

Chapter 11

Liquids and Intermolecular Forces

Content

WHAT'S AHEAD



11.1 A MOLECULAR COMPARISON OF GASES, LIQUIDS, AND SOLIDS

We begin with a comparison of solids, liquids, and gases from a molecular perspective. This comparison reveals the important roles that *temperature* and *intermolecular forces* play in determining the physical state of a substance.

11.2 INTERMOLECULAR FORCES

We then examine four intermolecular forces: *dispersion forces*, *dipole-dipole forces*, *hydrogen bonds*, and *ion-dipole forces*.

11.6 PHASE DIAGRAMS

We learn how to read *phase diagrams*, which are graphic representations of the equilibria among the gaseous, liquid, and solid phases.

11.3 SELECT PROPERTIES OF LIQUIDS We learn that the nature and strength of the intermolecular forces between molecules are largely responsible for many properties of liquids, including *viscosity* and *surface tension*.

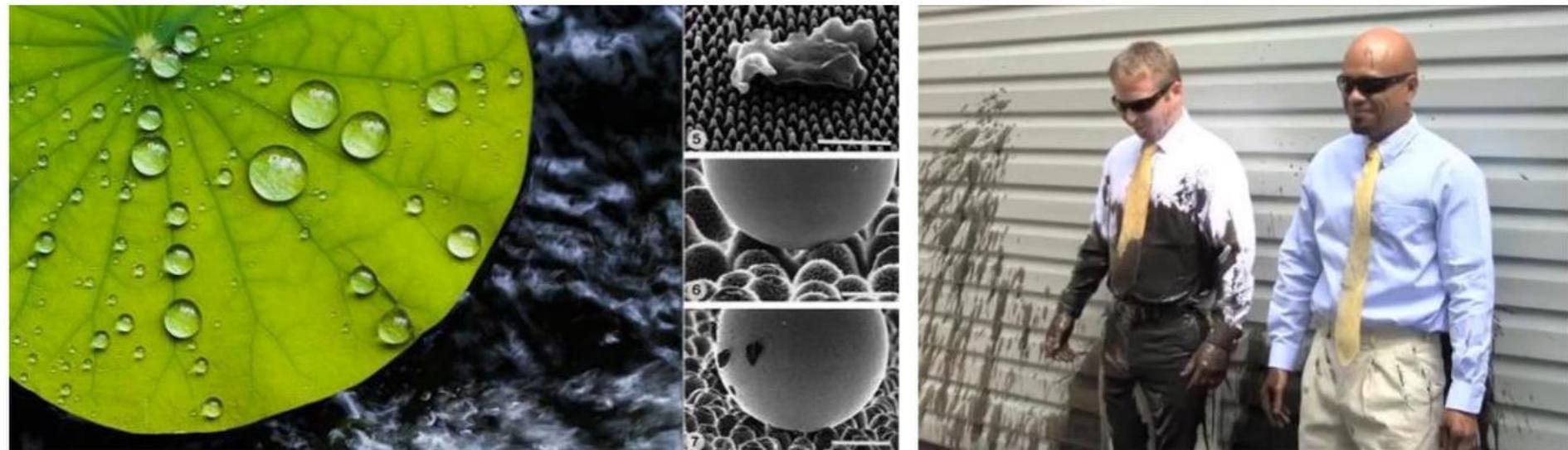
11.4 PHASE CHANGES We explore *phase changes*—the transitions of matter between the gaseous, liquid, and solid states—and their associated energies.

11.5 VAPOR PRESSURE We examine the *dynamic equilibrium* that exists between a liquid and its gaseous state and introduce *vapor pressure*.

11.7 LIQUID CRYSTALS We learn about substances that pass into a liquid crystalline phase, which is an intermediate phase between the solid and liquid states. A substance in the liquid crystalline phase has some of the structural order of a solid and some of the freedom of motion of a liquid.

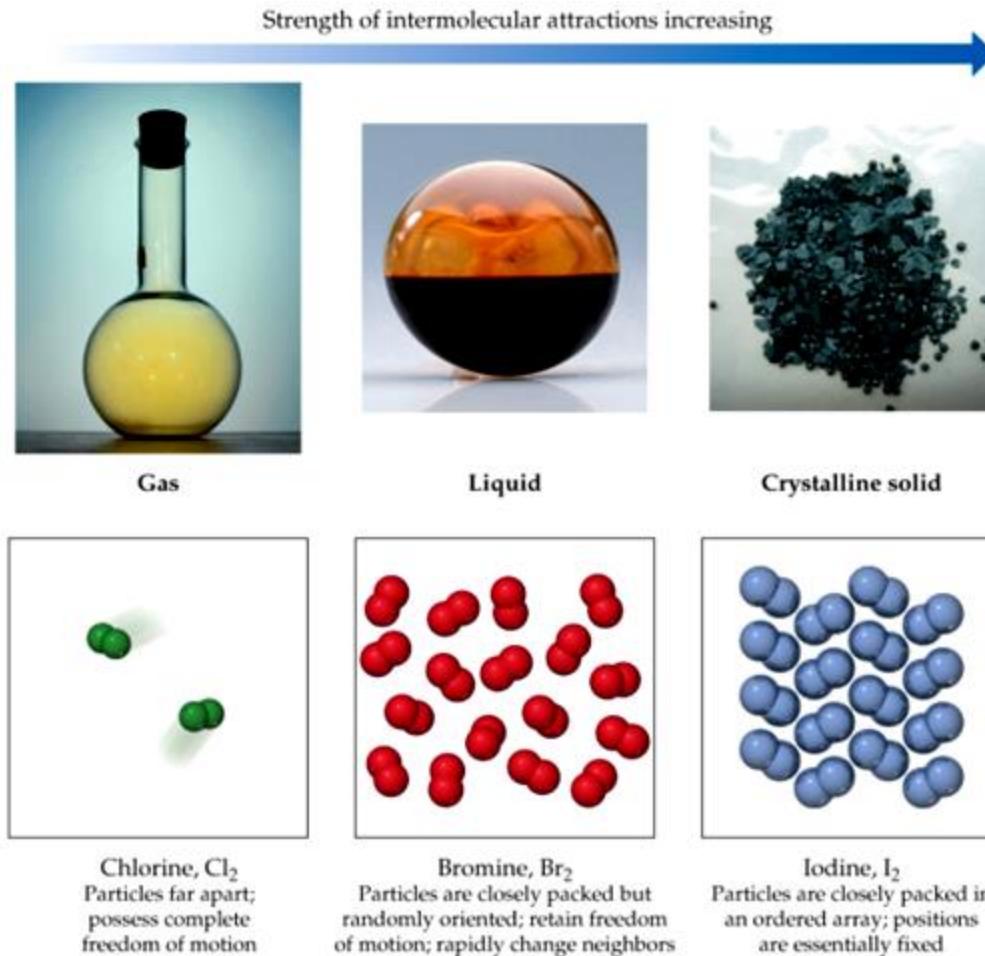


Hydrophobic, water repellent



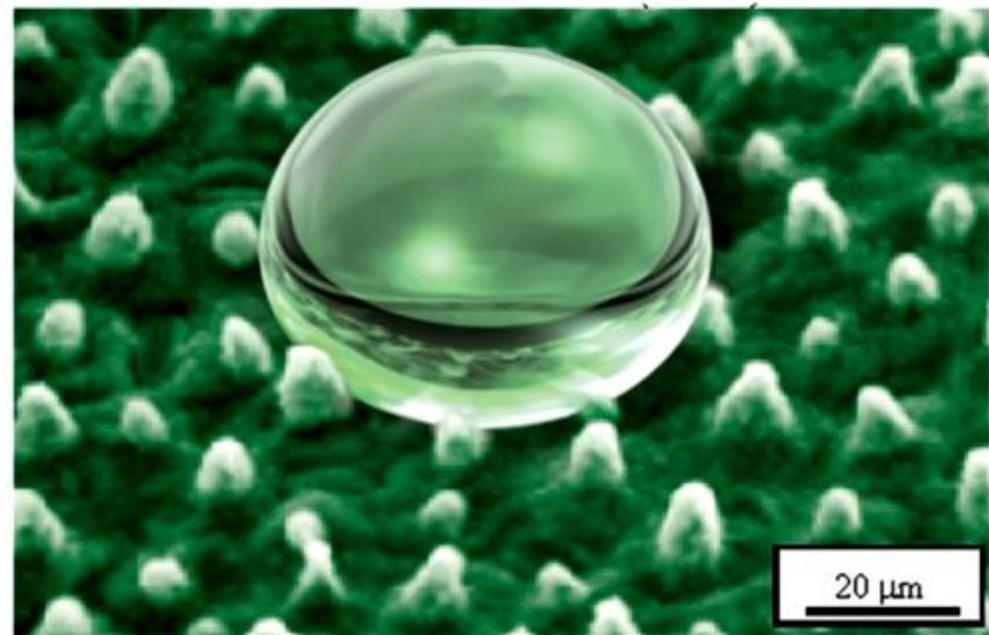
States of Matter

The fundamental difference between states of matter is the **distance between particles**.



States of Matter

Because in the solid and liquid states particles are closer together, we refer to them as **condensed phases**.



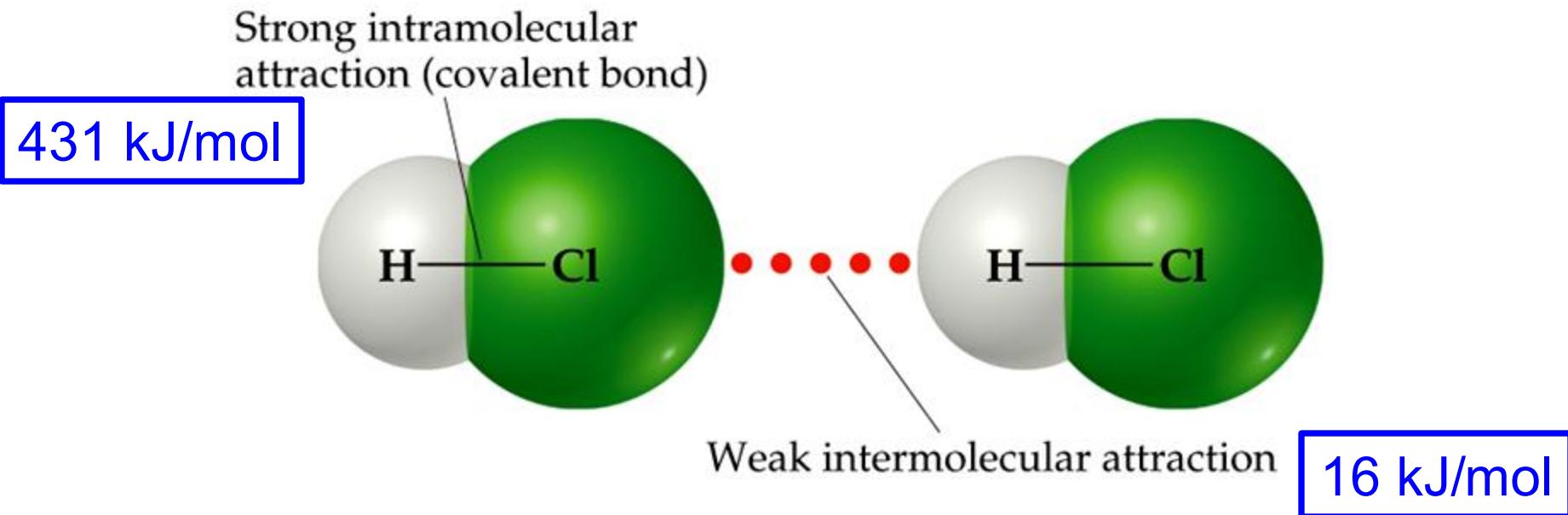
The States of Matter

- The state a substance at a particular temperature and pressure depends on two antagonistic entities:
 - The **kinetic energy** of the particles.
 - The **strength of the attractions** between the particles.

TABLE 11.1 • Some Characteristic Properties of the States of Matter

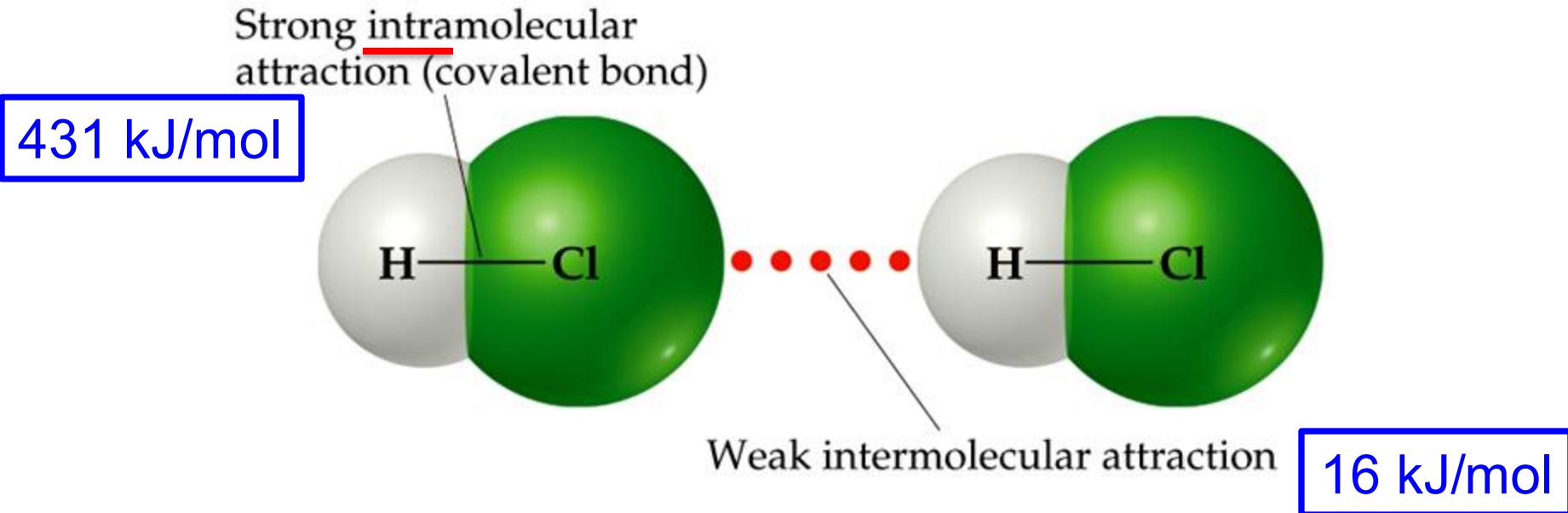
Gas	Assumes both volume and shape of its container Expands to fill its container Is compressible (压缩) Flows readily Diffusion within a gas occurs rapidly
Liquid	Assumes shape of portion of container it occupies Does not expand to fill its container Is virtually incompressible Flows readily Diffusion within a liquid occurs slowly
Solid	Retains own shape and volume Does not expand to fill its container Is virtually incompressible Does not flow Diffusion within a solid occurs extremely slowly

Intermolecular Forces 分子间力



The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compounds together.

Intermolecular Forces



These intermolecular attractions are, however, strong enough to control physical properties, such as **boiling** and **melting points**, **vapor pressures**, and **viscosities** (粘度).

van der Waals Forces (between neutral molecules 中性分子)

- London Disperse Forces (Dipole – induced dipole interactions)
- Dipole—dipole interactions
(偶极-偶极相互作用)
- Hydrogen bonding



Johannes Diderik van der Waals
1837–1923

· London Dispersion Forces 色散力

instantaneous dipole-induced dipole

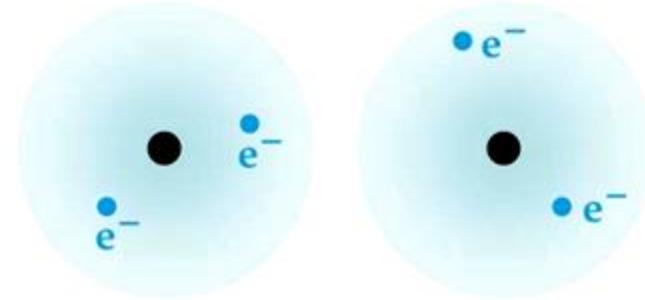
瞬时偶极感应偶极子

非极性分子相互靠拢时，它们的瞬时偶极矩之间会产生很弱的吸引力，这种吸引力称为色散力。色散力存在于一切分子之间。任何一个分子，都存在着瞬间偶极，这种瞬间偶极也会诱导邻近分子产生瞬间偶极，于是两个分子可以靠瞬间偶极相互吸引在一起。这种瞬间偶极产生的作用力称为色散力（dispersion force），又叫做伦敦力。



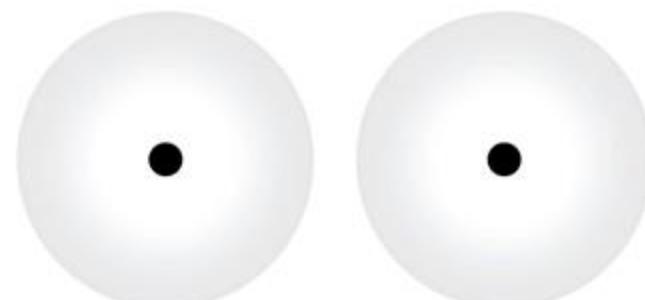
Fritz Wolfgang London
(1900–1954)

London Dispersion Forces



Atom A

Atom B



Atom A

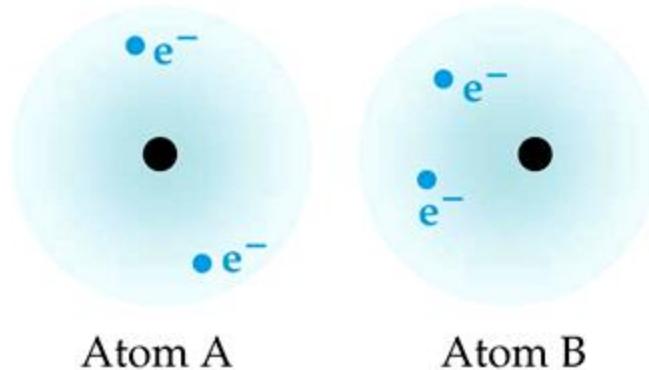
Atom B

(a) Two helium atoms, no polarization

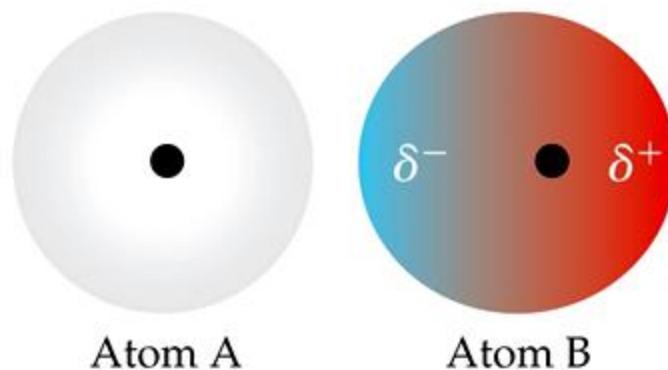
While the electrons in the 1s orbital of helium would repel (排斥) each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom.

London Dispersion Forces

Subatomic particle view



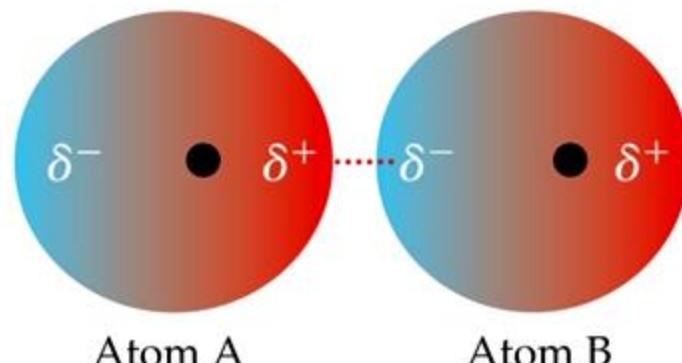
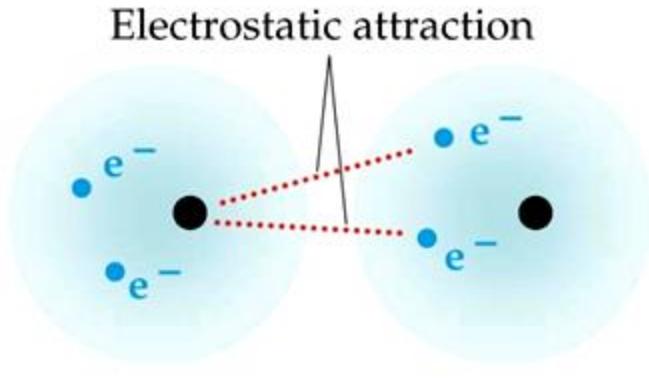
Polarization view



(b) Instantaneous dipole on atom B

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.

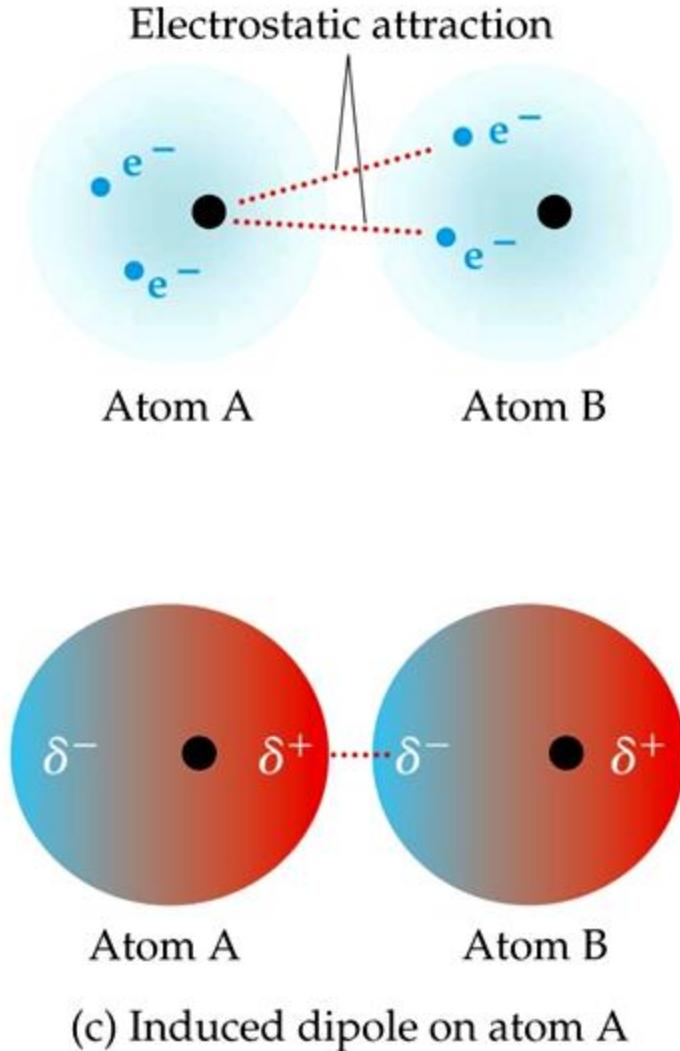
London Dispersion Forces



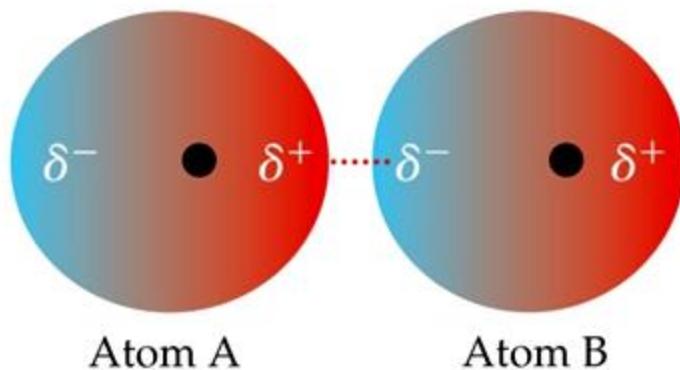
(c) Induced dipole on atom A

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 Dispersion Forces

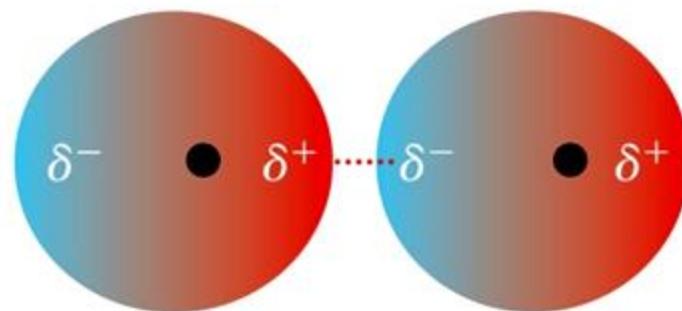
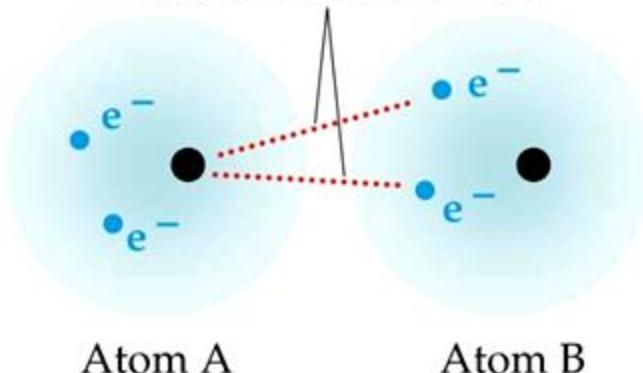


London dispersion forces, or dispersion forces (色散力), are **attractions** between an instantaneous dipole (瞬时偶极) and an induced dipole (感应偶极).



