/mol.<br>
•  $\Delta H_{vap}$  is positive because vaporization is endothermic;<br>
energy must be added to the wa
- $\Delta H_{\text{van}}$  is positive because vaporization is endothermic; energy must be added to the water to vaporize it.
- condenses, but the heat is emitted rather than absorbed.
- $\Delta H_{\text{cond}}$  is negative because condensation is exothermic; energy is given off as the water condenses.

Heat of Vaporization of Water

it of Vaporization of Water<br>H<sub>2</sub>O(*l*) → H<sub>2</sub>O(*g*) *ΔH* = +40.7 kJ (at 100 °C) H<sub>2</sub>O(*l*) → H<sub>2</sub>O(*g*) Δ*H* = +40.7 kJ (at 100 °C)<br>H<sub>2</sub>O(*g*) → H<sub>2</sub>O(*l*) Δ*H* = -40.7 kJ (at 100 °C)

### Heats of Vaporization



### TABLE 12.2 Heats of Vaporization of Several Liquids at Their Boiling Points and at 25 °C

- Use the heat of vaporization of a liquid to calculate the amount of heat energy required to vaporize a given amount of that liquid.
- Use the heat of vaporization as a conversion factor between moles of the liquid and the amount of heat required to vaporize it.

EXAMPLE: Using the Heat of Vaporization in Calculations Calculate the amount of water, in grams, that can be vaporized at its boiling point with 155 kJ of heat.

GIVEN: 155 kJ FIND:  $g H_2O$  LOOK UP:  $\Delta H_{\text{van}}$ 

SOLUTION MAP:



### Melting and Freezing

- As the temperature of a solid increases, thermal energy causes the molecules and atoms composing the solid to vibrate faster.
- At the melting point, atoms and molecules have enough thermal energy to overcome the intermolecular forces that hold them at their stationary points, and the solid turns into a liquid.

### Melting and Freezing

- When ice melts, water molecules break free from the solid structure and become liquid. Melting and Freezing<br>
• When ice melts, water<br>
molecules break free<br>
from the solid structure<br>
and become liquid.<br>
• As long as ice and<br>
water are both present,<br>
the temperature will be
- water are both present, the temperature will be  $0 °C$ .



Remember: Phase transitions for a pure substance, at a given pressure, occur at a constant temperature

- A mixture of water and ice will always have a A mixture of water *and* ice will always have a<br>temperature of 0 °C (at 1 atm pressure).<br>Only after all of the ice has melted will
- A mixture of water *and* ice will always have a<br>temperature of 0 °C (at 1 atm pressure).<br>• Only after all of the ice has melted will<br>additional heating raise the temperature of<br>the liquid water past 0 °C additional heating raise the temperature of the liquid water past 0 °C.

### Another "Heating Curve" for Water

### This time, a graph of the temperature of ice as it is heated from −20 °C to 35 °C (at the usual 1 atm)



During melting, the temperature of the solid and the liquid remains at 0 °C until the entire solid is melted.

### Energetics of Melting and Freezing

- A way to cool down a drink is to drop ice cubes into it.
- As the ice melts, the drink cools because melting is endothermic—heat is absorbed when a solid is converted Energetics of Melting and Freezing<br>A way to cool down a drink is to drop ice cubes into<br>As the ice melts, the drink cools because melting is<br>endothermic—heat is absorbed when a solid is con-<br>into a liquid. <u>Melting</u> of the
- Melting is endothermic because energy is required to partially overcome the attractions between molecules in the solid and free them into the liquid state. endothermic—heat is absorbed whe<br>into a liquid. <u>Melting</u> of the ice absor<br>Melting is endothermic because ene<br>partially overcome the attractions be<br>the solid and free them into the liqui<br>Freezing is exothermic—heat is rele
- Freezing is exothermic—heat is released when a liquid
- As water in a freezer turns into ice, it releases heat, which must be removed by the refrigeration system of the freezer.

