

Lecture Presentation

Chapter 11

Liquids and Intermolecular Forces

5) Gaseous mixtures _____.

- A) can only contain molecules
- B) are all heterogeneous
- C) can only contain isolated atoms
- D) are all homogeneous
- E) must contain both isolated atoms and molecules

18) The molar volume of a gas at STP is _____ L.

- A) 0.08206
- B) 62.36
- C) 1.00
- D) 22.4
- E) 14.7

36) Arrange the following gases in order of increasing average molecular speed at 25 °C.

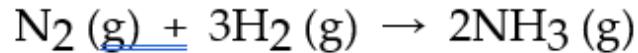


- A) He < N₂ < O₂ < CO₂
- B) He < O₂ < N₂ < CO₂
- C) CO₂ < O₂ < N₂ < He
- D) CO₂ < N₂ < O₂ < He
- E) CO₂ < He < N₂ < O₂

46) Which one of the following gases would deviate the least from ideal gas behavior?

- A) Ne
- B) CH₃Cl
- C) Kr
- D) CO₂
- E) F₂

14) The reaction of 50 mL of N₂ gas with 150 mL of H₂ gas to form ammonia via the equation:



will produce _____ mL of ammonia if pressure and temperature are kept constant.

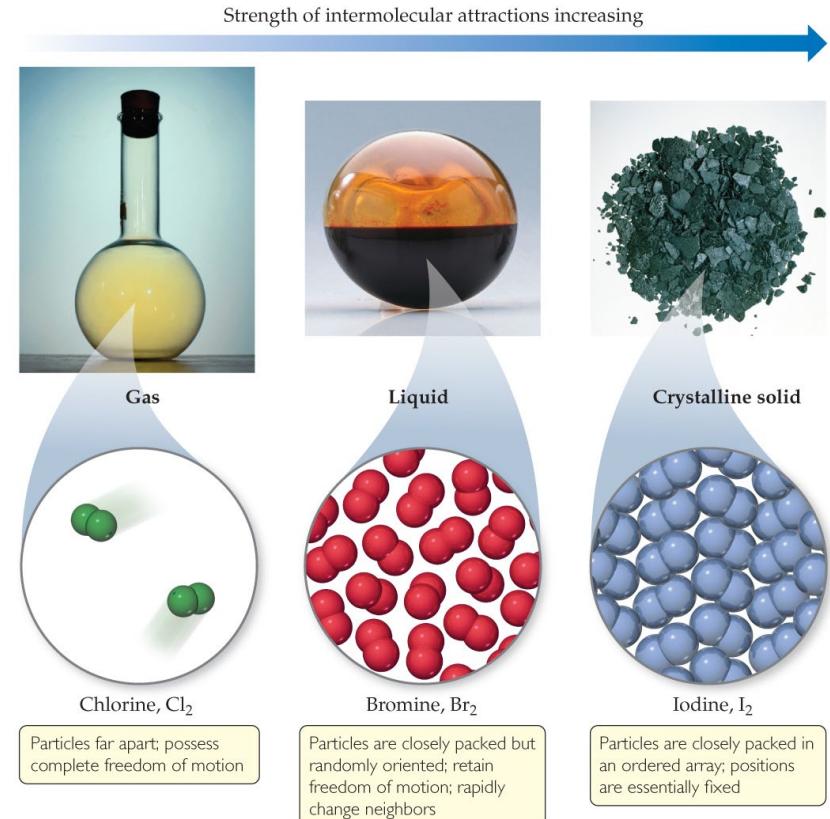
- A) 250
- B) 50
- C) 200
- D) 150
- E) 100

53) A mixture of He and Ne at a total pressure of 0.95 atm is found to contain 0.32 mol of He and 0.56 mol of Ne. The partial pressure of Ne is _____ atm.

- A) 1.7
- B) 1.5
- C) 0.60
- D) 0.35
- E) 1.0

States of Matter

- The fundamental difference between states of matter is the strength of the intermolecular forces of attraction.
- Stronger forces bring molecules closer together.
- Solids and liquids are referred to as the *condensed phases*.



Intermolecular
Forces

Differences in the States of Matter

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 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

*The atoms in a solid are able to vibrate in place. As the temperature of the solid increases, the vibrational motion increases.

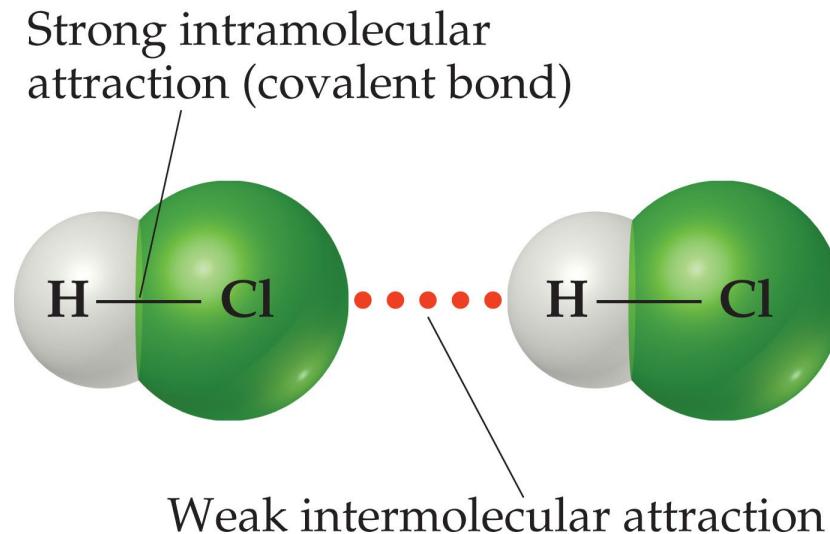
Which State of Matter?