London Dispersion Forces

Electrostatic attraction

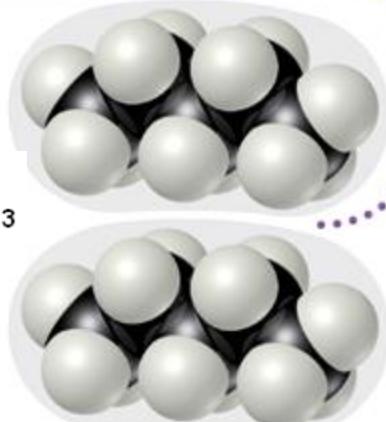


(c) Induced dipole on atom A

- These forces are present in *all* molecules, whether they are polar or nonpolar.
- The tendency of an electron cloud to **distort** (扭曲) in this way is called **polarizability** (极化率).

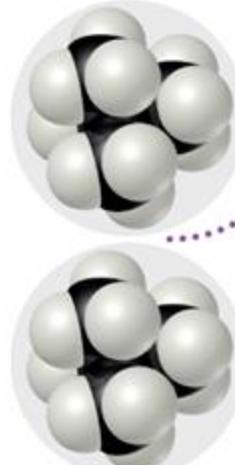
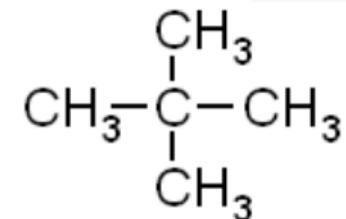
Factors Affecting London Forces

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



n-Pentane (C_5H_{12})
bp = 309.4 K

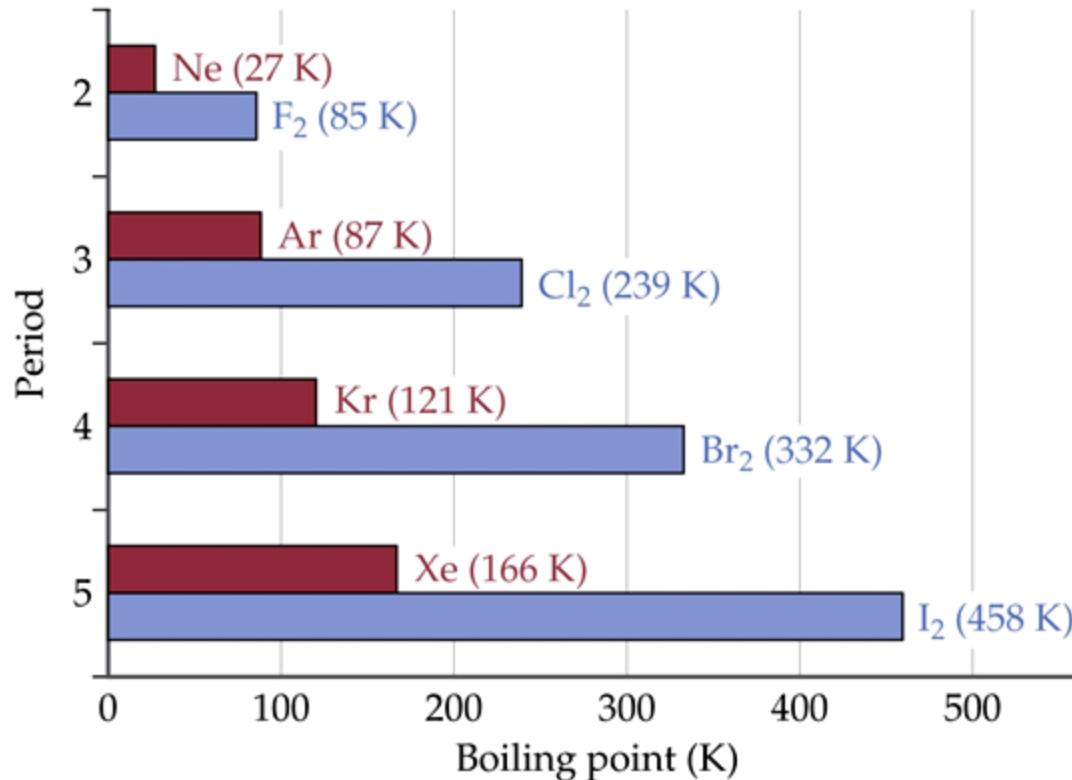
Spherical molecule, smaller surface area diminishes intermolecular contact and decreases dispersion force



Neopentane (C_5H_{12})
bp = 282.7 K

- The **shape** of the molecule affects the **strength** of dispersion forces: long, skinny (细长) molecules (like *n*-pentane) tend to have stronger dispersion forces than short, fat ones (like neopentane 新戊烷).
- This is due to the increased surface area in *n*-pentane.

Factors Affecting London Forces



- The strength of dispersion forces tends to increase with increased **molecular weight**.
- Larger atoms have larger electron clouds that are easier to polarize.



GIVE IT SOME THOUGHT

List the substances CCl_4 , CBr_4 , and CH_4 in order of increasing boiling point.

- A. $\text{CH}_4 < \text{CBr}_4 < \text{CCl}_4$
- B. $\text{CCl}_4 < \text{CH}_4 < \text{CBr}_4$
- C. $\text{CH}_4 < \text{CCl}_4 < \text{CBr}_4$
- D. $\text{CBr}_4 < \text{CCl}_4 < \text{CH}_4$



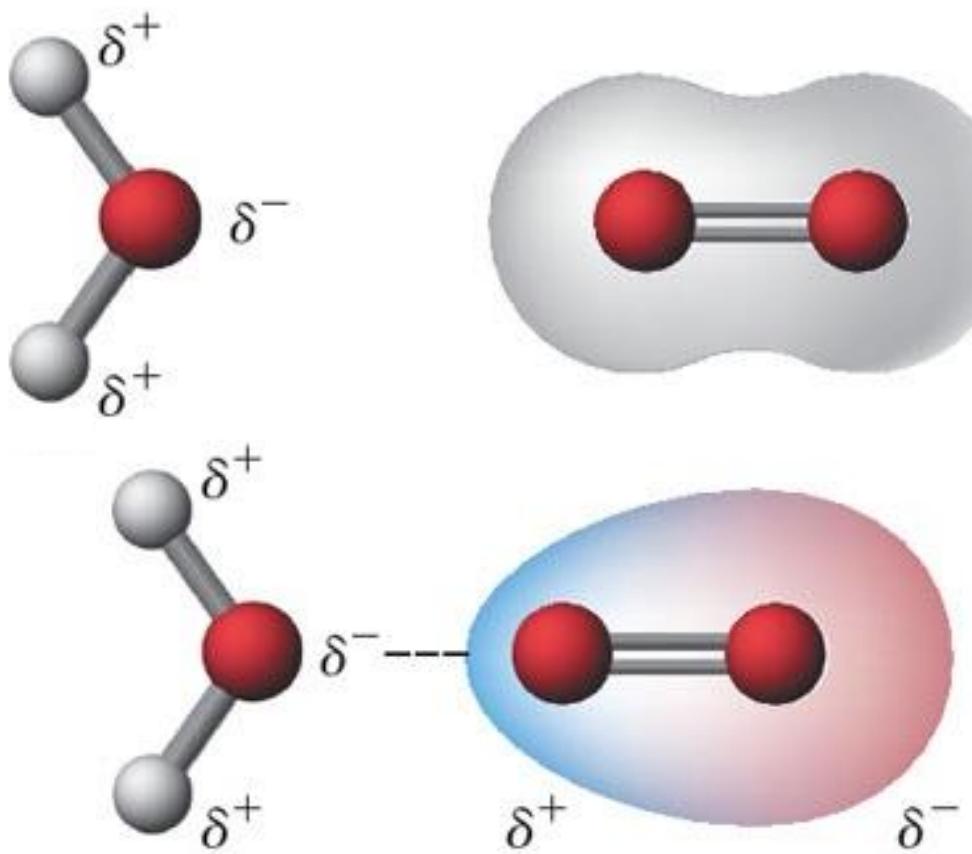
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- B. $\text{CCl}_4 < \text{CH}_4 < \text{CBr}_4$
- C. $\text{CH}_4 < \text{CCl}_4 < \text{CBr}_4$
- D. $\text{CBr}_4 < \text{CCl}_4 < \text{CH}_4$

Dipole – Induced Dipole Interactions

- A weak attraction that results when a polar molecule induces a dipole in an atom or in a nonpolar molecule by disturbing the arrangement of electrons in the nonpolar species.

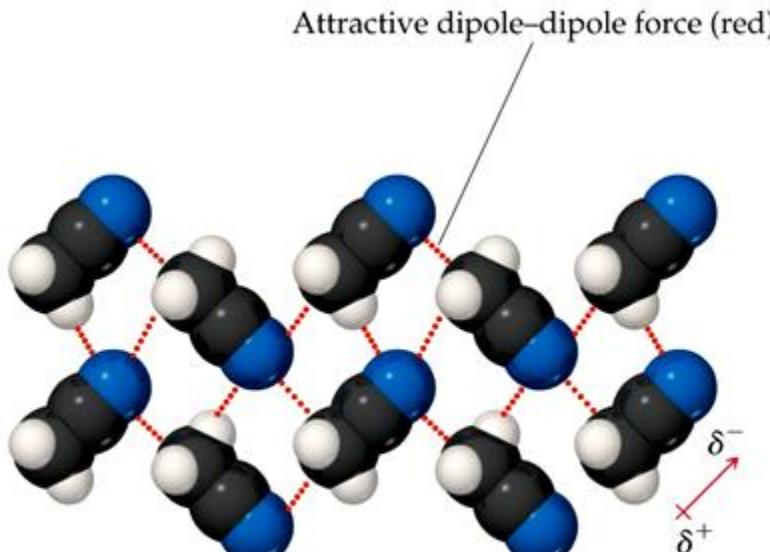


Oxygen dissolves in water:

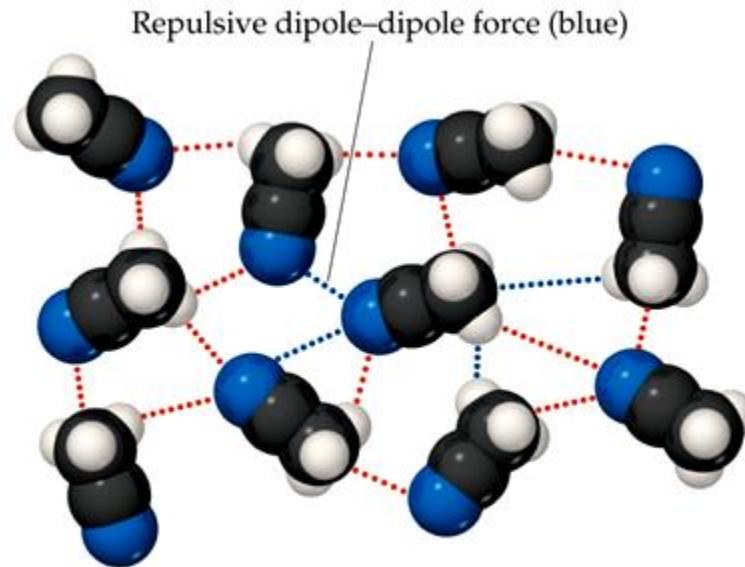
The dipole of water induces a dipole in O_2 by distorting the O_2 electron cloud.

Dipole–Dipole Interactions

- Molecules that have permanent dipoles (固有偶极) 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.

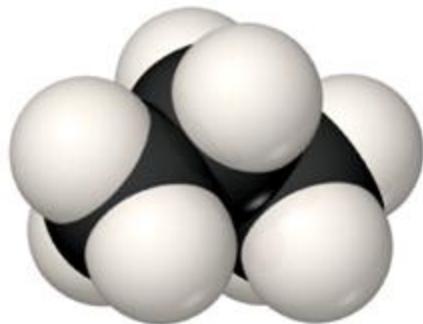


(a) Solid CH_3CN

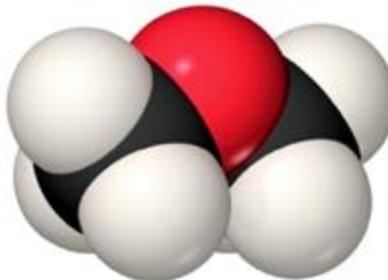


(b) Liquid CH_3CN

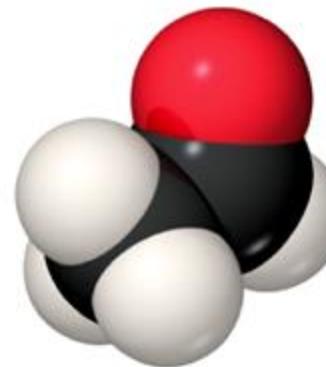
Dipole–Dipole Interactions



Propane
 $\text{CH}_3\text{CH}_2\text{CH}_3$
MW = 44 amu
 $\mu = 0.1 \text{ D}$
bp = 231 K



Dimethyl ether
 CH_3OCH_3
MW = 46 amu
 $\mu = 1.3 \text{ D}$
bp = 248 K



Acetaldehyde
 CH_3CHO
MW = 44 amu
 $\mu = 2.7 \text{ D}$
bp = 294 K



Acetonitrile
 CH_3CN
MW = 41 amu
 $\mu = 3.9 \text{ D}$
bp = 355 K

Increasing polarity
Increasing strength of dipole–dipole forces

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

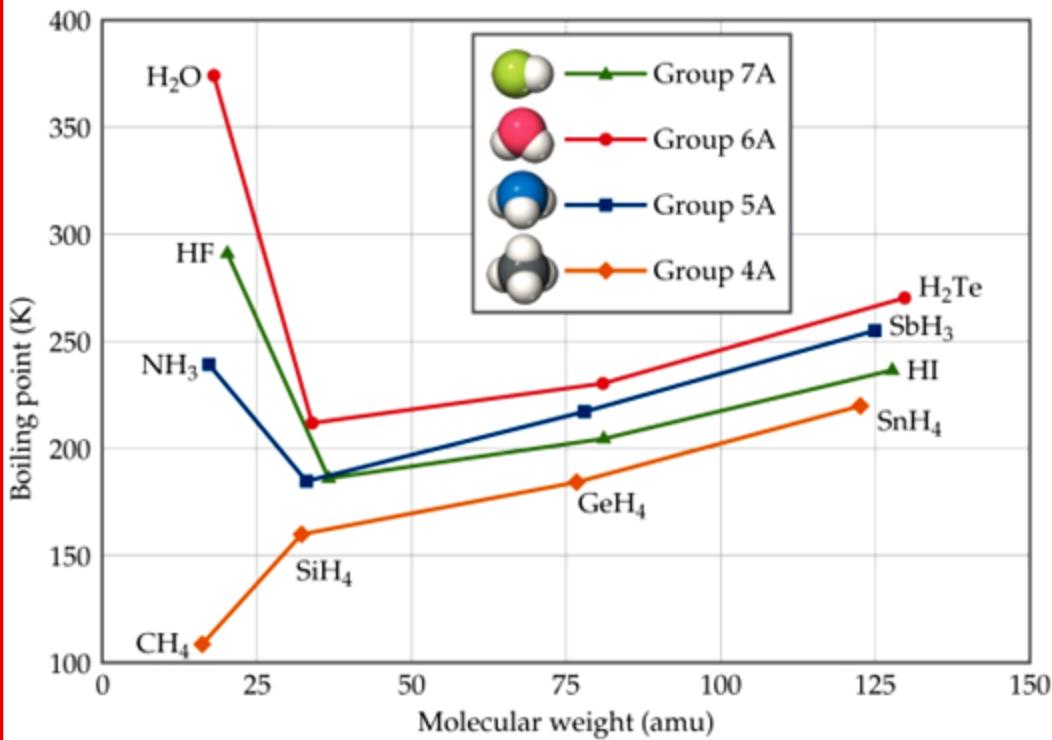
Which Have a Greater Effect?

Dipole–Dipole 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.

注意：这边所说的大小相近，判断的标准是相对分子质量是否相近。

How Do We Explain This?

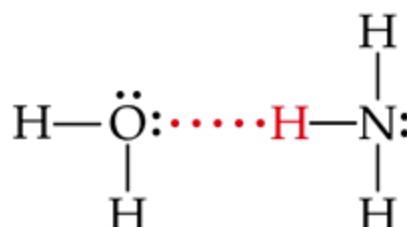
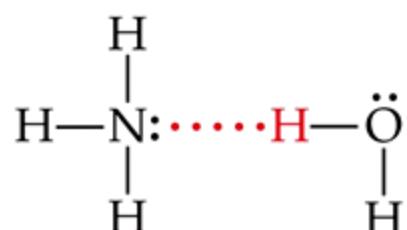
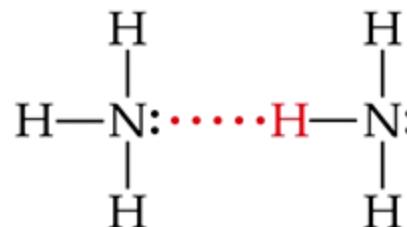
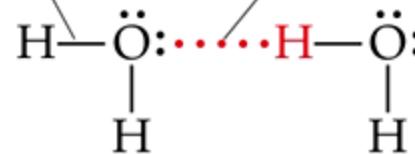


- The nonpolar series (SnH_4 to CH_4) follow the expected trend.
- The polar series follow the trend until you get to the smallest molecules in each group.

Hydrogen Bonding

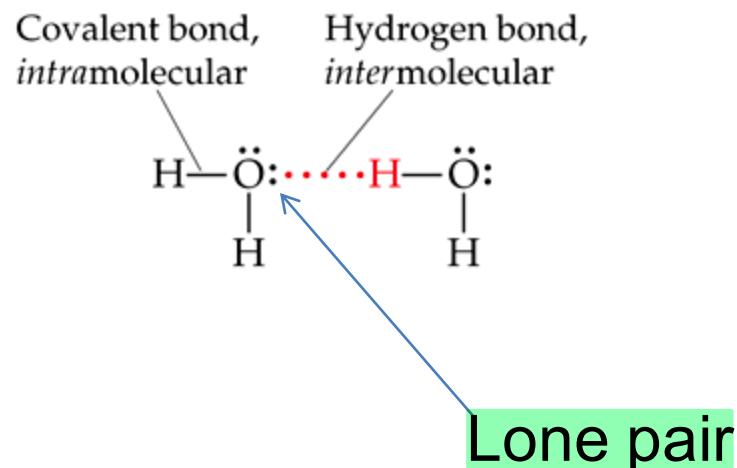
- The dipole–dipole interactions experienced when H is bonded to N, O, or F are unusually strong.
- We call these interactions **hydrogen bonds**.

Covalent bond,
intramolecular Hydrogen bond,
intermolecular



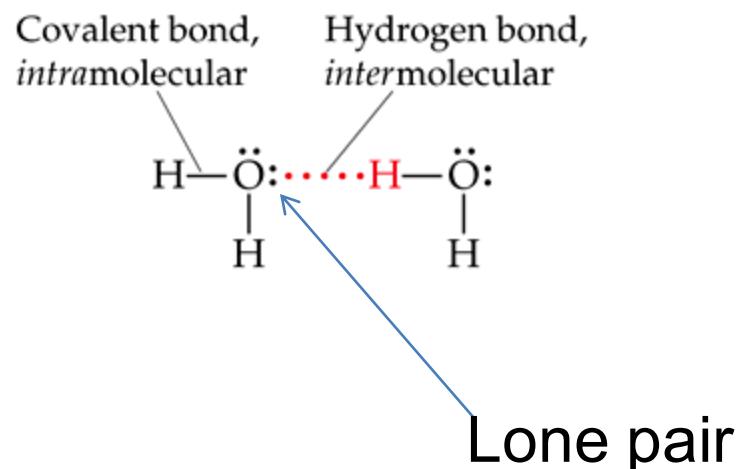
To form a hydrogen bond what must the non-hydrogen atom (N, O, or F) involved in the bond possess?

- A. The non-hydrogen atom must have a nonbonding electron pair.
- B. The non-hydrogen atom must have low electronegativity.
- C. The non-hydrogen atom must have a large atomic size.
- D. The non-hydrogen atom must have a small electron affinity.