### Heat of Fusion

**Heat of Fusion**<br>"Fusion": An old-fashioned term for melting<br>So, we are talking about "Heat of Melting" here<br>The amount of heat required to melt 1 mol of a sc<br>is the **heat of fusion (Δ** $H_{\text{fus}}$ **).**<br>The heat of fusion for "Fusion": An old-fashioned term for melting So, we are talking about "Heat of Melting" here

- **Heat of Fusion**<br>
"Fusion": An old-fashioned term for melting<br>
So, we are talking about "Heat of Melting" here<br>
 The amount of heat required to melt 1 mol of a solid<br>
is the **heat of fusion (** $\Delta H_{\text{fus}}$ **).**<br>
 The beat o
- The heat of fusion for water is 6.02 kJ/mol.
- $\Delta H_{\text{fus}}$  is positive because melting is endothermic; energy must be added to the ice to melt it.
- The same amount of heat is involved when The amount of heat required to melt 1 mol of a solid<br>is the **heat of fusion (** $\Delta H_{\text{fus}}$ **).**<br>The heat of fusion for water is 6.02 kJ/mol.<br> $\Delta H_{\text{fus}}$  is positive because melting is endothermic;<br>energy must be added to th rather than absorbed.
	- $\triangleright$  ΔH is negative because freezing is exothermic; energy is given off as the water freezes.

Heat of Fusion of Water

$$
f \text{Fusion of Water}
$$
\n
$$
H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = +6.02 \text{ kJ}
$$

# $H_2O(s) \to H_2O(l)$   $\Delta H = +6.02$  kJ<br> $H_2O(l) \to H_2O(s)$   $\Delta H = -6.02$  kJ



- Use the heat of fusion to calculate the amount of heat energy required to melt a given amount of a solid.
- Use the heat of fusion as a conversion factor between moles of a solid and the amount of heat required to melt them.

EXAMPLE: Using the Heat of Fusion in Calculations Calculate the amount of ice in grams that, upon melting (at 0 °C), absorbs 237 kJ of heat.

GIVEN: 237 kJ FIND:  $g H_2O$  LOOK UP:  $\Delta H_{fus}$ 

SOLUTION MAP:



### A Heating Curve for Ice

The diagram shows a heating curve for ice beginning at –25 °C and ending at 125 °C. Correlate sections i, ii, and iii with the correct states of water.



- Sublimation is a physical change in which a substance changes from its solid state directly to its gaseous state.
- When a substance sublimes, molecules leave the surface of the solid, where they are held less tightly than in the **Sublimation**<br> **Sublimation** is a physical change in which<br>
changes from its solid state directly to its<br>
When a substance sublimes, molecules le<br>
of the solid, where they are held less tight<br>
interior, and become gaseous.
- Dry ice, which is solid carbon dioxide, does not melt under atmospheric pressure (at any temperature).
- At  $-78$  °C, the CO<sub>2</sub> molecules have enough energy to leave the surface of the dry ice and become gaseous, in a process analogous to boiling – Its vapor pressure is equal to 1 atm
- Solids sublime to some extent at every temperature, just like liquids. It's usually a lot less, so we just don't notice it.

• Dry ice is solid carbon dioxide. The solid does not melt but rather sublimes. It transforms directly from solid carbon dioxide to gaseous carbon dioxide.



- Regular ice will slowly sublime at temperatures below 0 °C.
- In cold climates, ice or snow lying on the ground gradually disappears, even if the temperature remains below 0 °C.
- Similarly, ice cubes left in the freezer for a long time slowly become smaller, even though the freezer is always below 0 °C.

- Ice sublimes out of frozen foods.
- You can see this in food that has been frozen in an airtight plastic bag for a long time.
- The ice crystals that form in the bag are water that has sublimed out of the food and redeposited on the surface of the bag.
- Food that remains frozen for too long becomes dried out.
- This can be avoided by freezing foods to colder temperatures (further below 0 °C), a process called deepfreezing.
- The colder temperature lowers the rate of sublimation and preserves the food longer.

Intermolecular forces also affect whether two substances will be soluble in one another

If there were no intermolecular forces, everything would freely dissolve in everything else.

If dissolution of two substances would disrupt the intermolecular forces, their energy would go up.