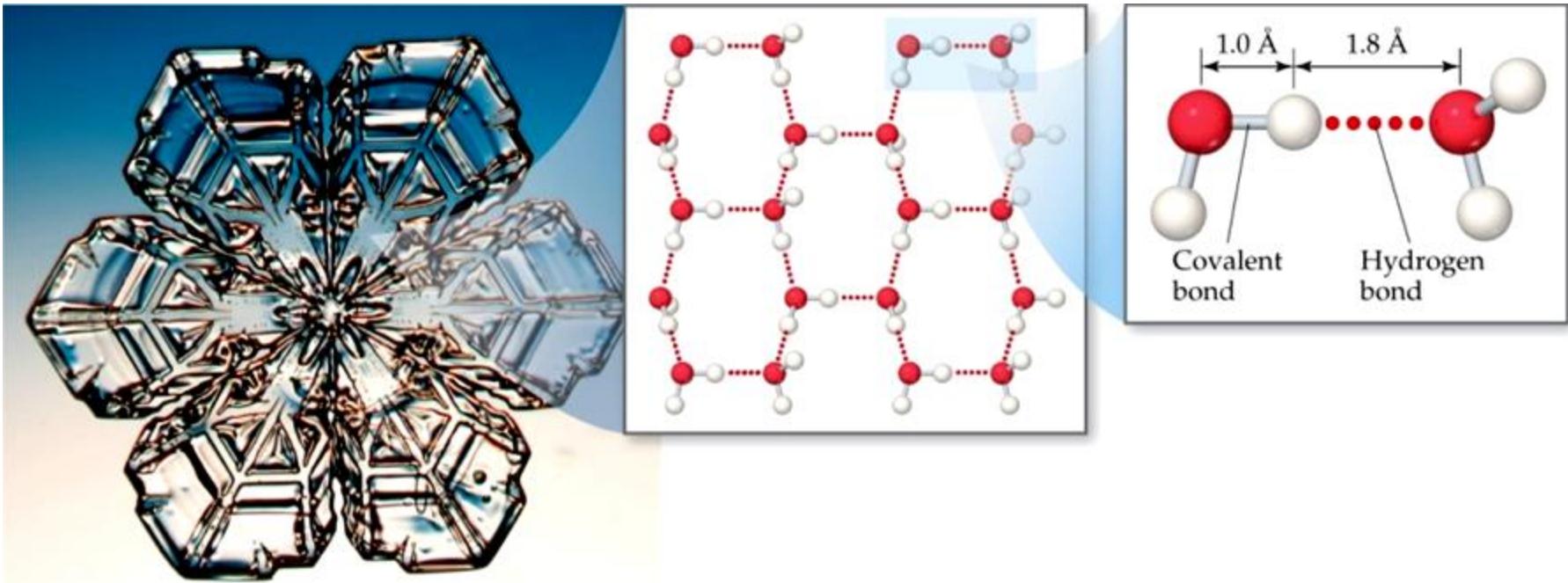


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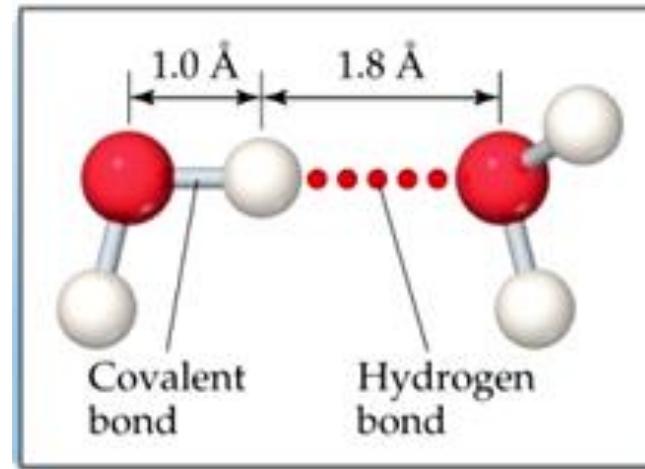
Hydrogen Bonding



- Hydrogen bonding arises in part from the **high electronegativity** of nitrogen, oxygen, and fluorine.
Also, when hydrogen is bonded to one of those very electronegative elements, the hydrogen nucleus is exposed.

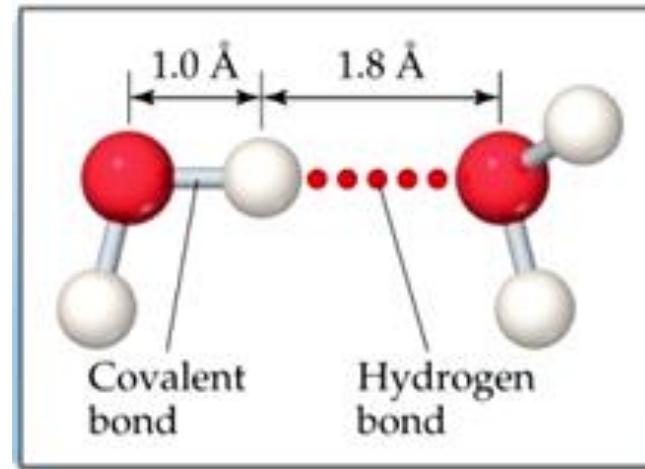
What is the approximate H—O $\cdots\cdots$ H bond angle in ice, where H—O is the covalent bond and O $\cdots\cdots$ H is the hydrogen bond?

- A. Approximately 90°
- B. Approximately 109°
- C. Approximately 120°
- D. Approximately 180°



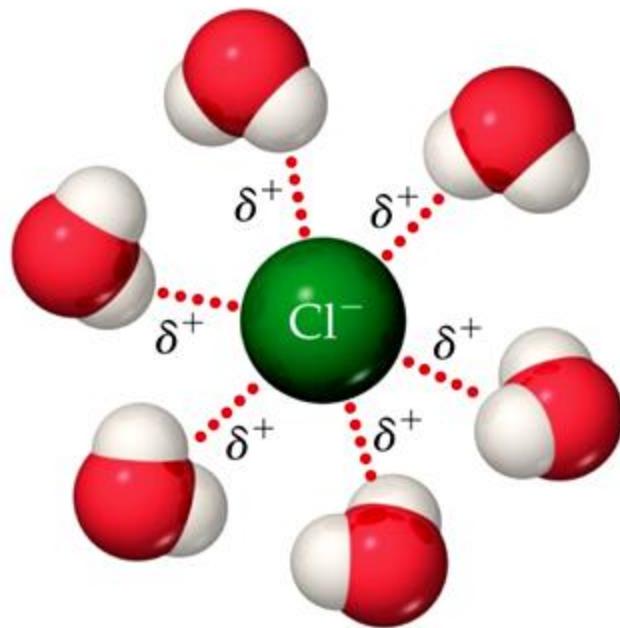
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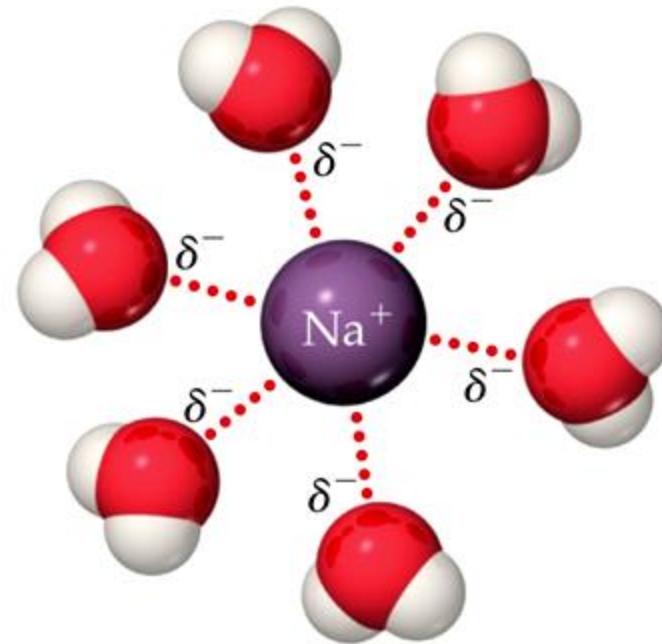


Ion–Dipole Interactions

- Ion–dipole interactions (**a fourth type of force**) are important in solutions of ions.
- The strength of these forces is what makes it possible for **ionic substances to dissolve in polar solvents**.



Positive ends of polar molecules
are oriented toward negatively
charged anion



Negative ends of polar molecules
are oriented toward positively
charged cation



GIVE IT SOME THOUGHT

In which mixture do you expect to find ion–dipole forces: CH₃OH in water or Ca(NO₃)₂ in water?

- A. CH₃OH in water, because CH₃OH is a strong electrolyte and forms ions.
- B. Ca(NO₃)₂ in water, because Ca(NO₃)₂ is a strong electrolyte and forms ions.
- C. CH₃OH in water, because CH₃OH is a weak electrolyte and forms ions.
- D. Ca(NO₃)₂ in water, because Ca(NO₃)₂ is a weak electrolyte and forms ions.

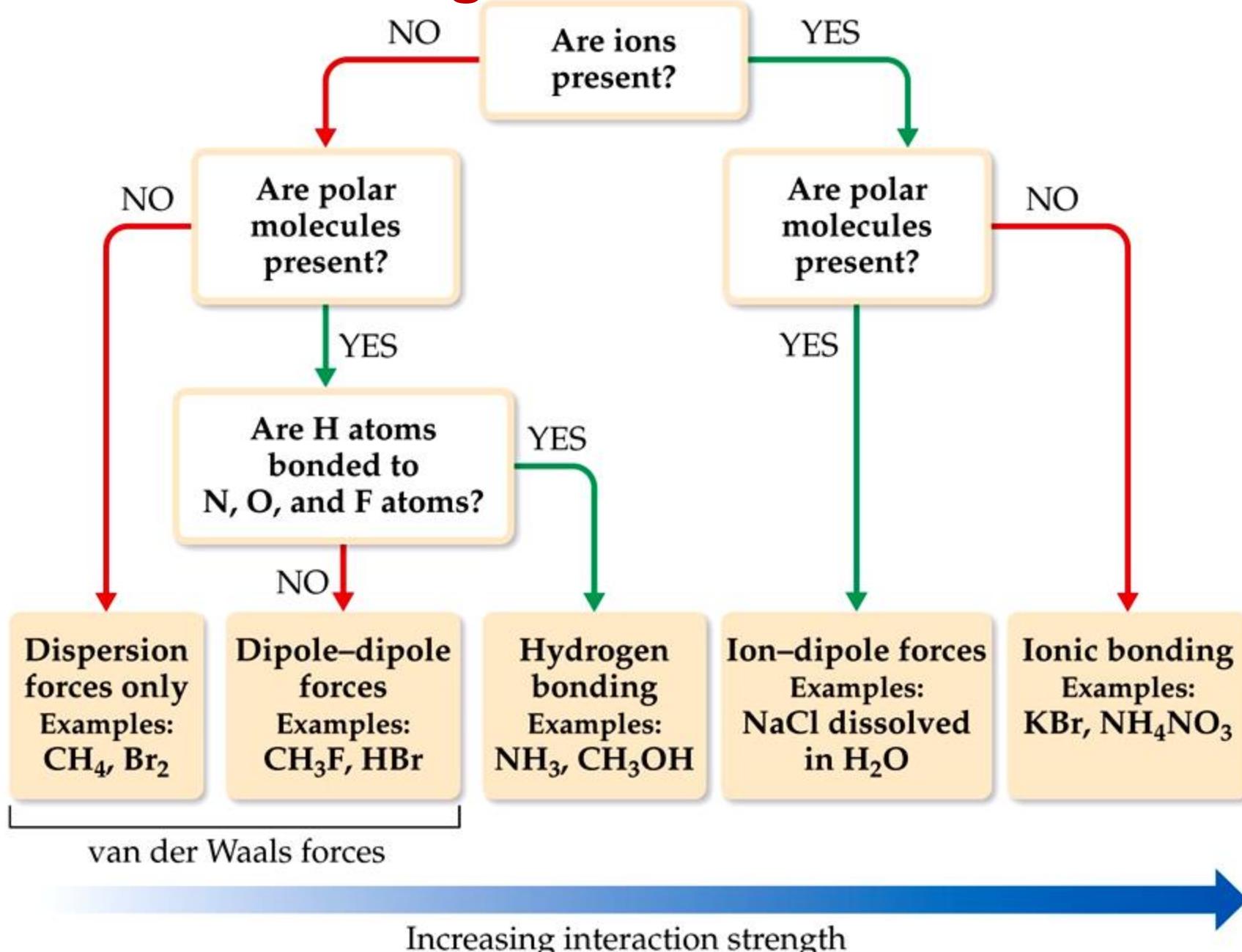


GIVE IT SOME THOUGHT

In which mixture do you expect to find ion–dipole forces: CH₃OH in water or Ca(NO₃)₂ in water?

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- C. CH₃OH in water, because CH₃OH is a weak electrolyte and forms ions.
- D. Ca(NO₃)₂ in water, because Ca(NO₃)₂ is a weak electrolyte and forms ions.

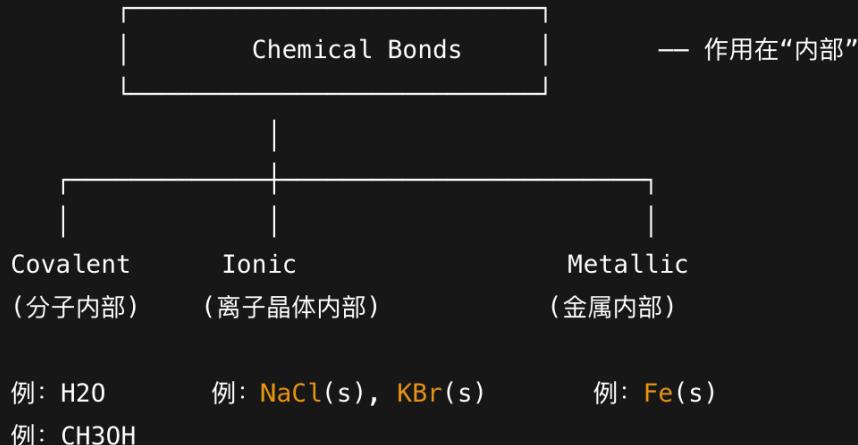
Summarizing Intermolecular Forces



第一层：粒子内部是什么键？ (Chemical Bonds)

scss

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这里要注意：

离子化合物（无论极性/非极性）其本质内部键都是“离子键”。

第二层：粒子之间有什么相互作用？ (Intermolecular Forces)

SCSS

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注意到了吗？

Ion-dipole 和 **Ionic bonding** 分别描述“不同情境”：

- **Ionic bonding** → 固态晶体内的离子键 (intramolecular / 结构力)
- **Ion-dipole** → 离子被溶剂包裹后的粒子间作用 (intermolecular)

极性离子化合物当然“有离子键”，只是：

- ▶ 在固态时 → 显示为 Ionic Bonding (强)

例如：

NaCl(s) 晶体中 Na^+ - Cl^- 靠强不可逆的“离子键”排成晶格。

- ▶ 在溶液中 → 晶格破碎，主要作用变成 Ion-dipole (弱)

例如：

NaCl(aq) → Na^+ 被水分子氧端包围

Cl^- 被水分子氢端包围

于是主导作用力不是离子键，而是离子-偶极力。

也就是说：

同一个离子化合物，固态时用“离子键”描述，溶液中用“离子-偶极力”描述，它们是不同层级的作用力，不冲突。

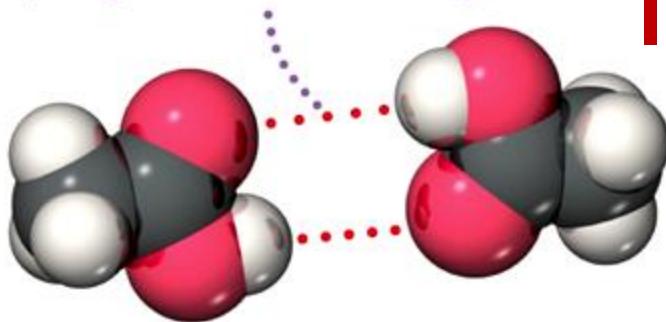
化学键（作用于粒子内部）

- |
- └ 共价键 (H2O, CH3OH)
- └ 离子键 (NaCl(s), KBr(s))
- └ 金属键 (Fe, Cu)

分子间作用力（作用于粒子之间）

- |
- └ 色散力 (CH4)
- └ 偶极–偶极 (HBr)
- └ 氢键 (NH3, CH3OH)
- └ 离子–偶极 (Na+ 与 H2O)
- └ 离子–离子（也可作为晶格作用力来描述）

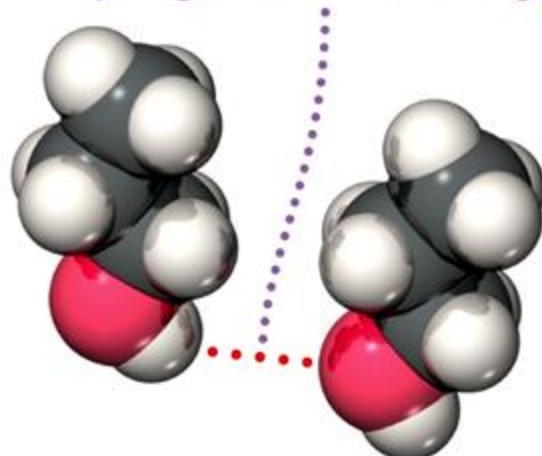
Each molecule can form two hydrogen bonds with a neighbor



Acetic acid, CH_3COOH

MW = 60 amu
bp = 391 K

Each molecule can form one hydrogen bond with a neighbor



1-Propanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$

MW = 60 amu
bp = 370 K

Intermolecular Forces Affect Many Physical Properties

The strength of the attractions between particles can greatly affect the properties of a substance or solution.

Exercise Predicting Types and Relative Strengths of Intermolecular At attractions

List the substances BaCl_2 , H_2 , CO, HF, and Ne in order of increasing boiling point.

Solution

Plan The boiling point depends in part on the attractive forces in each substance. We need to order these according to the relative strengths of the different kinds of intermolecular attractions.

Solve

- (1) The attractive forces are stronger for ionic substances than for molecular ones, so BaCl_2 should have the highest boiling point.
- (2) The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are H_2 (2), CO (28), HF (20), and Ne (20).
- (3) The boiling point of H_2 should be the lowest because it is nonpolar and has the lowest molecular weight. The molecular weights of CO, HF, and Ne are similar.
- (4) Because HF can hydrogen bond, however, it should have the highest boiling point of the three. Next is CO, which is slightly polar and has the highest molecular weight. Finally, Ne, which is nonpolar, should have the lowest boiling point of these three.

Exercise Predicting Types and Relative Strengths of Intermolecular Attraction

List the substances BaCl_2 , H_2 , CO , HF , and Ne in order of increasing boiling point.

Solution

Plan The boiling point depends in part on the attractive forces in each substance. We need to order these according to the relative strengths of the different kinds of intermolecular attractions.

Solve The predicted order of boiling points is, therefore,



Check The boiling points reported in the literature are H_2 (20 K), Ne (27 K), CO (83 K), HF (293 K), and BaCl_2 (1813 K)—in agreement with our predictions.

Viscosity 粘度



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

Substance	Formula	Viscosity (kg/m·s)
Hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	3.26×10^{-4}
Heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	4.09×10^{-4}
Octane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	5.42×10^{-4}
Nonane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	7.11×10^{-4}
Decane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	1.42×10^{-3}

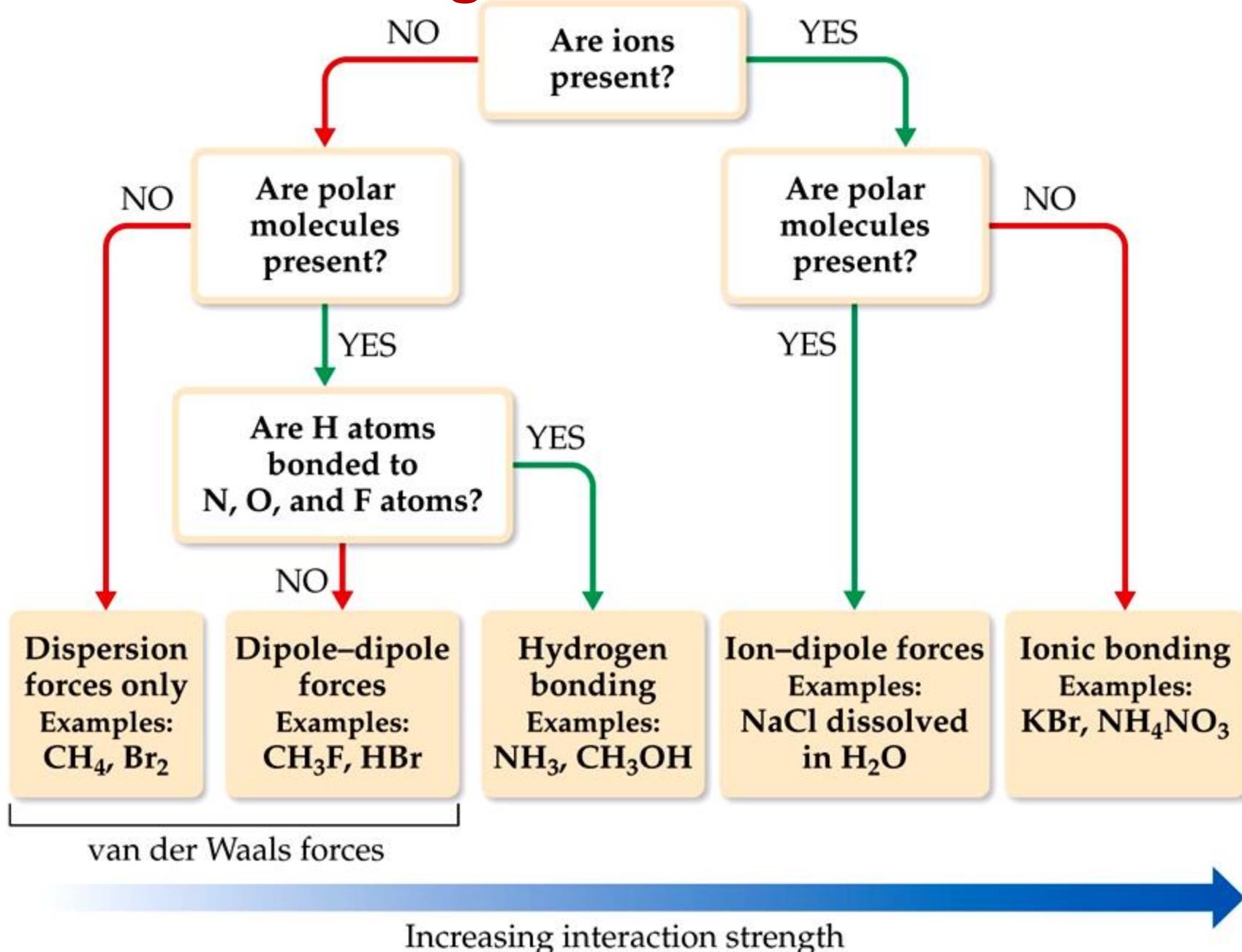
SAE 40
higher number
higher viscosity
slower pouring

SAE 10
lower number
lower viscosity
faster pouring

- Resistance of a liquid to flow is called **viscosity**.
- It is related to the ease with which molecules can move past each other.
- Viscosity increases with stronger intermolecular forces and decreases with higher temperature.