– Dissolving unfavorable; little solubility

If the two substances have intermolecular forces similar in nature, they tend to be "miscible"

– they dissolve in each other in a wide range of ratios

### "like dissolves like"



## $H_2O$  and CH<sub>3</sub>OH both have dipole-dipole and hydrogen bonding interactions Intermolecular Forces -- "like dissolves like"<br>Doth have dipole-dipole

– Miscible (can dissolve in all proportions)



both have basically only London dispersion forces

– Miscible (can dissolve in all proportions)

 $H<sub>2</sub>O$  has strong hydrogen bonding forces and significant dipole-dipole forces, but very little dispersion Intermolecular Forces -- "like dissolves like"<br>honding forces and significant



para-Xylene has strong London dispersion forces Intermolecular Forces -- "like dissolves like"<br>as strong hydrogen bonding forces and significant<br>--dipole forces, but very little dispersion<br>para-Xylene has strong London dispersion forces<br>(actually a bit stronger than the  $H<sub>2</sub>O$  molecules), but no other forces

Water and para-Xylene are insoluble in each other

Dissolution is especially bad for water:

H-bonding and dipole-dipole interactions would be lost, and it simply doesn't have enough electrons to have strong Londondispersion forces to replace what's lost.

Intermolecular Forces -- "like dissolves like"<br>gen bonding, dipole-dipole<br>therefore polar) and



Ethanol and para-Xylene are miscible

Since ethanol has a strong component of dispersion forces between its molecules, it is compatible enough with a substance that has only dispersion forces. Ethanol and para-Xylene are **miscible**<br>
Since ethanol has a strong component of dispersion forces<br>
between its molecules, it is compatible enough with a<br>
substance that has only dispersion forces.<br>
Ethanol can be seen as

ractice<br>hoose the substance in that boils at a higher theck your answer on the next page<br>a) CH<sub>3</sub>OH CH<sub>3</sub>CHF<sub>2</sub> Choose the substance in that boils at a higher temperature Practice<br>Choose the substance in that boils at a higher temperature<br>Check your answer on the next page<br>2) CHOH CHCHE

## heck your answer on the next pag<br>
a) CH<sub>3</sub>OH CH<sub>3</sub>CHF<sub>2</sub><br>
b) CH<sub>3</sub>-O-CH<sub>2</sub>CH<sub>3</sub> CH<sub>3</sub>CH<sub>3</sub> b)  $CH_3$ -O-CH<sub>2</sub>CH<sub>3</sub> CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

Choose the substance in that boils at a higher temperature

a) 
$$
(CH_3OH)
$$
  $CH_3CHF_2$    
\nH-bonding   
\nDipole-dipole   
\nb)  $CH_3-O-CH_2CH_3$    
\n $CH_3CH_2CH_2N$    
\n $can H-bond$ 

H-bonding Dipole-dipole



CH3OH CH3 Choose the substance in that boils at a higher temperature Practice<br>Choose the substance in that boils at a higher temperature<br>Check your answer on the next page





Choose the substance in that boils at a higher temperature



Choose the substance in that boils at a higher temperature Practice<br>Choose the substance in that boils at a higher temperature<br>Check your answer on the next page<br> $CH_3$ 

 $CH<sub>3</sub>$  $CH_3$  -  $\dot{C}$  -  $CH_3$  $CH<sub>3</sub>$ C

 $CH<sub>3</sub>CH<sub>3</sub>$ 

Choose the substance in that boils at a higher temperature

 $CH<sub>3</sub>CH<sub>3</sub>$ 

No dipole-dipole (symmetric)

Dispersion (by 18 e<sup>-</sup>) )



Choose the substance in that boils at a higher temperature **Practice**<br>Choose the substance in that boils at a higher temperature<br>Check your answer on the next page<br> $\left( \begin{array}{cc} \n\frac{H}{C} & \n\end{array} \right)_{C=C} \left( \begin{array}{cc} \n\frac{H}{C} & \n\end{array} \right)_{C=C} \left( \begin{array}{cc} \n\frac{H}{C} & \n\end{array} \right)_{C=C}$ 