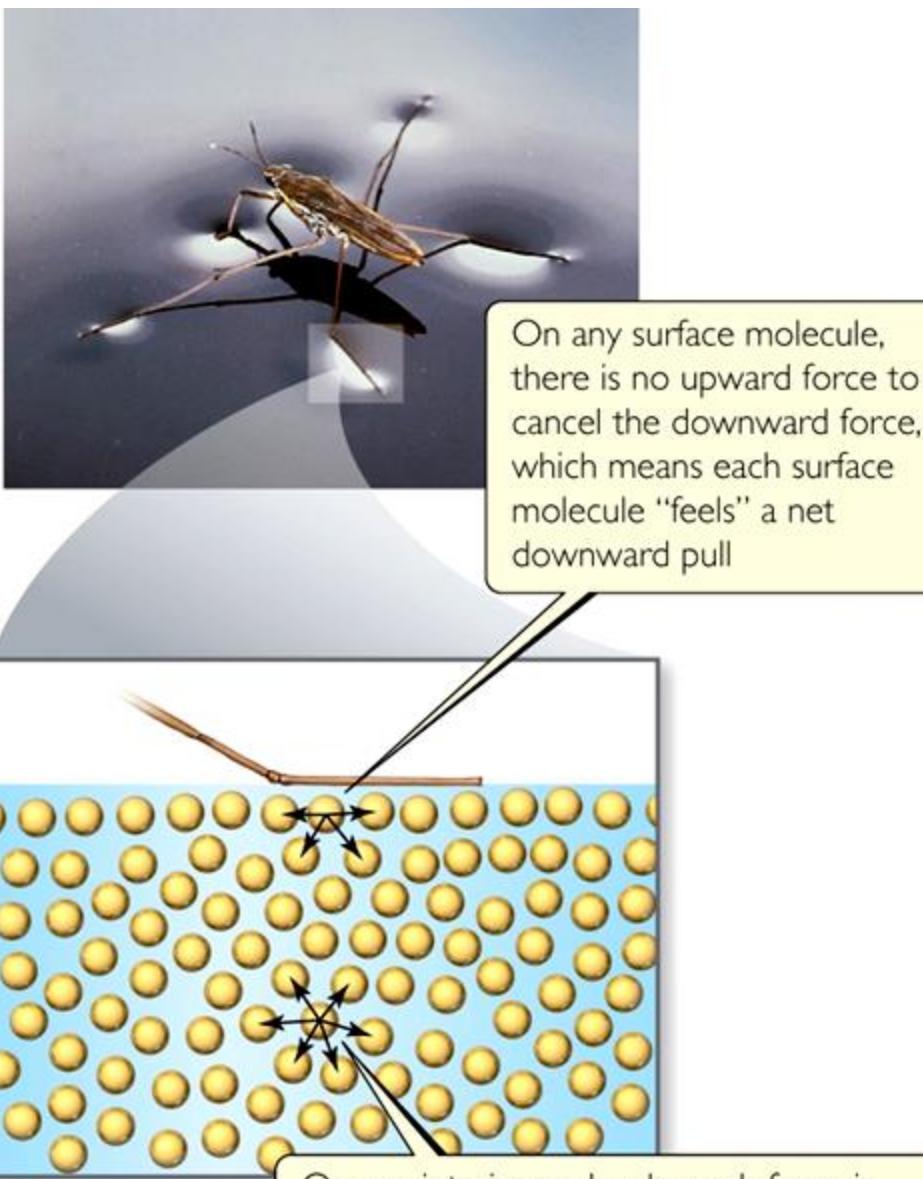
- London Disperse Forces (Dipole-induced dipole interactions)
- Dipole–dipole interactions
- Hydrogen bonding
- Ion–Dipole Interactions

Summarizing Intermolecular Forces



van der Waals forces

Increasing interaction strength



Surface Tension

表面张力

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

It is the energy required to increase area of a liquid by a unit amount (J/m^2)

表面张力指液体表面任意二相邻部分之间垂直于它们的单位长度分界线相互作用的拉力。



GIVE IT SOME THOUGHT

How do viscosity and surface tension change

- a. as temperature increases,
 - b. as intermolecular forces of attraction become stronger?
-
- A. Viscosity increases as intermolecular forces increase while surface tension decreases. Both viscosity and surface tension increase with increasing temperature.
 - B. Viscosity decreases as intermolecular forces increase while surface tension increases. Both viscosity and surface tension increase with decreasing temperature
 - C. Both viscosity and surface tension increase as intermolecular forces increase and temperature decreases.
 - D. Both viscosity and surface tension decrease as intermolecular forces increase and temperature increases.

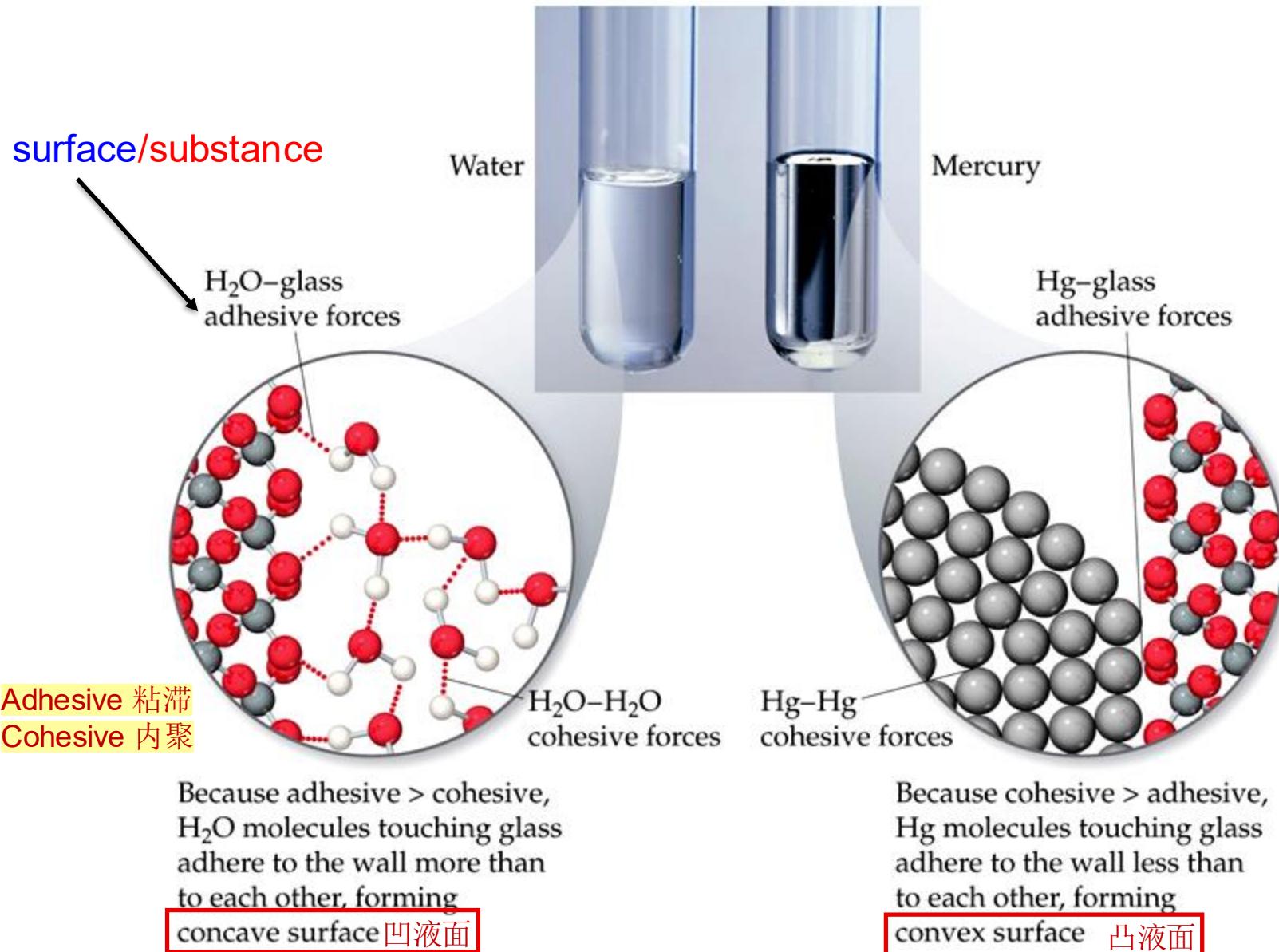


GIVE IT SOME THOUGHT

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 - C. Both viscosity and surface tension increase as intermolecular forces increase and temperature decreases.
 - D. Both viscosity and surface tension decrease as intermolecular forces increase and temperature increases.

Wetting and Non-Wetting



If the inside surface of each tube were coated with wax (蜡), would the general shape of the water meniscus(弯月面) change? Would the general shape of the mercury (汞) meniscus change?

Shape of Water Meniscus

- A. Yes, Inverted U
- B. No change
- C. No change
- D. Yes, Inverted U

Shape of Hg Meniscus

- Yes, downward U
- Yes, downward U
- No change
- No change

If the inside surface of each tube were coated with wax (蜡), would the general shape of the water meniscus change? Would the general shape of the mercury (汞) meniscus change?

Shape of Water Meniscus

- A. Yes, Inverted U
- B. No change
- C. No change
- D. Yes, Inverted U

Shape of Hg Meniscus

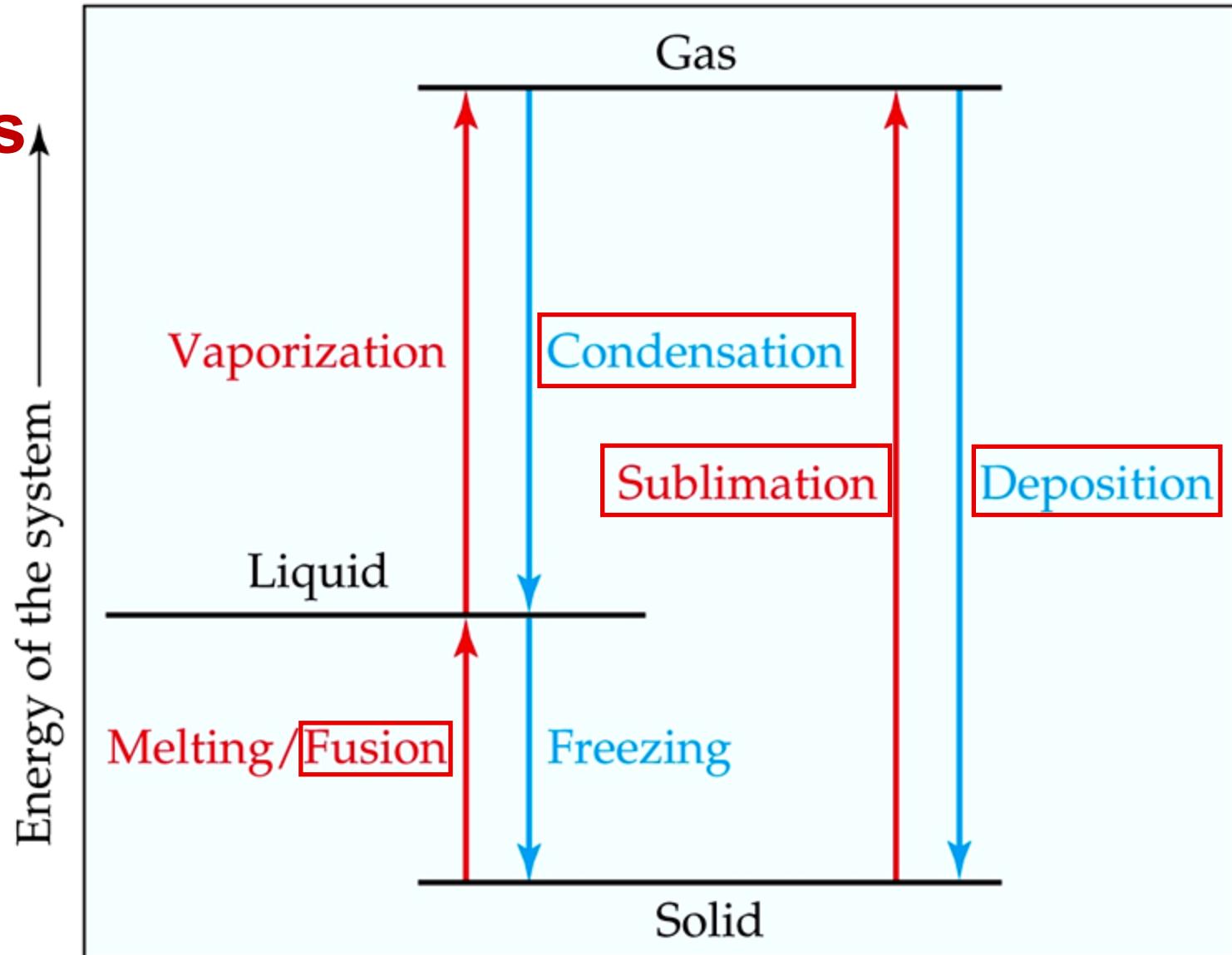
- Yes, downward U
- Yes, downward U
- No change
- No change

Water-Repellent Legs of Water Striders

Water striders (*Gerris remigis*) have remarkable non-wetting legs that enable them to stand effortlessly and move quickly on water, a feature believed to be due to a surface-tension effect caused by secreted wax (蜡).

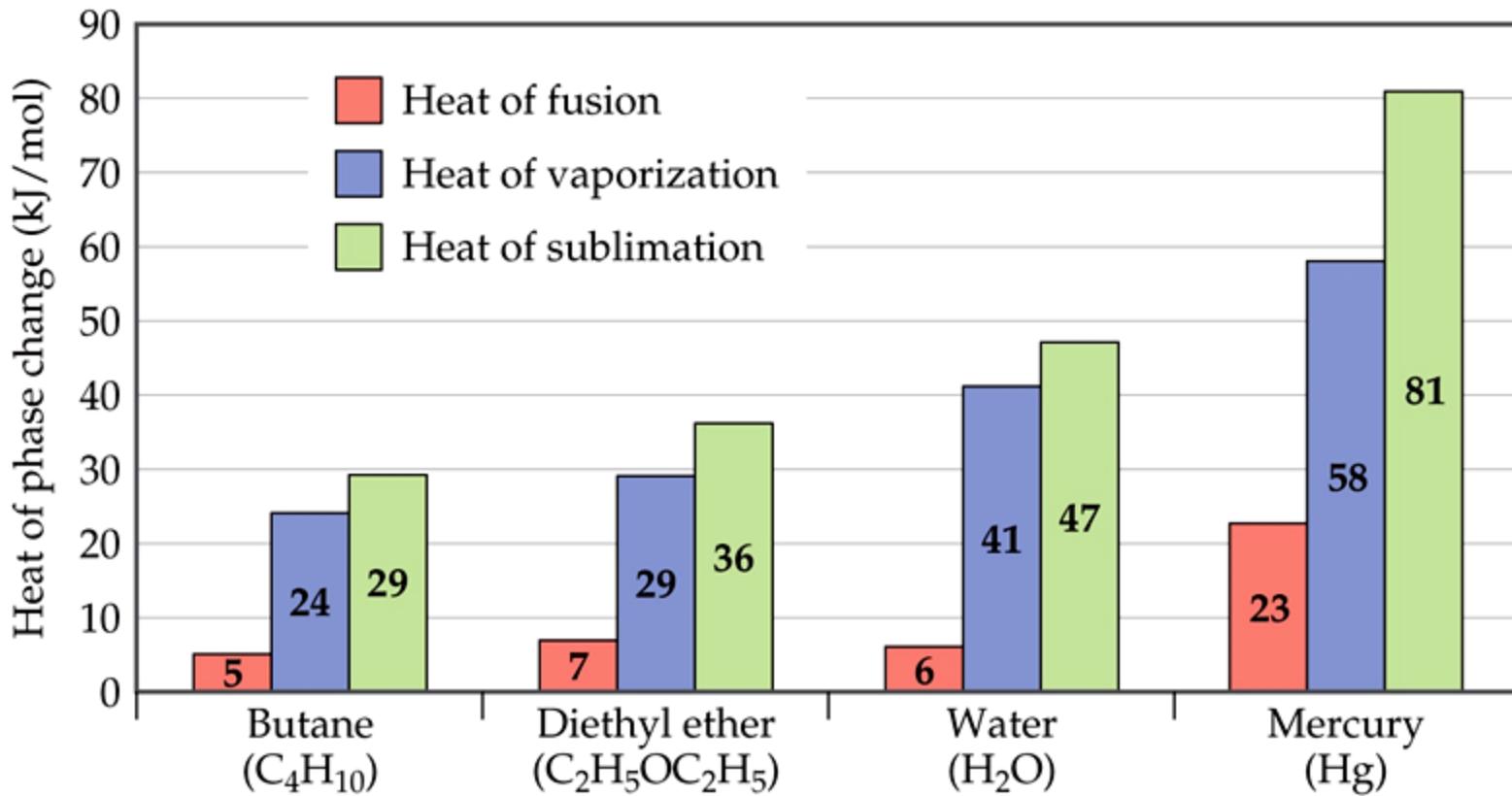


Phase Changes



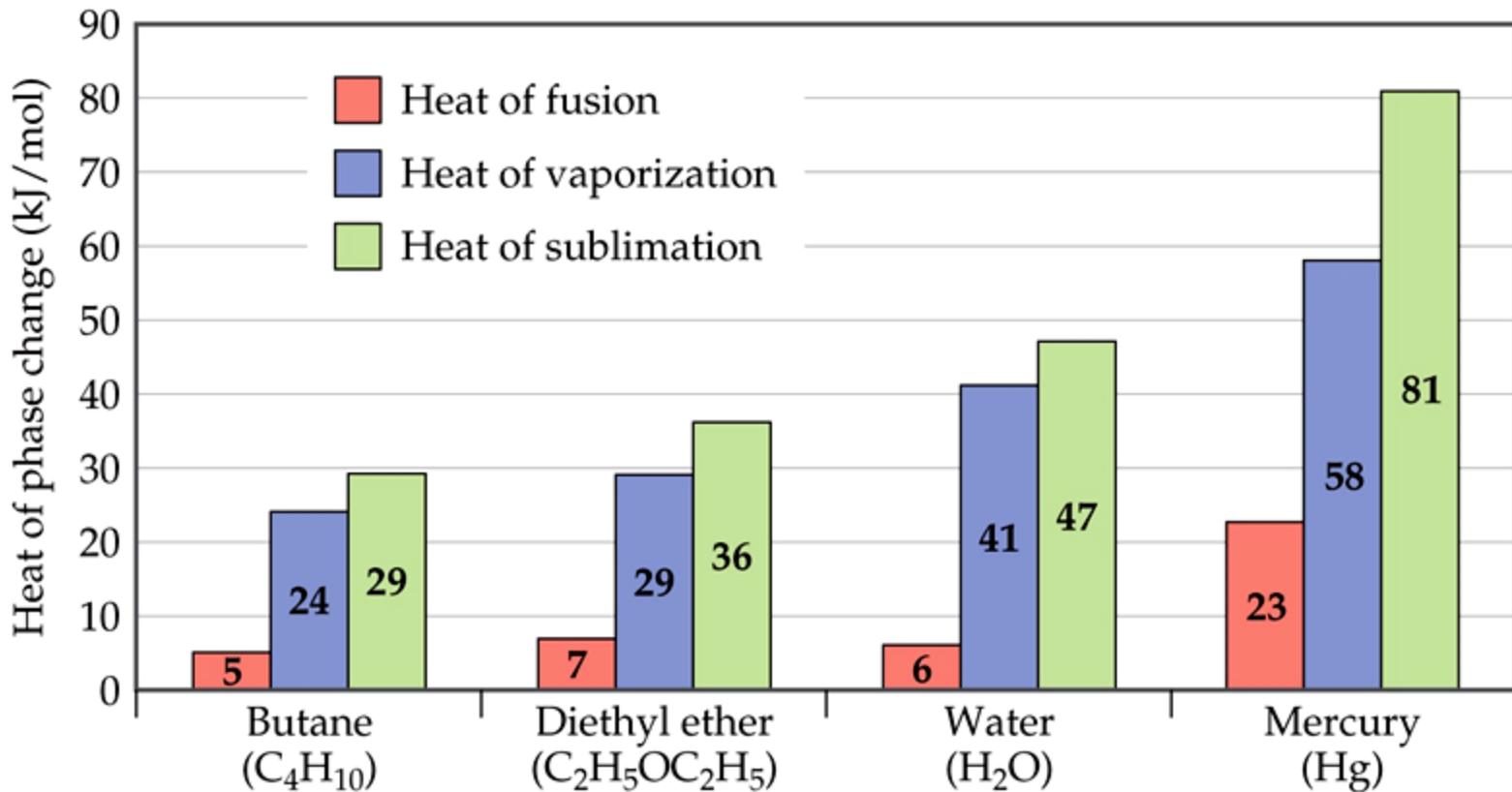
- Endothermic process (energy added to substance)
- Exothermic process (energy released from substance)

Energy Changes Associated with Changes of State



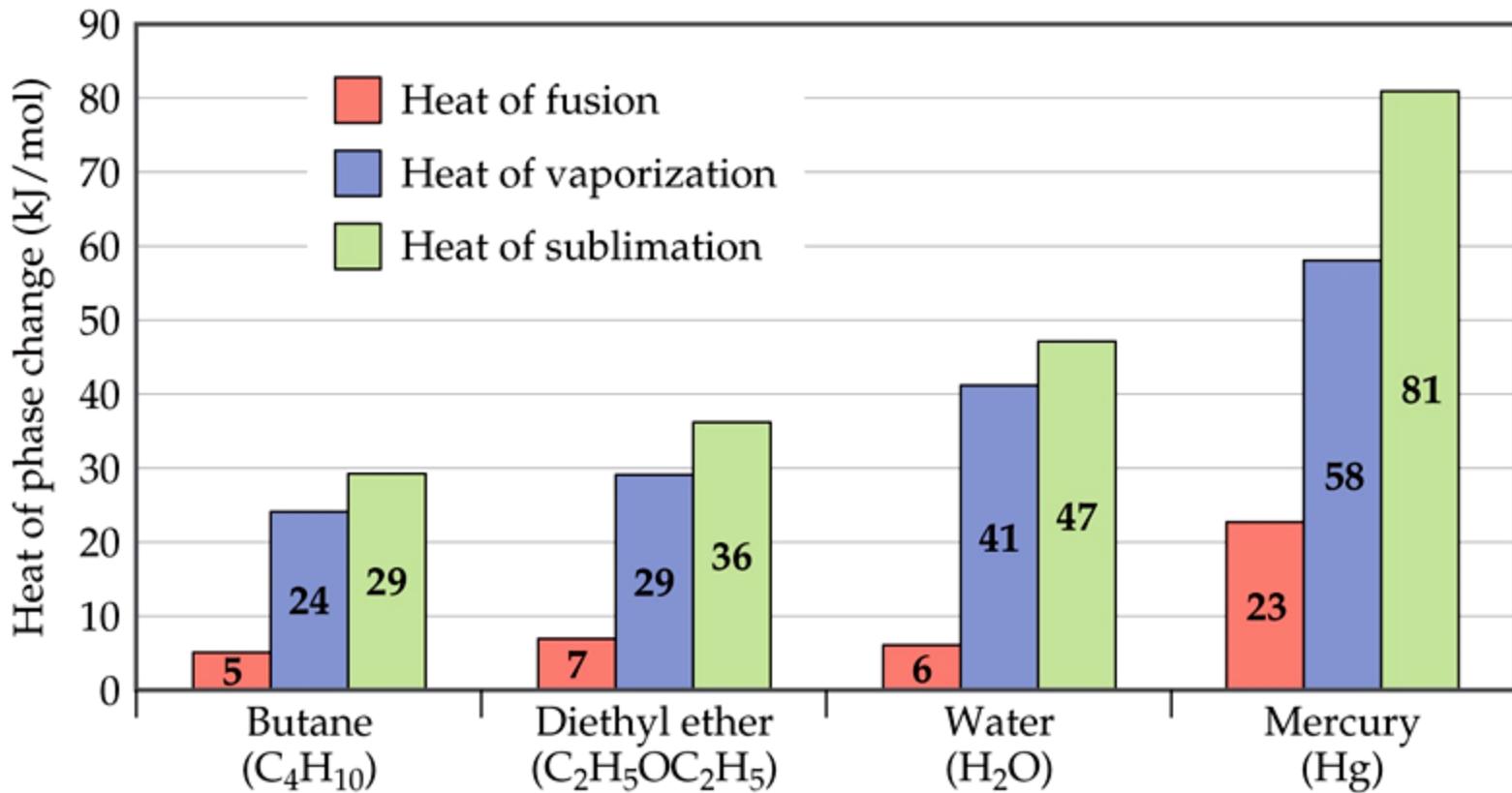
The **heat of fusion** (熔化热) is the energy required to change a solid at its melting point to a liquid.

Energy Changes Associated with Changes of State



The **heat of vaporization** (蒸发热) is defined as the energy required to change a liquid at its boiling point to a gas.

Energy Changes Associated with Changes of State



The **heat of sublimation** (升华热) is defined as the energy required to change a solid directly to a gas.

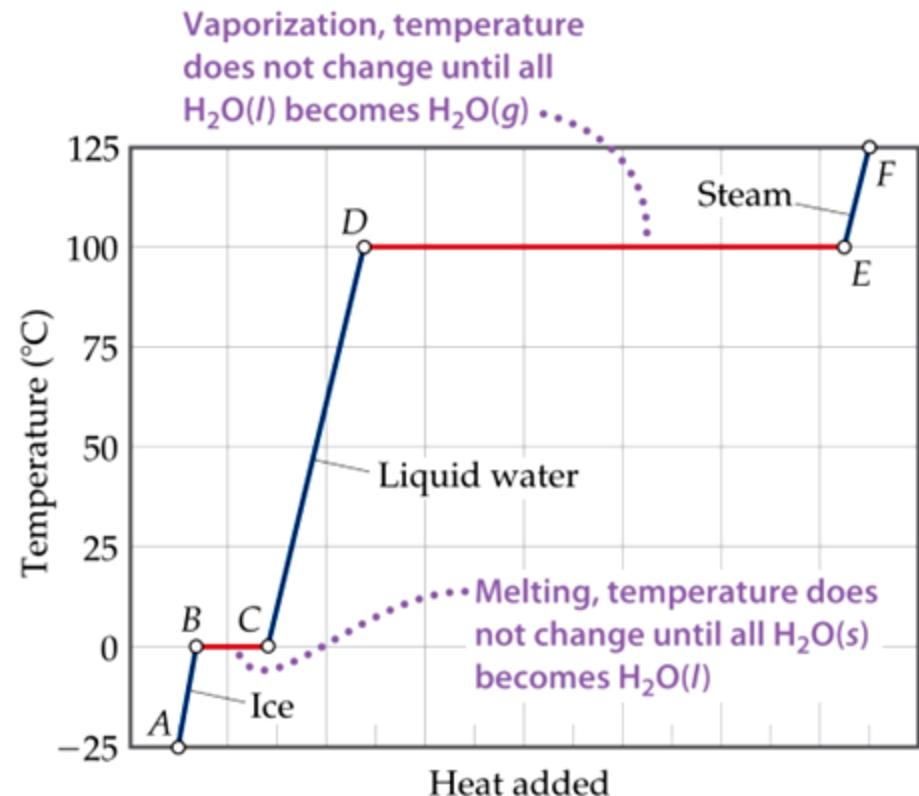
Is it possible to calculate the heat of sublimation for a substance given its heats of vaporization and fusion? If so, what is the relationship?

- A. No, because we are not dealing with state functions.
- B. No, because we need heat of melting.
- C. Yes, $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
- D. Yes, $\Delta H_{sub} = \Delta H_{fus} - \Delta H_{vap}$

Is it possible to calculate the heat of sublimation for a substance given its heats of vaporization and fusion? If so, what is the relationship?

- A. No, because we are not dealing with state functions.
- B. No, because we need heat of melting.
- C. Yes, $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
- D. Yes, $\Delta H_{sub} = \Delta H_{fus} - \Delta H_{vap}$

Energy Changes Associated with Changes of State



- The heat added to the system at the melting and boiling points goes into pulling the molecules farther apart from each other.
- The temperature of the substance does not rise during a phase change.

Exercise Calculating ΔH for Temperature and Phase Changes

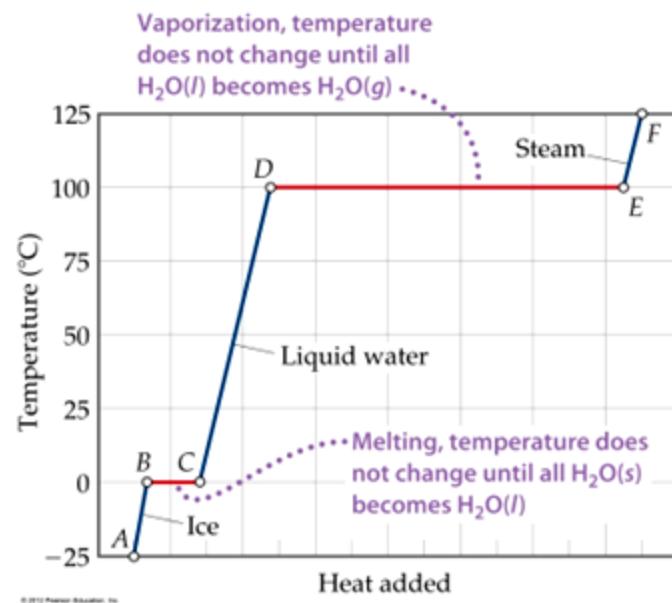
Calculate the enthalpy change upon converting 1.00 mol of ice at $-25\text{ }^{\circ}\text{C}$ to steam at $125\text{ }^{\circ}\text{C}$ under a constant pressure of 1 atm. The specific heats of ice, liquid water, and steam are 2.03 J/g-K, 4.18 J/g-K, and 1.84 J/g-K, respectively. For H_2O , $\Delta H_{\text{fus}} = 6.01\text{ kJ/mol}$ and $\Delta H_{\text{vap}} = 40.67\text{ kJ/mol}$.

Solution

Plan We can calculate the enthalpy change for each segment and then sum them to get the total enthalpy change (Hess's law, Section 5.6).

Solve For segment *AB* in Figure 11.22, we are adding enough heat to ice to increase its temperature by $25\text{ }^{\circ}\text{C}$. A temperature change of $25\text{ }^{\circ}\text{C}$ is the same as a temperature change of 25 K, so we can use the specific heat of ice to calculate the enthalpy change during this process:

$$\text{AB: } \Delta H = (1.00\text{ mol})(18.0\text{ g/mol})(2.03\text{ J/g-K})(25\text{ K}) = 914\text{ J} = 0.91\text{ kJ}$$



Exercise Calculating ΔH for Temperature and Phase Changes (continued)

For segment BC in Figure 11.22, in which we convert ice to water at 0°C , we can use the molar enthalpy of fusion directly:

$$\textcolor{red}{BC}: \Delta H = (1.00 \text{ mol})(6.01 \text{ kJ/mol}) = 6.01 \text{ kJ}$$

The enthalpy changes for segments CD , DE , and EF can be calculated in similar fashion:

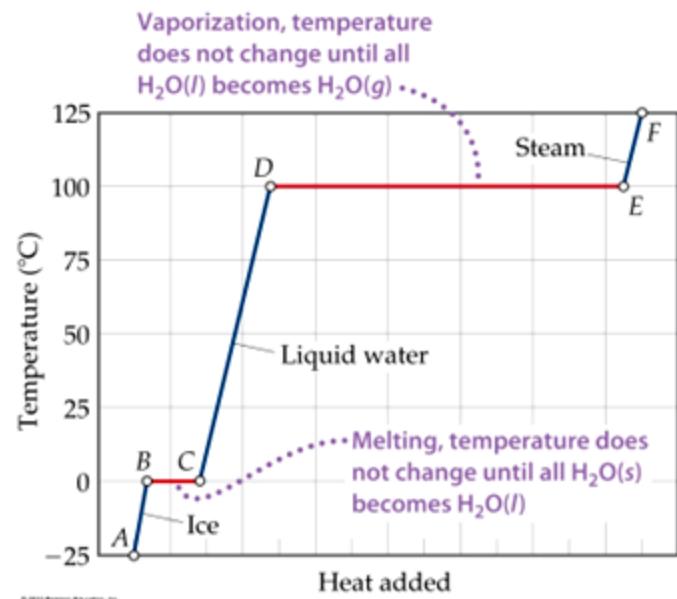
$$\textcolor{red}{CD}: \Delta H = (1.00 \text{ mol})(18.0 \text{ g/mol})(4.18 \text{ J/g-K})(100 \text{ K}) \\ = 7520 \text{ J} = 7.52 \text{ kJ}$$

$$\textcolor{red}{DE}: \Delta H = (1.00 \text{ mol})(40.67 \text{ kJ/mol}) = 40.7 \text{ kJ}$$

$$\textcolor{red}{EF}: \Delta H = (1.00 \text{ mol})(18.0 \text{ g/mol})(1.84 \text{ J/g-K})(25 \text{ K}) = 830 \text{ J} = 0.83 \text{ kJ}$$

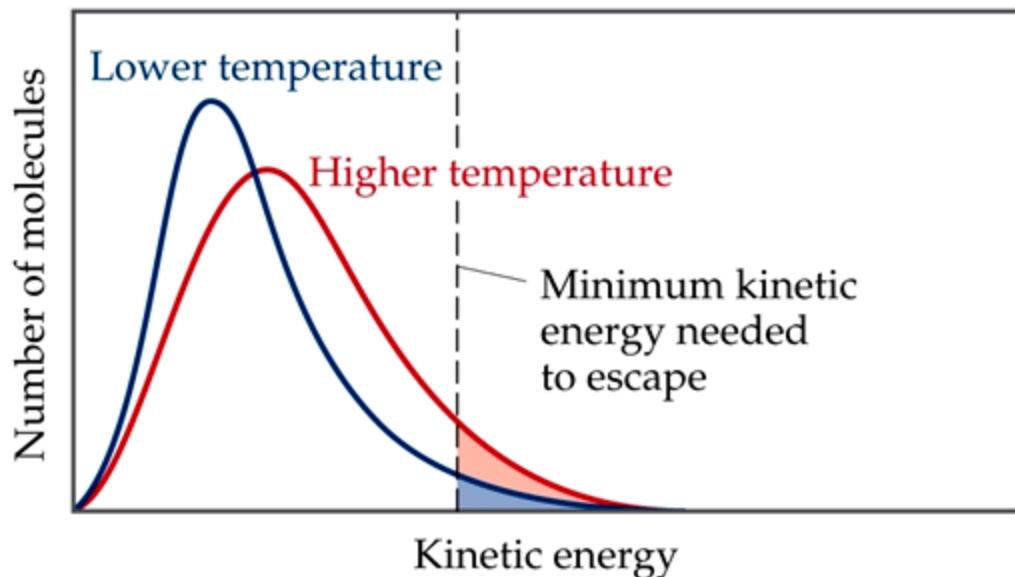
The total enthalpy change is the sum of the changes of the individual steps:

$$\Delta H = 0.91 \text{ kJ} + 6.01 \text{ kJ} + 7.52 \text{ kJ} + 40.7 \text{ kJ} + 0.83 \text{ kJ} \\ = 56.0 \text{ kJ}$$



Vapor Pressure

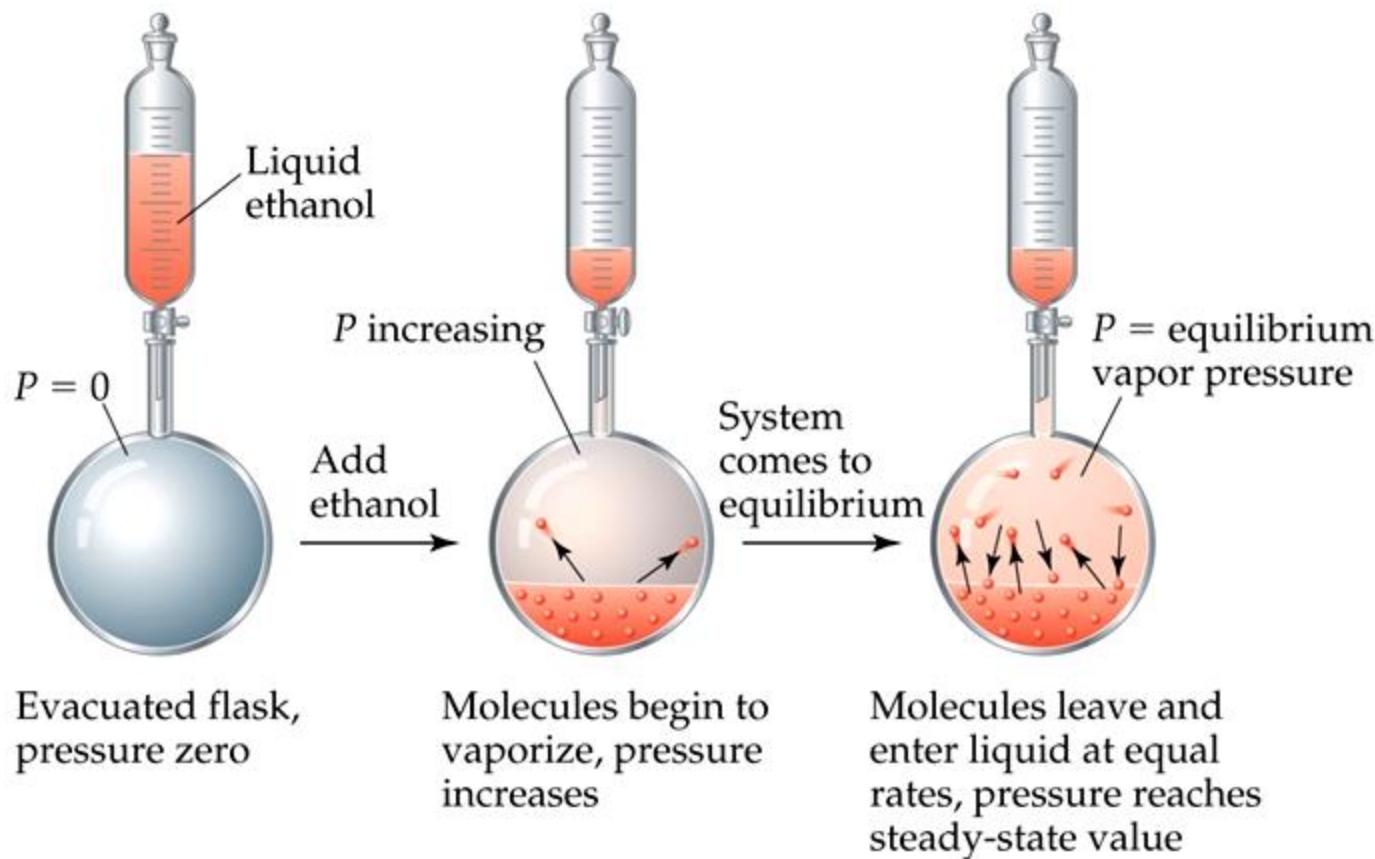
- At any temperature some molecules in a liquid have enough energy to break free.
- As the temperature rises, the fraction of molecules that have enough energy to break free increases.



Blue area = number of molecules having enough energy to evaporate at lower temperature

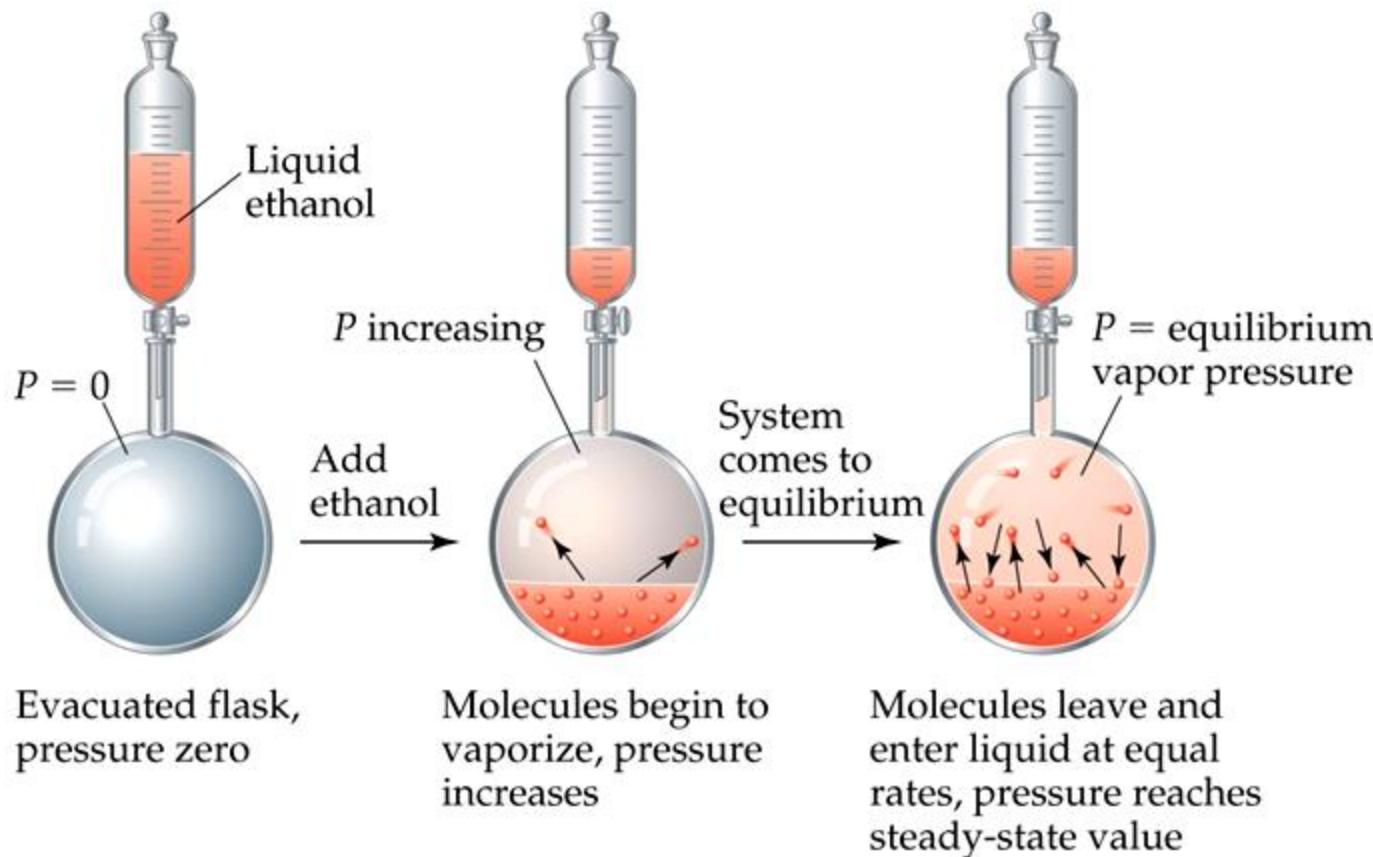
Red + blue areas = number of molecules having enough energy to evaporate at higher temperature

Vapor Pressure



As more molecules escape the liquid,
the pressure they exert increases.

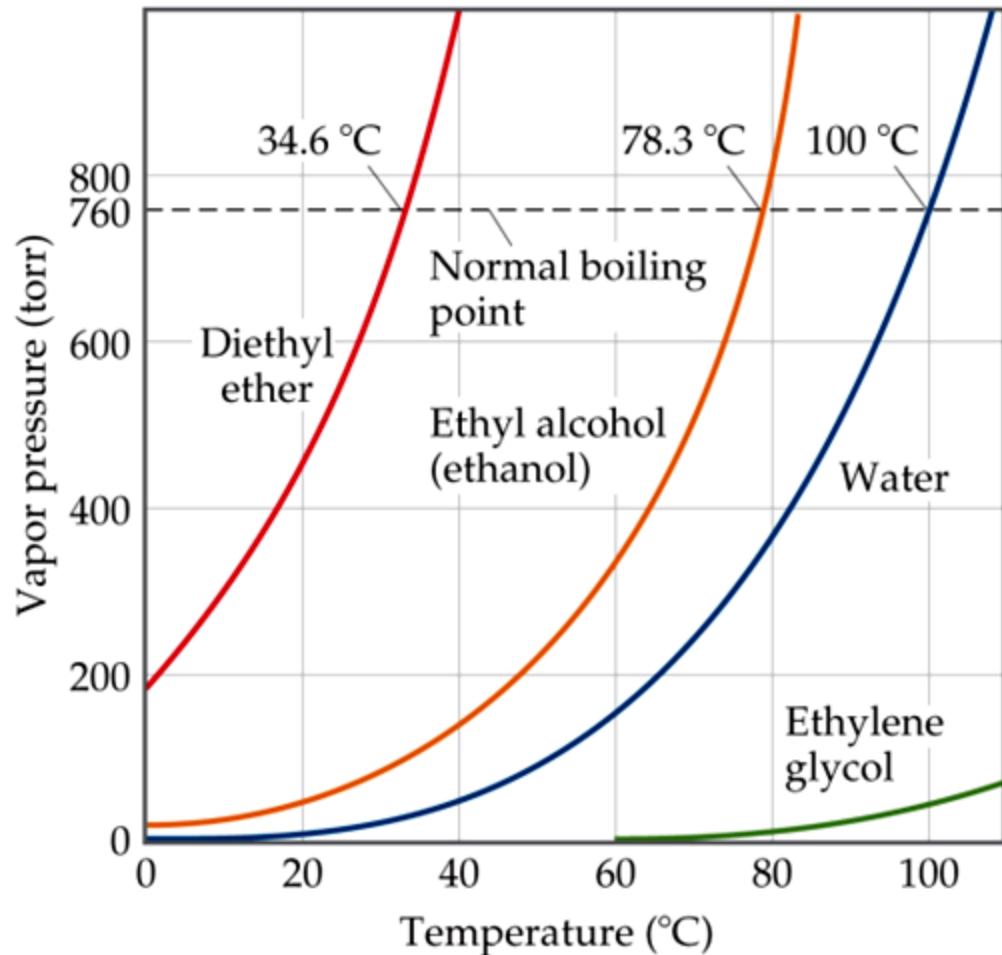
Vapor Pressure



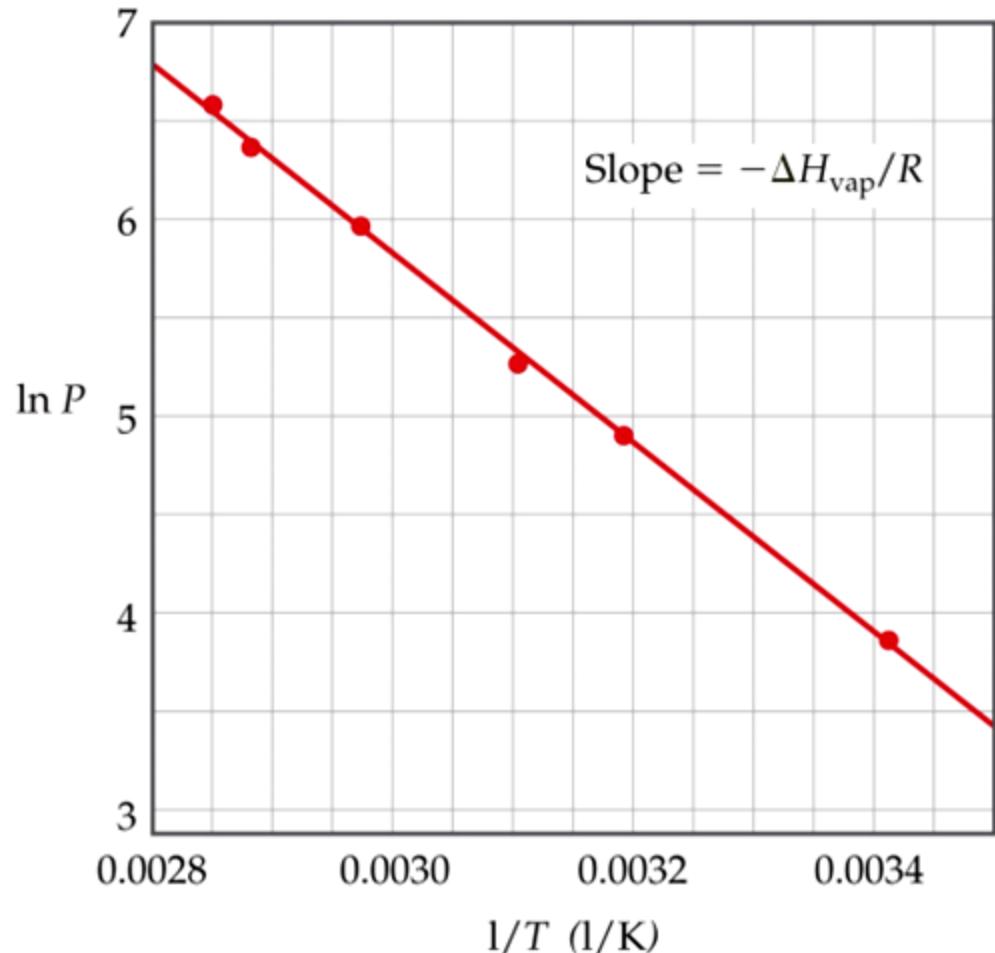
The liquid and vapor reach a state of dynamic equilibrium: liquid molecules evaporate and vapor molecules condense *at the same rate*.