Choose the substance in that boils at a higher temperature



Both lack hydrogen-bonding

Both have the same number of electrons & comparable size

The polar molecule has dipole-dipole forces, whereas the nonpolar molecule doesn't

### Chemistry and Life: Hydrogen Bonding in DNA

- A DNA molecule is composed of thousands of repeating units called nucleotides.
- Each nucleotide contains a base: adenine, thymine, cytosine, or guanine (abbreviated A, T, C, and G).
- The order of these bases along DNA encodes the instructions that specify how proteins are made in each cell of the body.
- DNA consists of two complementary strands wrapped around each other in the now-famous double helix.
- Each strand is held to the other by *hydrogen bonds* that occur between the bases on each strand.

### Chemistry and Life: Hydrogen Bonding in DNA

- DNA replicates because each base (A, T, C, and G) has a Chemistry and Life:<br>Hydrogen Bonding in DNA<br>DNA replicates because each base (A, T, C, and G) has a<br>complementary partner with which it hydrogen-bonds.<br>Adenine (A) hydrogen-bonds with thymine (T).
- Adenine (A) hydrogen-bonds with thymine (T).
- Cytosine (C) hydrogen-bonds with guanine (G).
- The *hydrogen bonds* are so specific that each base will pair only with its complementary partner.

### Chemistry and Health: Hydrogen Bonding in DNA

- When a cell is going to divide, the DNA unzips across the hydrogen bonds that run along its length.
- New bases, complementary to the bases in each half, add along each of the halves, forming *hydrogen* **bonds** with their complement.
- The result is two identical copies of the original DNA.
#### Hydrogen Bonding in DNA



# Types of Crystalline Solids: Molecular, Ionic, and Atomic

- Solids may be crystalline (a well-ordered array of atoms or molecules) or amorphous (having no long-range order).
- Crystalline solids can be divided into three categories—molecular, ionic, and atomic—based on the individual units that compose the solid.

# Types of Crystalline Solids



# Molecular Solids

- Molecular solids are solids whose composite units are molecules.
- Ice (solid  $H_2O$ ) and dry ice (solid  $CO_2$ ) are examples of molecular solids.
- Molecular solids are held together by intermolecular forces dispersion forces, dipole–dipole forces, and hydrogen bonding. • Molecular solids are held together by intermolecular forces—<br>dispersion forces, dipole–dipole forces, and hydrogen<br>bonding.<br>• Ice is held together by hydrogen bonds, and dry ice is held<br>together by dispersion forces.<br>• M
- Ice is held together by hydrogen bonds, and dry ice is held together by dispersion forces.
- low melting points.
- Ice melts at 0 °C and dry ice sublimes at −78 °C.

## Ionic Solids

- **Ionic solids** are solids composed of *formula units*, the smallest electrically neutral collection of cations and anions that compose the compound.
- Table salt (NaCl) and calcium fluoride (CaF<sub>2</sub>) are good examples of ionic solids.
- Ionic solids are held together by electrostatic attractions between cations and anions.
- In NaCl, the attraction between the Na<sup>+</sup> cation and the Cl– anion holds the solid lattice together because the lattice is composed of alternating cations and anions in a three-dimensional array.

### Ionic Solids

- The forces that hold ionic solids together are actual ionic bonds.
- Since *ionic bonds are* much *stronger than* any of the intermolecular forces discussed previously, ionic solids tend to have much higher melting points than molecular solids. \*
- Sodium chloride, an ionic solid, melts at 801 °C, while carbon disulfide, a molecular solid with a higher molar mass, melts at −110 °C. \*

\* These observations mainly apply to small molecules and simple ionic compounds There are many molecular compounds that melt higher than many "ionic liquids"

### Atomic Solids

- Atomic solids are solids whose composite units are individual atoms.
- Diamond (C), iron (Fe), and solid xenon (Xe) are good examples of atomic solids.
- Atomic solids can be divided into three categories— Atomic solids are solids whose composite units are<br>individual atoms.<br>Diamond (C), iron (Fe), and solid xenon (Xe) are good<br>examples of atomic solids.<br>Atomic solids can be divided into three categories—<br>covalent atomic soli metallic atomic solids—each held together by a different kind of force.