Vapor Pressure

- The **boiling point** of a liquid is the temperature at which its vapor pressure equals atmospheric pressure.
- The **normal boiling point** is the temperature at which its vapor pressure is 760 torr.

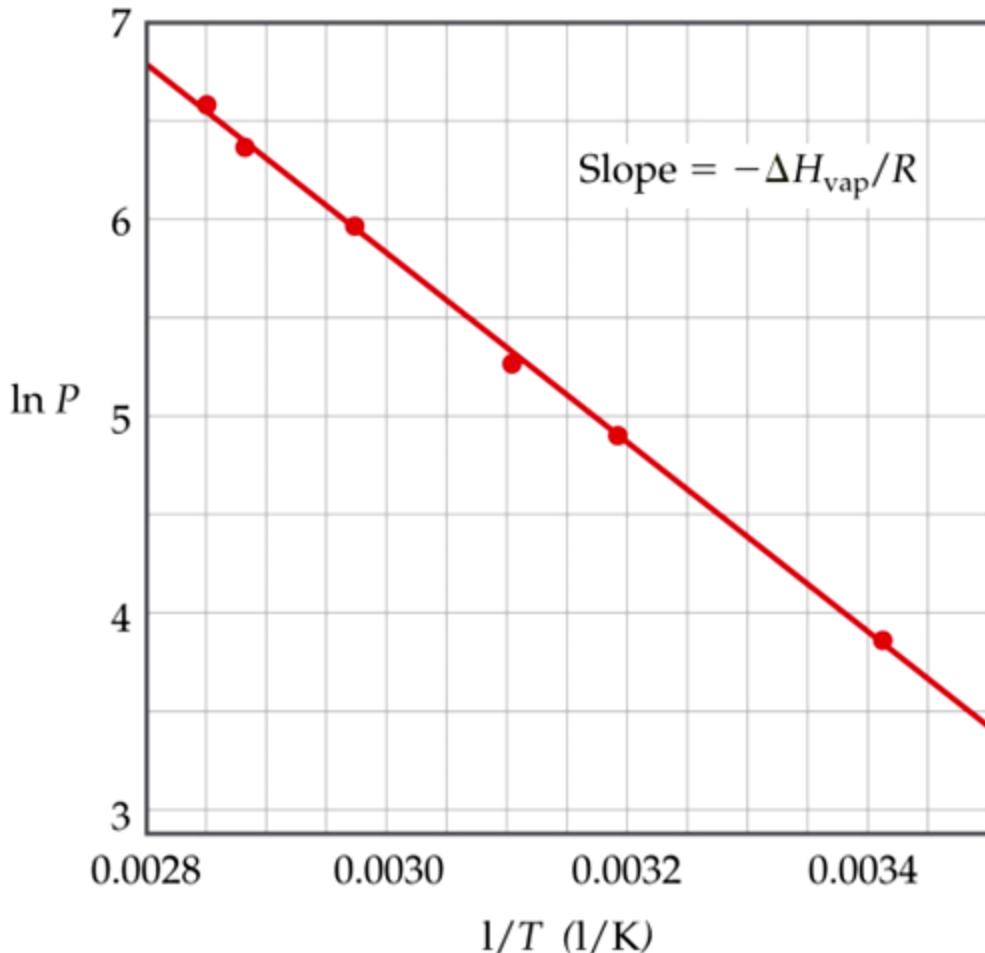


Vapor Pressure



The natural log of the vapor pressure of a liquid is inversely proportional to its temperature.

Vapor Pressure



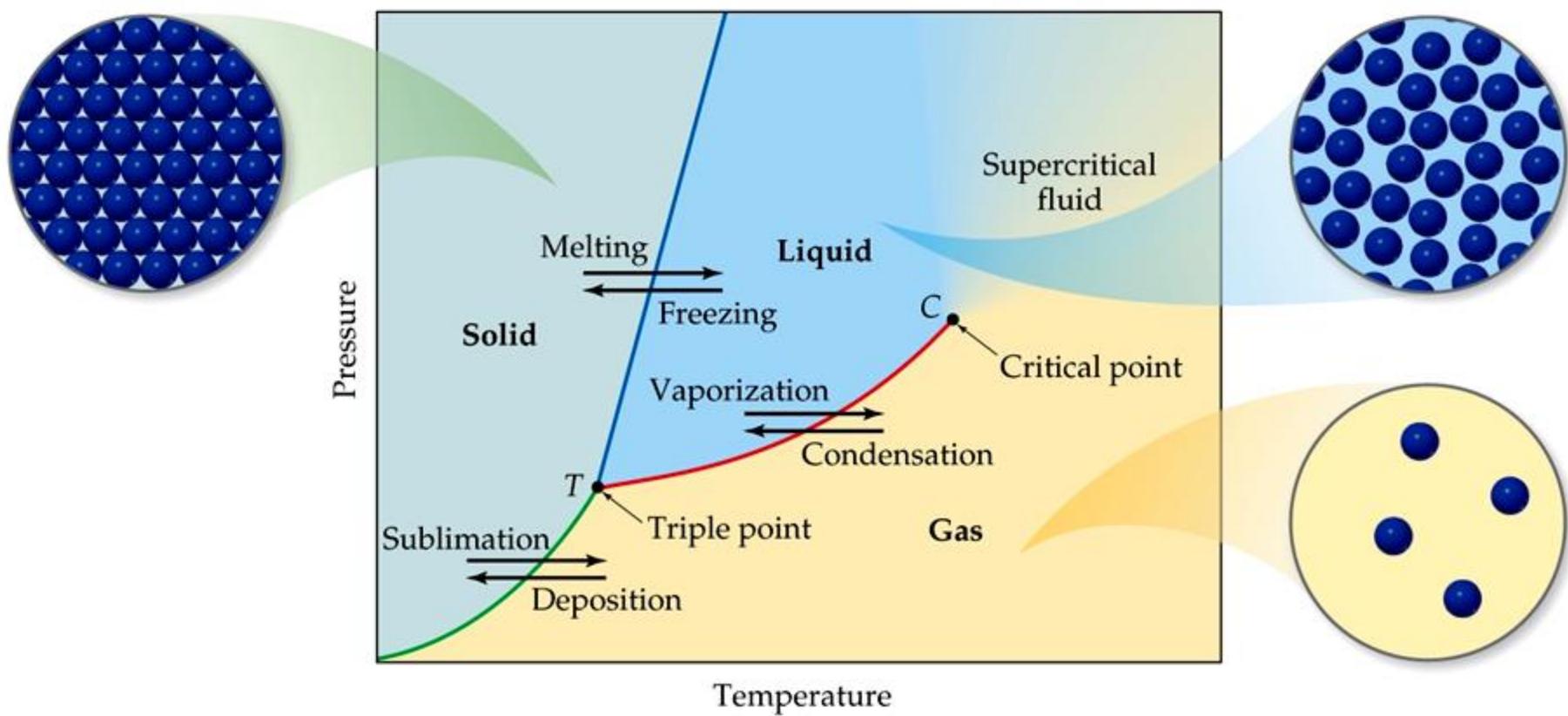
This relationship is quantified in the **Clausius–Clapeyron equation:**

$$\ln P = -\Delta H_{\text{vap}}/RT + C,$$

where C is a constant.

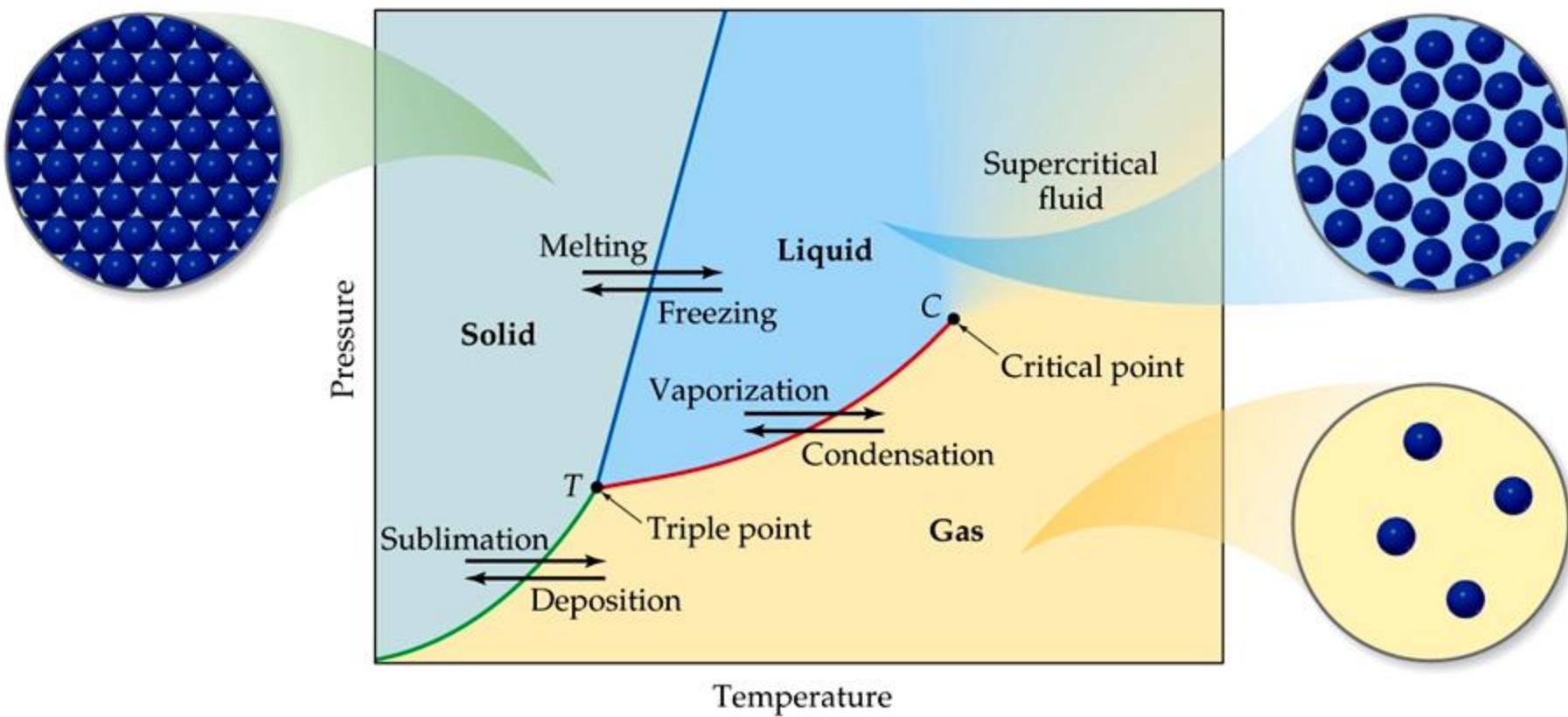
Phase Diagrams

Phase diagrams display the state of a substance at various pressures and temperatures, and the places where equilibria exist between phases.



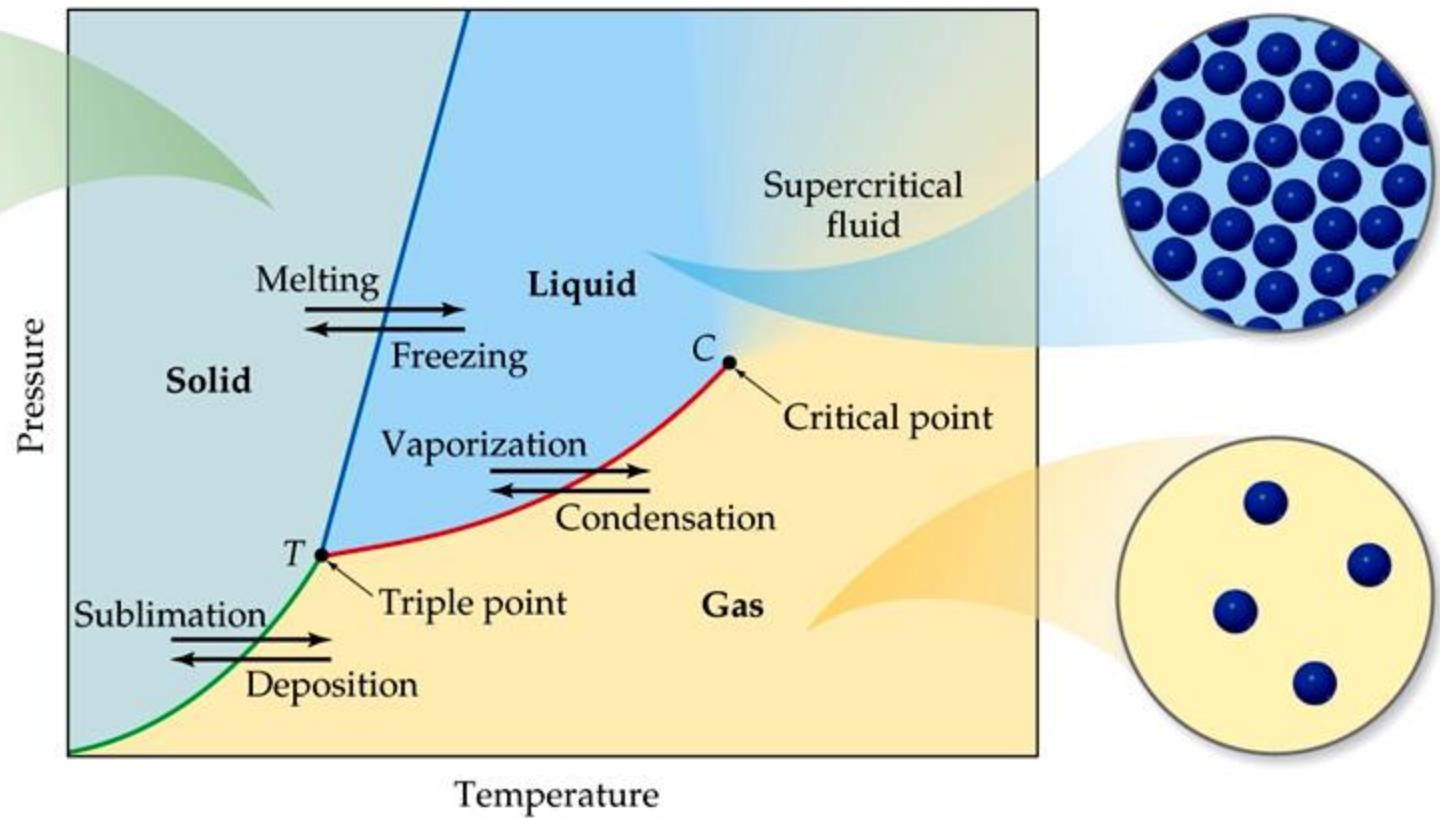
Phase Diagrams

The liquid–vapor interface starts at the **triple point (T)**, at which all three states are in equilibrium, and ends at the **critical point (C)**, above which the liquid and vapor are indistinguishable from each other.



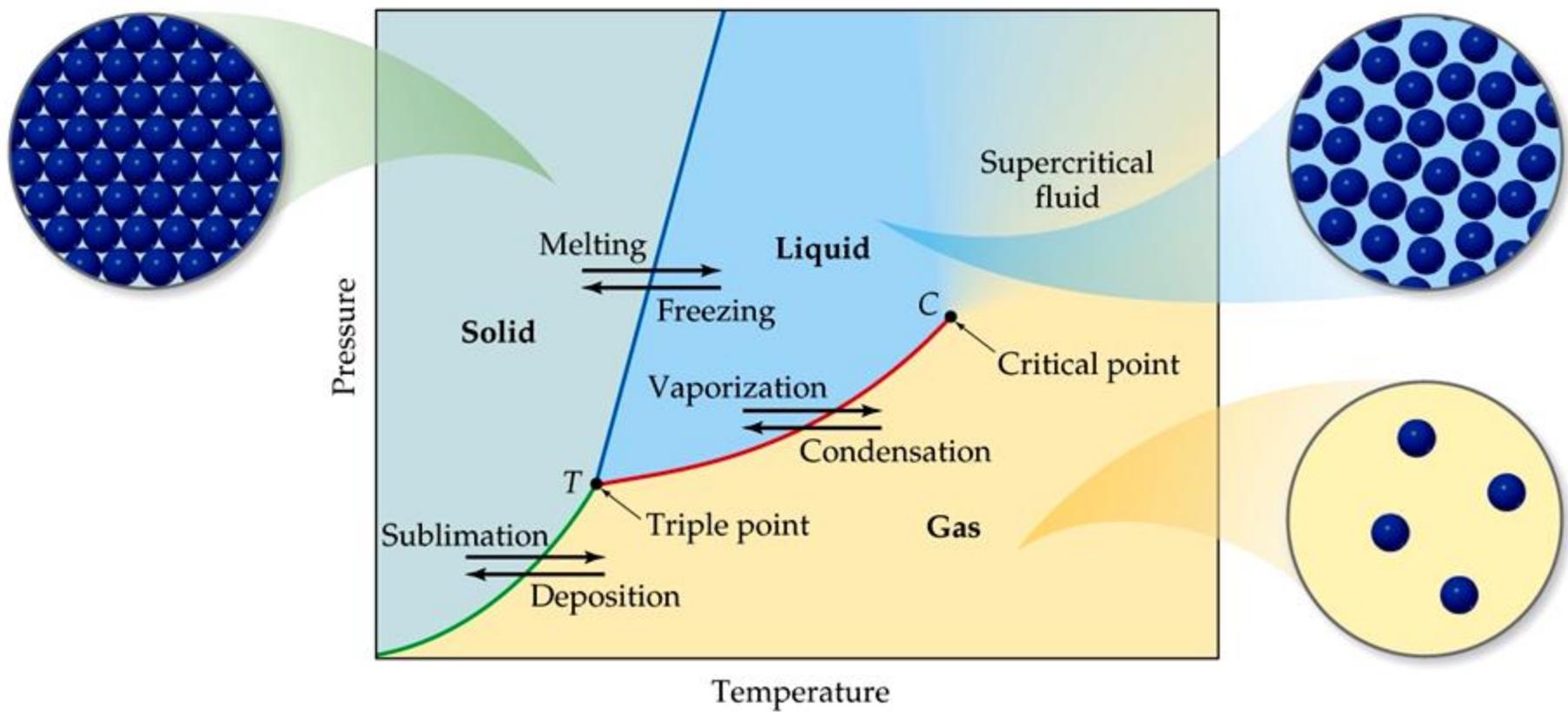
Phase Diagrams

Each point along this line is the boiling point of the substance at that pressure.



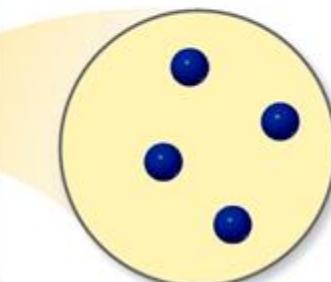
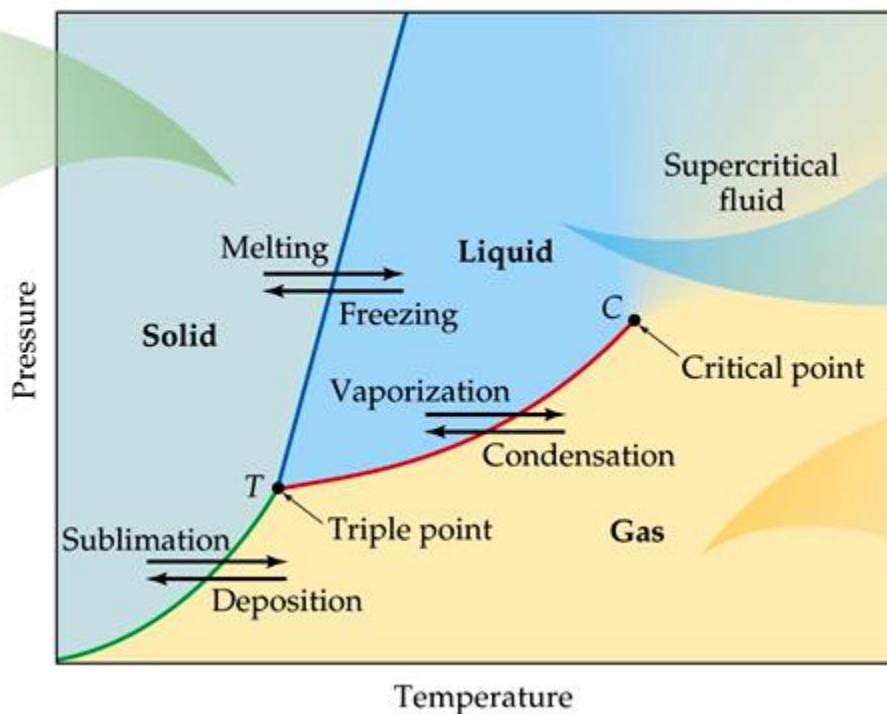
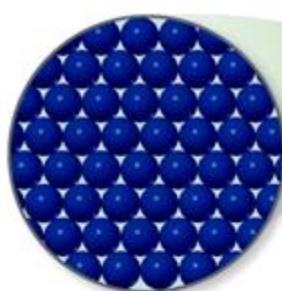
Phase Diagrams

The interface between liquid and solid marks the melting point of a substance at each pressure.