## Types of Atomic Solids



## Covalent Atomic Solids

- Covalent atomic solids, such as diamond, are held together by covalent bonds.
- In diamond, each carbon atom forms four covalent bonds to four other carbon atoms in a tetrahedral geometry.
- This structure extends throughout the entire crystal, so that a diamond crystal can be thought of as a giant molecule held together by these covalent bonds.
- Since covalent bonds are very strong, covalent atomic solids have high melting points. Diamond is estimated to melt at about 3800 °C.

### Diamond: A Covalent Atomic Solid

In diamond, carbon atoms form covalent bonds in a three-dimensional hexagonal pattern.



Nonbonding Atomic Solids

- Nonbonding atomic solids, such as solid xenon, are held together by relatively weak dispersion forces.
- Xenon atoms have stable electron configurations and therefore do not form covalent bonds with each other.
- Consequently, solid xenon, like other nonbonding atomic solids, has a very low melting point (about  $-112$  °C).

### Metallic Atomic Solids

- Metallic atomic solids, such as iron, silver, and lead, have variable melting points.
- Metals are held together by metallic bonds that, in the simplest model, consist of positively charged ions in a sea of electrons.
- Metallic bonds are of varying strengths, with some metals, such as mercury, having melting points below room temperature (−39 °C) and other metals, such as iron, having relatively high melting points (iron melts at 1809 °C).

#### Structure of a Metallic Atomic Solid

- In the simplest model of a metal, each atom donates one or more electrons to an "electron sea."
- The metal consists of the metal cations in a negatively charged electron sea.



- Water has a low molar mass (18.02 g/mol), yet it is a liquid instead of a gas at room temperature.
- Water's relatively high boiling point can be understood by examining the structure of the water molecule.



- The bent geometry of the water molecule and the Water: A Remarkable Molecule<br>The bent geometry of the water molecule and the<br>highly polar nature of the O — H bonds result in a<br>molecule with a significant dipole moment.<br>Water's two Q — H bonds (bydrogen directly bonded molecule with a significant dipole moment.
- **Water: A Remarkable Molecule**<br>
 The bent geometry of the water molecule and the<br>
highly polar nature of the  $O H$  bonds result in a<br>
molecule with a significant dipole moment.<br>
 Water's two  $O H$  bonds (hydrogen direct to oxygen) allow water molecules to form strong hydrogen bonds with other water molecules, resulting in a relatively high boiling point.
- Water's high polarity also allows it to dissolve many other polar and ionic compounds.
- Consequently, water is the main solvent of living organisms, transporting nutrients and other important compounds throughout the body.

- Life is impossible without water, and in most places on Earth where liquid water exists, life exists.
- Recent evidence of water on Mars—that either existed in the past or exists in the present—has fueled hopes of finding life or evidence of life there.

- Water: A Remarkable Molecule<br>• The way water freezes is unique. Most other substances<br>contract upon freezing, but water expands upon freezing.<br>• Because liquid water expands when it freezes, ice is less contract upon freezing, but water expands upon freezing.
- Because liquid water expands when it freezes, ice is less dense than liquid water. Water reaches its maximum density at 4.0 °C.
- Consequently, ice cubes and icebergs float.
- The frozen layer of ice at the surface of a winter lake insulates the water in the lake from further freezing.
- If ice were to sink, liquid water would remain exposed and keep freezing. Life in the body of water would die.
- Life survived extreme ice ages ("snowball earth") because of this! Otherwise even the oceans would have frozen solid!

- The expansion of water upon freezing is one reason that most organisms do not survive freezing.
- When the water within a cell freezes, it expands and often ruptures the cell, just as water freezing within a pipe bursts the pipe.
- Many foods, especially those with high water content, do not survive freezing very well either.
- Industrial flash-freezing of fruits and vegetables happens so rapidly that the water molecules cannot align into the expanded phase and so the cells are not ruptured.