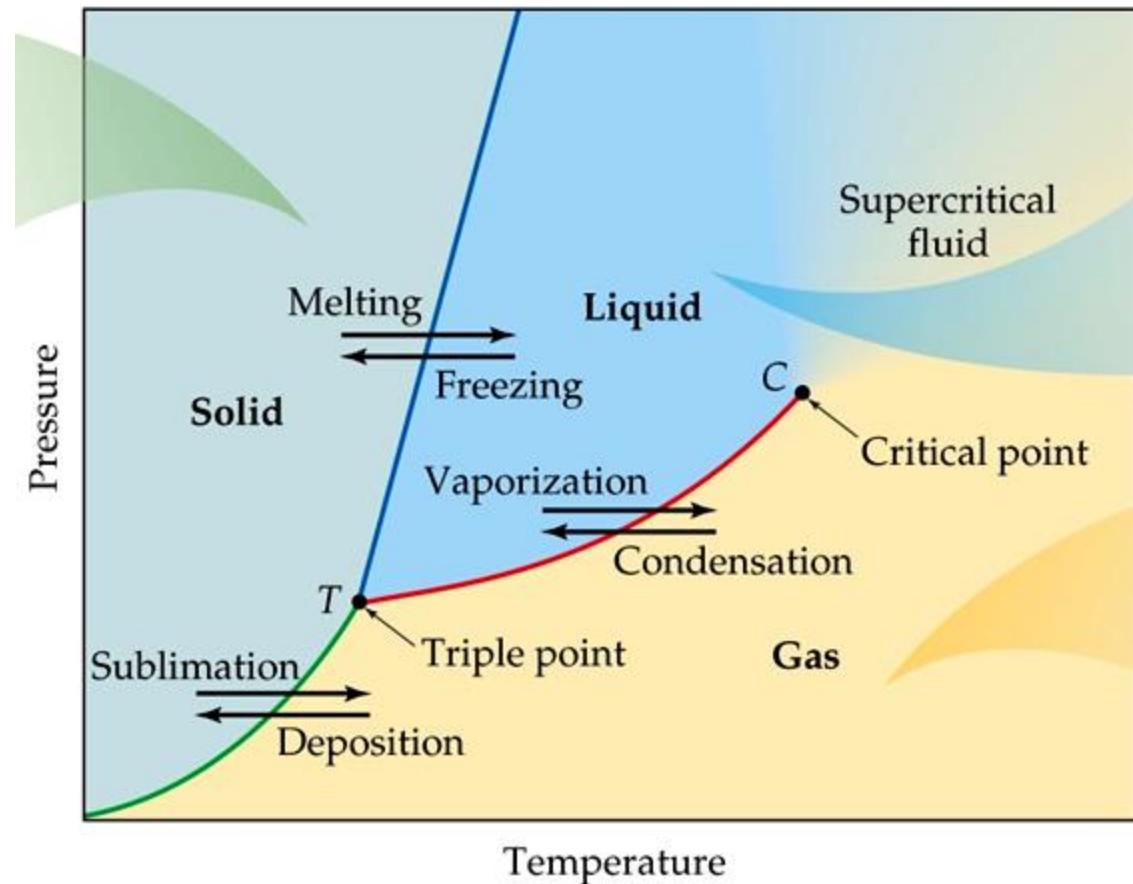
Phase Diagrams

- Below the triple point the substance cannot exist in the liquid state.
- Along the solid–gas line those two phases are in equilibrium; the sublimation point at each pressure is along this line.



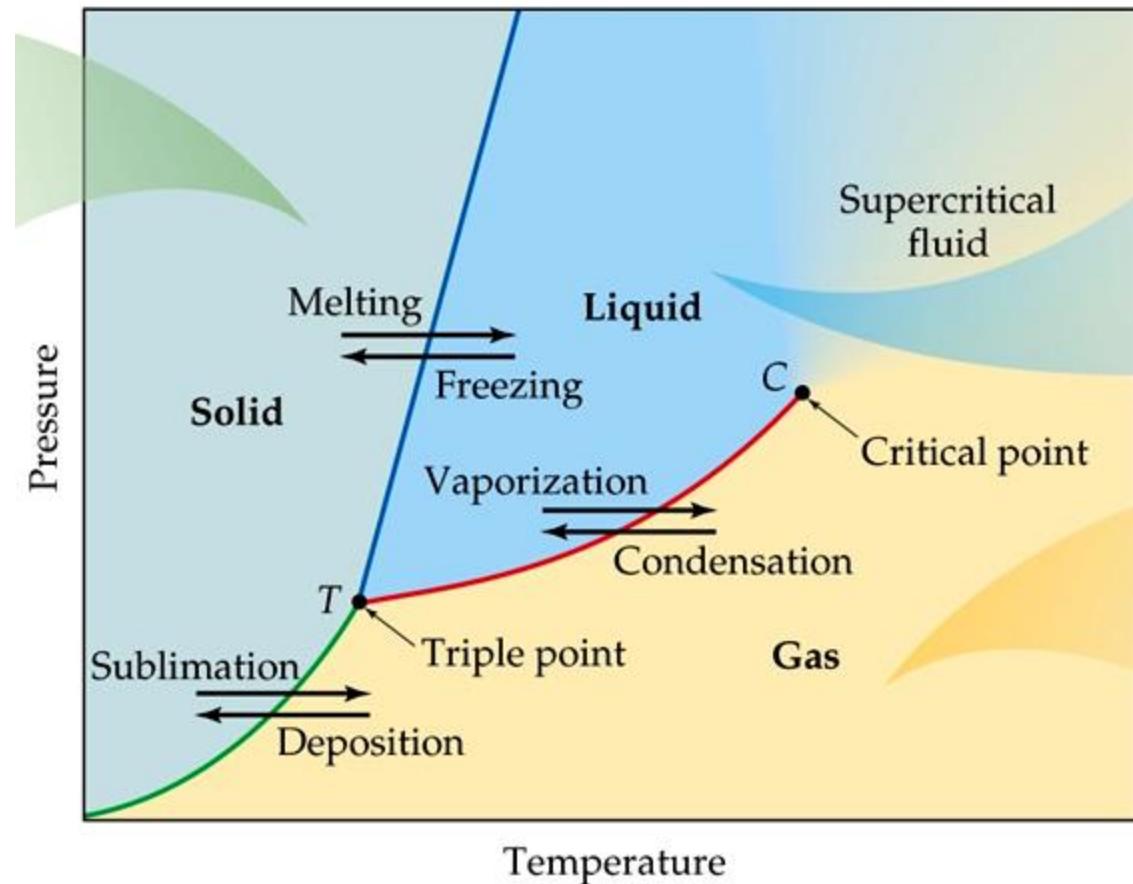
If the pressure exerted on a liquid is increased, while the temperature is held constant, what type of phase transition will eventually occur?

- A. Freezing
- B. Melting
- C. Vaporization
- D. Condensation



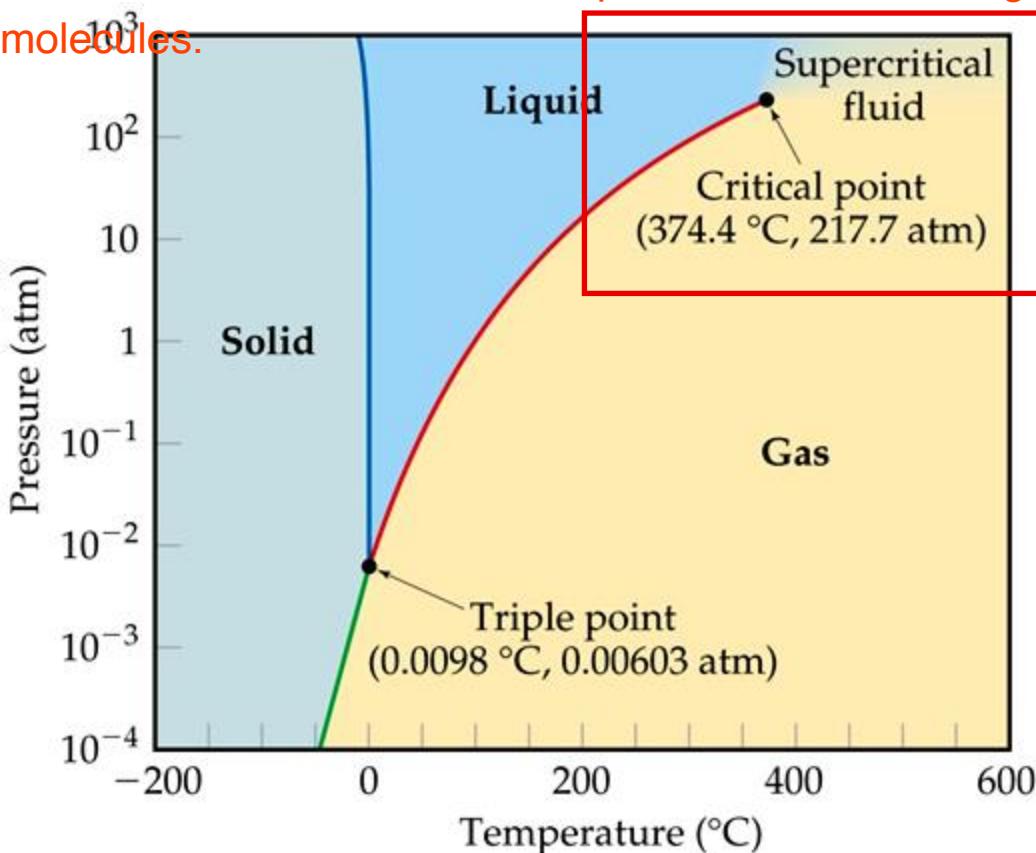
If the pressure exerted on a liquid is increased, while the temperature is held constant, what type of phase transition will eventually occur?

- A. Freezing
- B. Melting
- C. Vaporization
- D. Condensation



Phase Diagram of Water

Critical temperature (T_c) is a direct measure of the strength of intermolecular forces. A higher T_c means it is harder to keep the substance as a gas, implying stronger attraction between molecules.

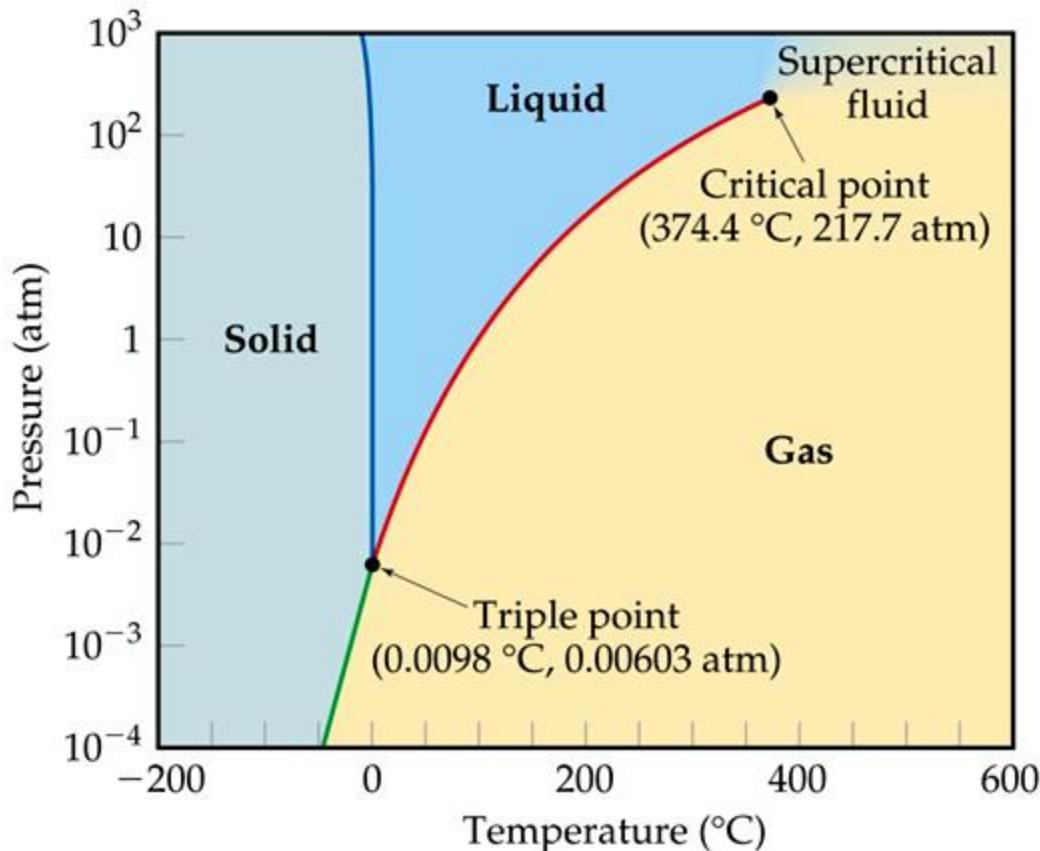


- Note the high critical temperature and critical pressure.
 - These are due to the strong van der Waals forces between water molecules.

Critical temperature is the highest temperature at which a substance can be liquefied from a gas, regardless of the pressure applied.

Critical pressure is the minimum pressure needed to liquefy a gas at its critical temperature

Phase Diagram of Water

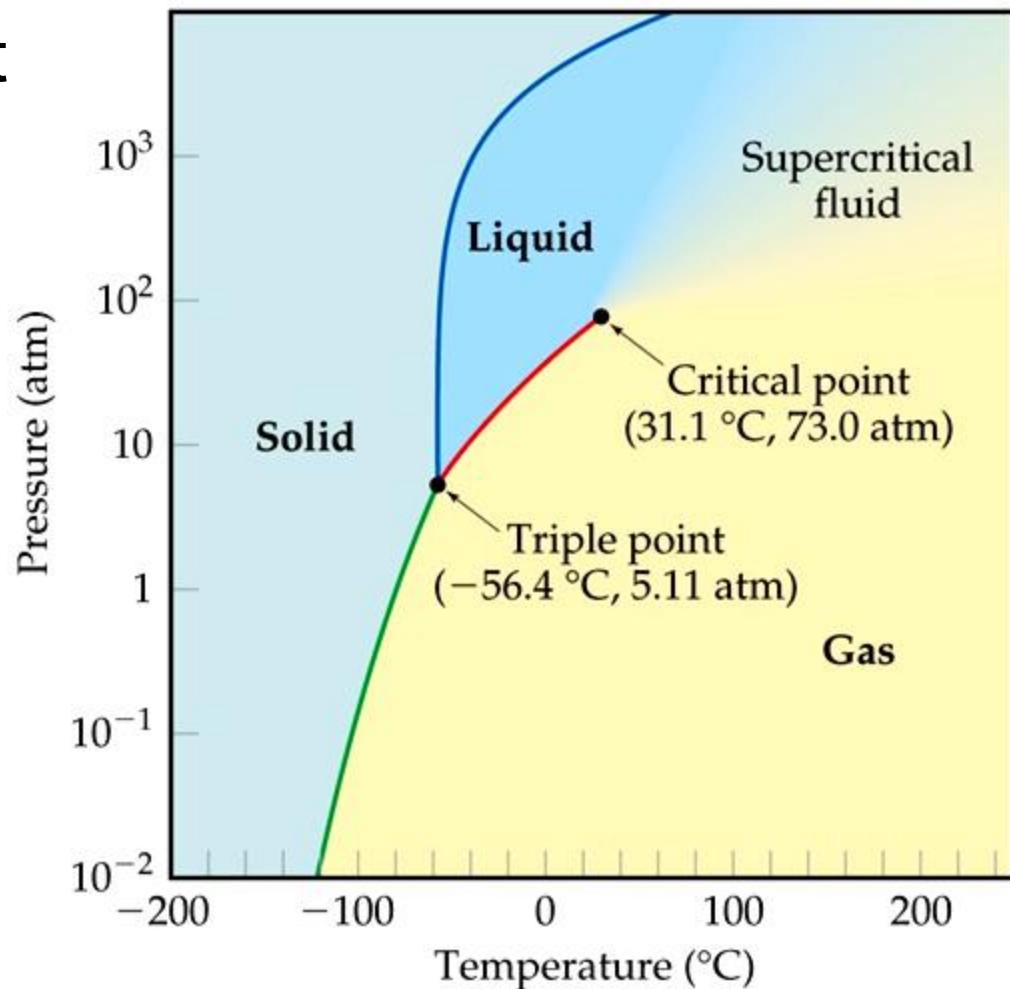
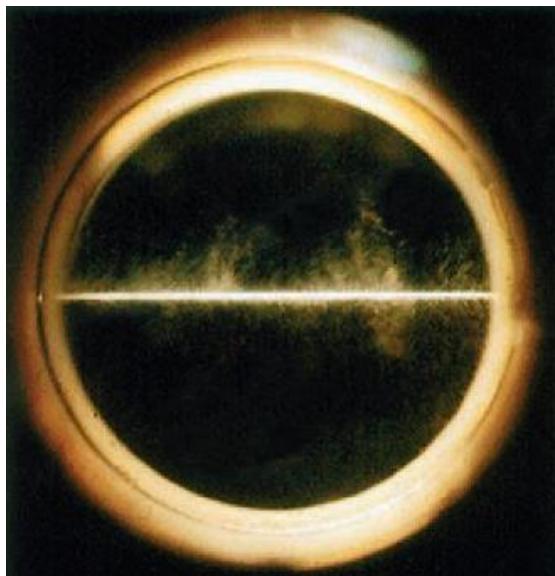


The slope of the solid–liquid line is negative.

- This means that as the pressure is increased at a temperature just below the melting point, water goes from a solid to a liquid.

Phase Diagram of Carbon Dioxide

Carbon dioxide cannot exist in the liquid state at pressures below 5.11 atm; CO_2 sublimes at normal pressures.

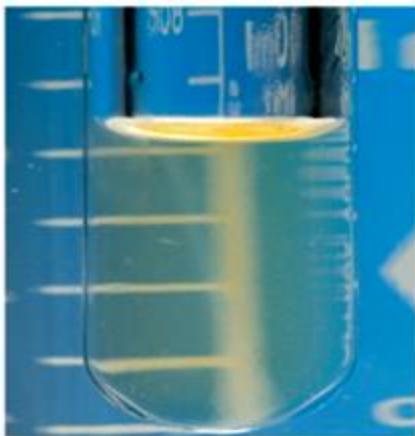


Supercritical Fluid of CO_2

Liquid Crystals

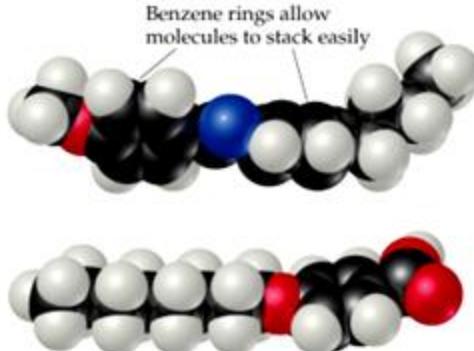
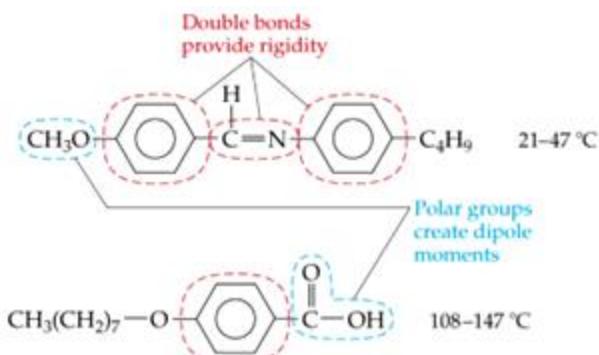


$145\text{ }^{\circ}\text{C} < T < 179\text{ }^{\circ}\text{C}$
Liquid crystalline phase

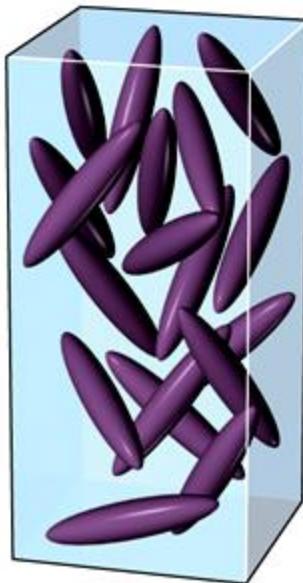


$T > 179\text{ }^{\circ}\text{C}$
Liquid phase

- Some substances do not go directly from the solid state to the liquid state.
- In this intermediate state, liquid crystals have some traits of solids and some of liquids.

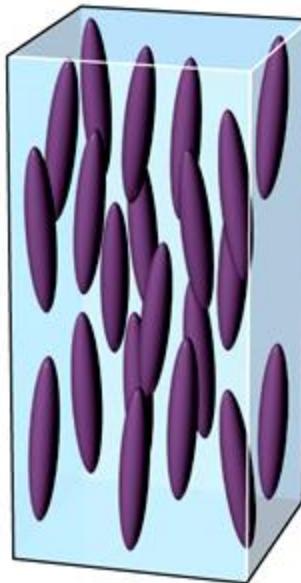


Liquid Crystals



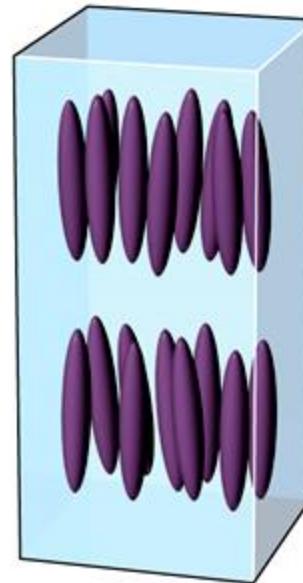
Liquid phase

Molecules
arranged
randomly



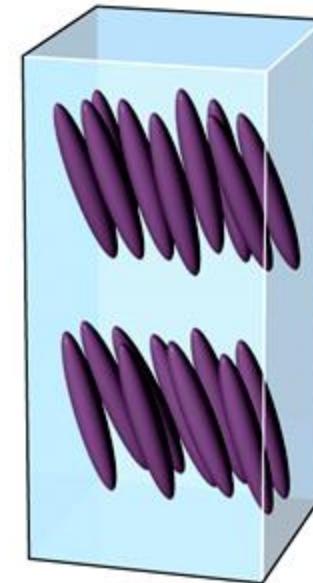
**Nematic liquid
crystalline phase**

Long axes of
molecules
aligned, but ends
are not aligned



**Smectic A liquid
crystalline phase**

Molecules aligned
in layers, long
axes of molecules
perpendicular to
layer planes

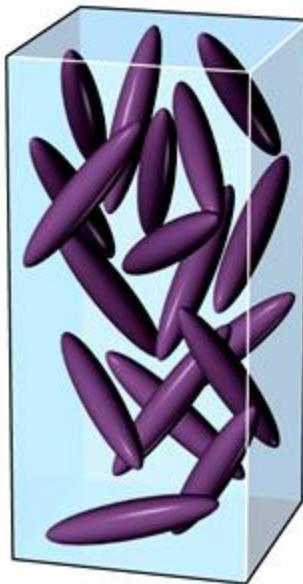


**Smectic C liquid
crystalline phase**

Molecules aligned
in layers, long
axes of molecules
inclined with
respect to layer
planes

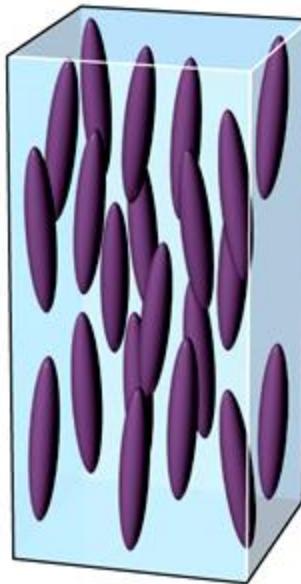
Unlike liquids, molecules in liquid crystals have some degree of order.

Liquid Crystals



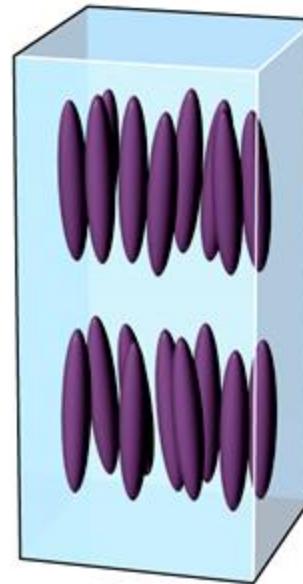
Liquid phase

Molecules arranged randomly



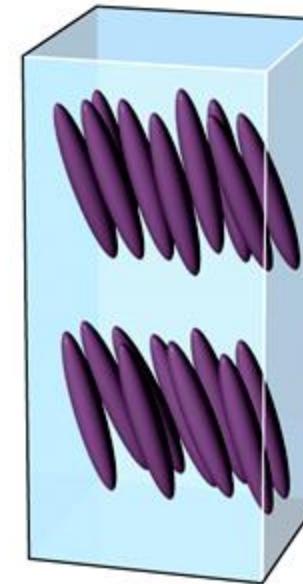
Nematic liquid crystalline phase

Long axes of molecules aligned, but ends are not aligned



Smectic A liquid crystalline phase

Molecules aligned in layers, long axes of molecules perpendicular to layer planes

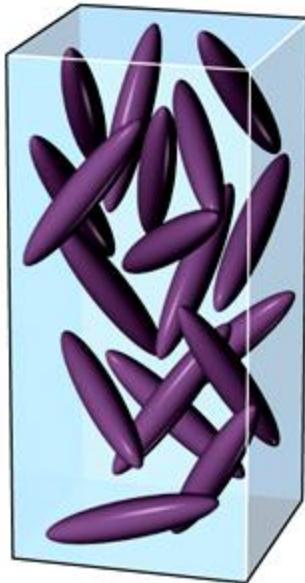


Smectic C liquid crystalline phase

Molecules aligned in layers, long axes of molecules inclined with respect to layer planes

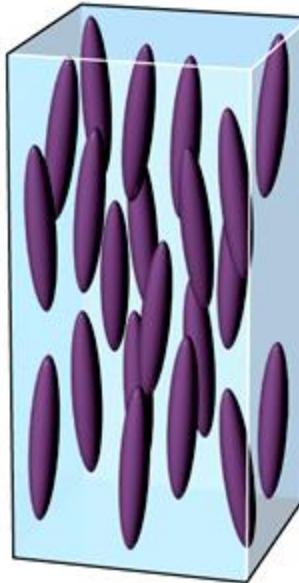
In **nematic liquid crystals** (向列液晶), molecules are only ordered in one dimension, along the long axis.

Liquid Crystals



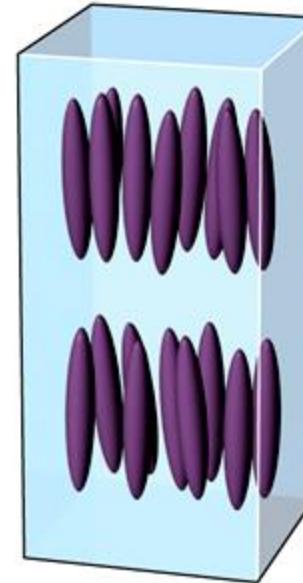
Liquid phase

Molecules
arranged
randomly



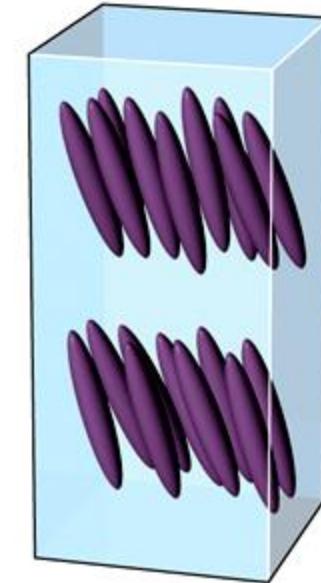
**Nematic liquid
crystalline phase**

Long axes of
molecules
aligned, but ends
are not aligned



**Smectic A liquid
crystalline phase**

Molecules aligned
in layers, long
axes of molecules
perpendicular to
layer planes

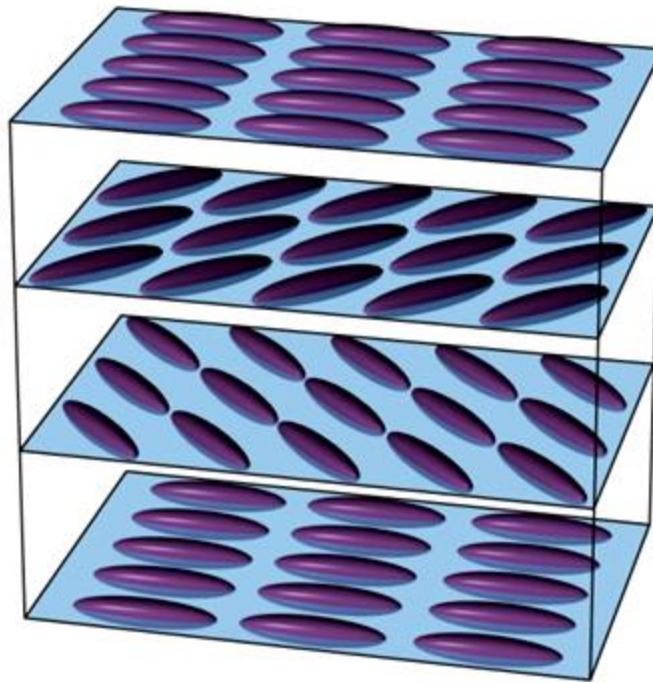


**Smectic C liquid
crystalline phase**

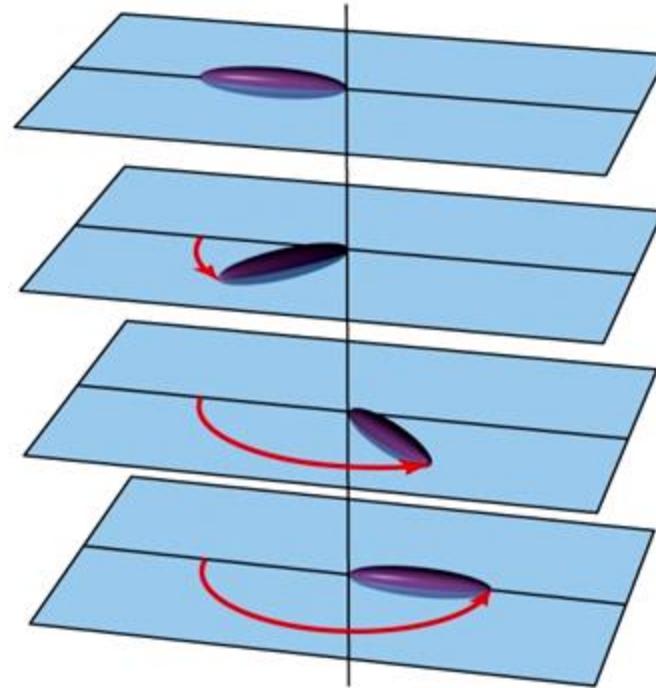
Molecules aligned
in layers, long
axes of molecules
inclined with
respect to layer
planes

In **smectic liquid crystals** (近晶型), molecules are ordered in two dimensions, along the long axis and in layers.

Liquid Crystals



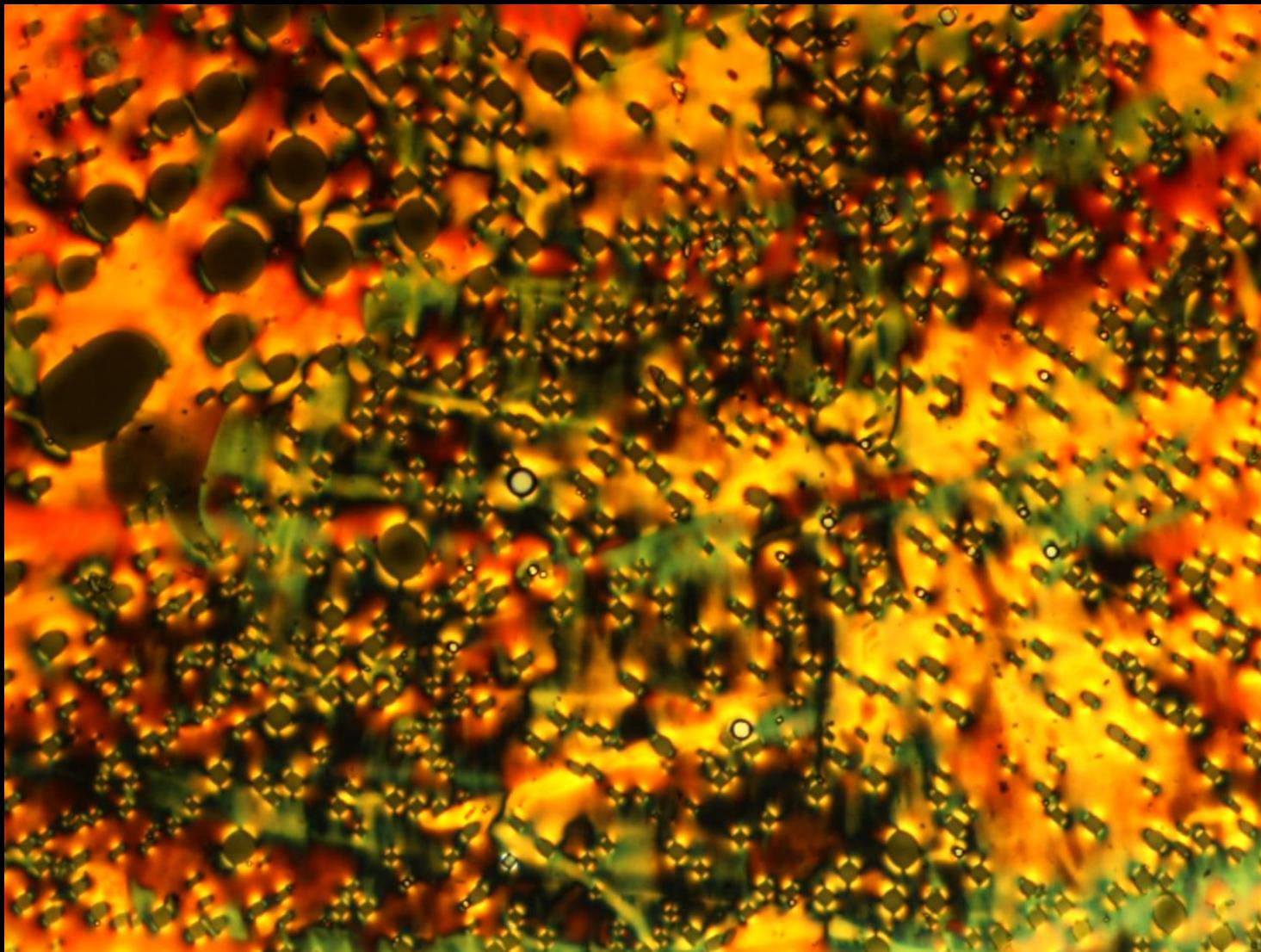
In a cholesteric liquid crystal the molecules pack into layers; the long axis of each molecule is oriented parallel to its neighbors within the same layer



The direction along which the molecules point rotates from one layer to the next, resulting in a spiraling pattern resembling the threads of a screw

In cholesteryl (胆固醇) liquid crystals, nematic-like crystals are layered at angles to each other.

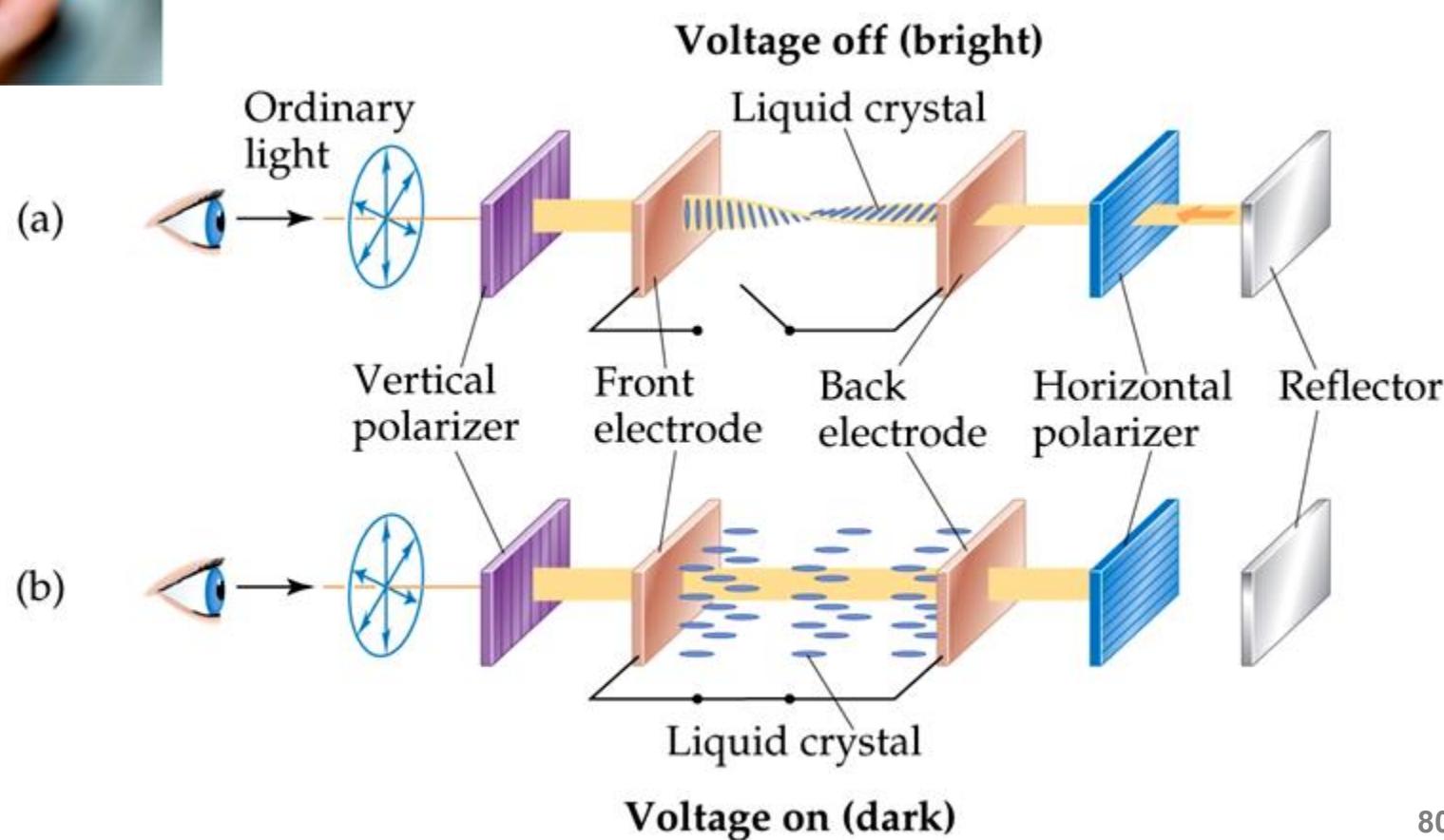
The Beauty of Liquid Crystals





Liquid Crystals

These crystals can exhibit color changes with changes in temperature.



Ionic Liquids - Green Solvents for the Future

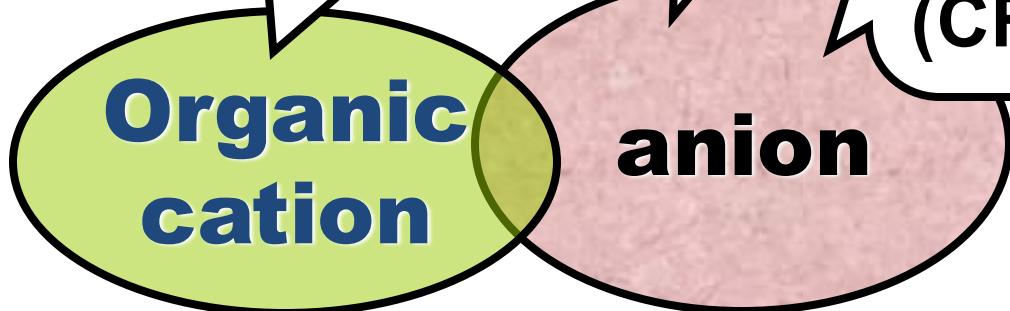
- Salts that are liquid at ambient temperatures.
- Low melting organic salts
- Very low vapor pressure
- Non-flammable
- Wide liquid range (300 °C)
- Moderate to high viscosity (bad)
- Solvent properties different from molecular solvents
- Solvent properties can be controlled by selection of anion and cation – hence often termed designer solvents (good).

Ionic Liquids - Green Solvents for the Future

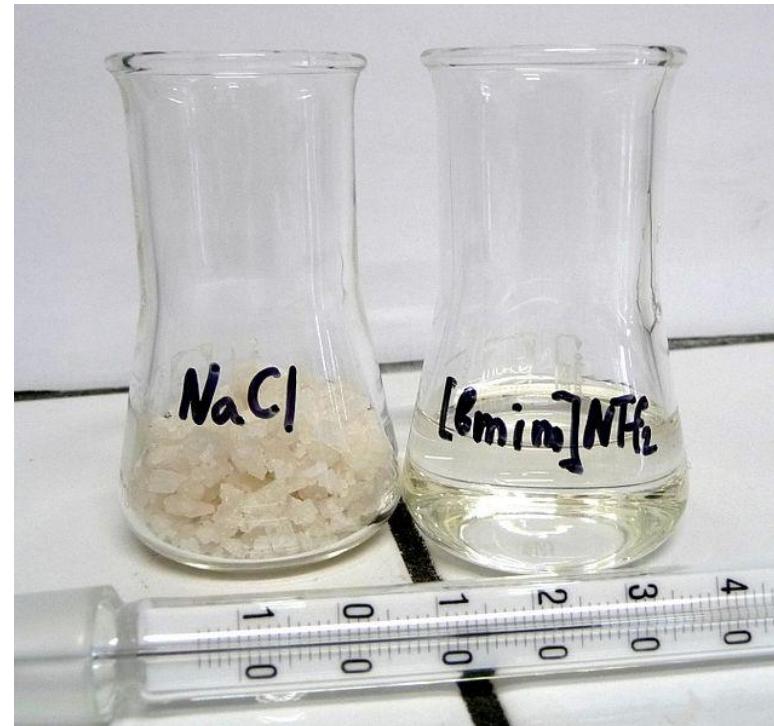
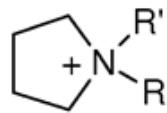
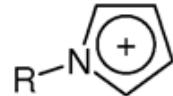
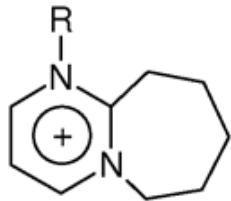
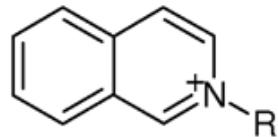
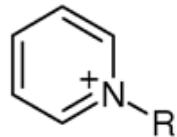
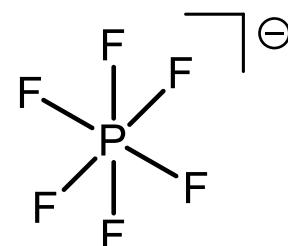
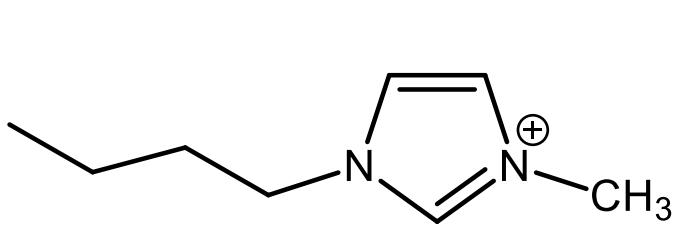
Alkylammonium
Alkylphosphonium
Alkylnitride
N,N'-dialkylimidazolium
N-alkylpyridinium

Halide-based (Cl^- , Br^- , F^-)
Halogeno-based (BF_4^- , PF_6^-)
Halogenoaluminium(III)

NO_3^- , ClO_4^- , HSO_4^-
 SO_3^- , CF_3SO_3^-
 $(\text{CF}_3\text{SO}_2)_2\text{N}^-$
 $(\text{CF}_3\text{SO}_2)_3\text{C}^-$



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Which force below is the strongest intermolecular attractive force ?

- a. Hydrogen bonding
- b. Ion-dipole forces
- c. Dipole-dipole forces
- d. London dispersion forces



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Which compound below is not capable of forming hydrogen bonds?

- a. CH_4
- b. NH_3
- c. H_2O
- d. HF



Which compound below is not capable of forming hydrogen bonds?

- a. CH₄
- b. NH₃
- c. H₂O
- d. HF



Which compound below has the highest boiling point?

- a. H_2O
- b. H_2S
- c. H_2Se
- d. H_2Te



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Which element below has the highest boiling point?

- a. Kr
- b. F₂
- c. Cl₂
- d. Br₂



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- c. Cl₂
- d. Br₂



Which substance below has a greater density in its liquid state than in its solid state?

- a. Iron
- b. Glass
- c. Water
- d. Carbon dioxide



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- c. Water
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The resistance of a liquid to flow is called the _____ of the liquid.

- a. density
- b. viscosity
- c. potential energy
- d. flow rate



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The energy required to cause
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- a. boiling point
- b. freezing point
- c. heat of vaporization
- d. heat of fusion



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Isopropyl alcohol feels cool to the touch because it has an (X) heat of (Y).

- a. X = exothermic, Y = vaporization
- b. X = endothermic, Y = vaporization
- c. X = exothermic, Y = fusion
- d. X = endothermic, Y = fusion



When heat is added to ice at zero degrees Celsius, what will happen?

- a. The temperature will increase.
- b. The temperature will decrease.
- c. The temperature will not change.
- d. A supercritical fluid will form.



The highest temperature at which a substance can exist in its liquid state is called its _____ point.

- a. boiling
- b. freezing
- c. triple
- d. critical



The temperature and pressure at which all three phases exist simultaneously is called the _____ point of a substance.

- a. boiling
- b. freezing
- c. triple
- d. critical



At high altitudes (海拔), the boiling point of water is

- a. 100 degrees Celsius.
- b. greater than 100 degrees Celsius.
- c. less than 100 degrees Celsius.
- d. equal to its freezing point.



Substance X has a boiling point of 150 degrees Celsius and a freezing point of 15 degrees Celsius. The condensation point of X

- a. is 150 degrees Celsius.
- b. is 15 degrees Celsius.
- c. is 165 degrees Celsius.
- d. is 135 degrees Celsius.



Which of the terms below does NOT describe a type of liquid crystal?

- a. Eutectic (共晶)
- b. Nematic
- c. Smectic
- d. Cholesteric