- The answer to this question largely relies on the
 - balance between the kinetic energies of the particles.
 - interparticle energies of attraction.

Table 11.2 Comparing Kinetic Energies and Energies of Attractions for States of Matter

Gas	Kinetic energies >> energies of attraction
Liquid	Comparable kinetic energies and energies of attraction
Solid	Energies of attraction >> kinetic energies

Intermolecular Forces



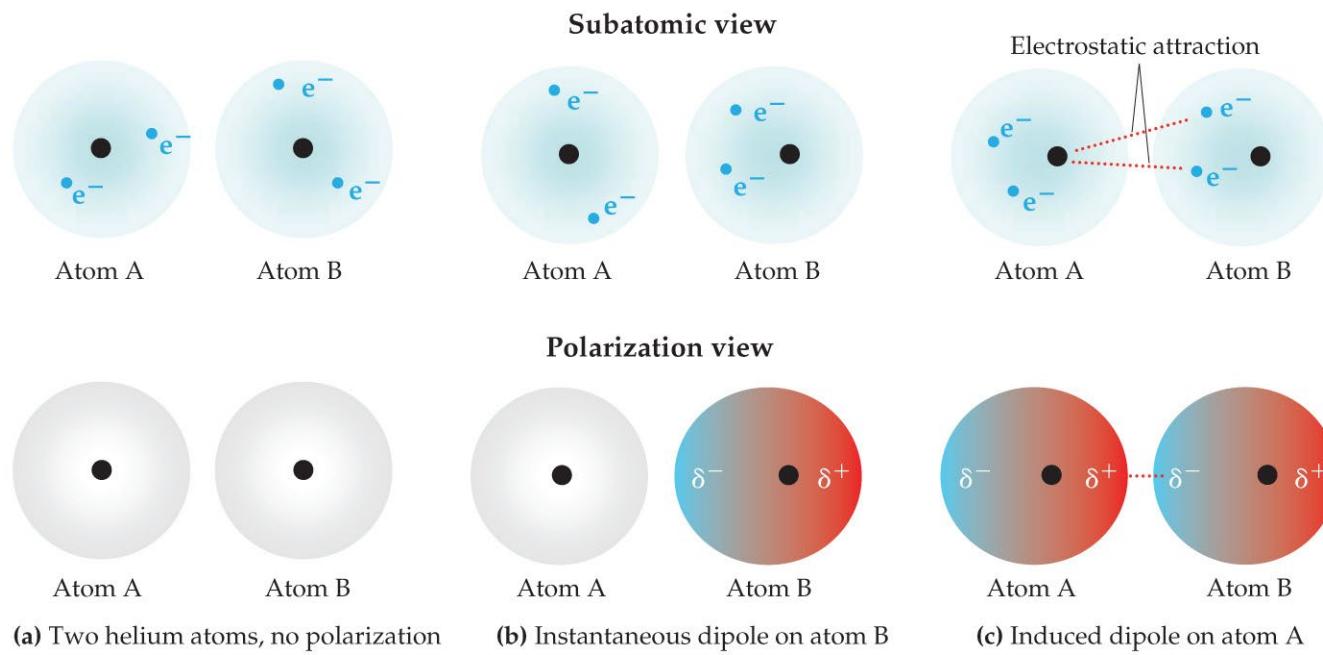
- The attractions between molecules are not nearly as strong as the intramolecular attractions (bonds) that hold compounds together.
- Many physical properties reflect intermolecular forces, like boiling points, melting points, viscosity, surface tension, and capillary action.

Types of Intermolecular Force

- Weakest to strongest forces:
 - dispersion forces (or London dispersion forces)
 - dipole–dipole forces
 - hydrogen bonding (a special dipole–dipole force)
 - ion–dipole forces
- Note: The first two types are also referred to collectively as *van der Waals forces*.

Dispersion Forces

- The figure below shows how a nonpolar particle (in this case a helium atom) can be temporarily polarized to allow dispersion force to form.
 - The tendency of an electron cloud to distort is called its **polarizability**.

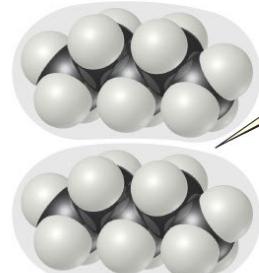


Intermolecular Forces

Factors Which Affect Amount of Dispersion Force in a Molecule

- number of electrons in an atom (**more electrons, more dispersion force**)
- size of atom or molecule/molecular weight
- shape of molecules with similar masses (more contact, larger dispersion force)

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



n-Pentane (C₅H₁₂)
bp = 309.4 K

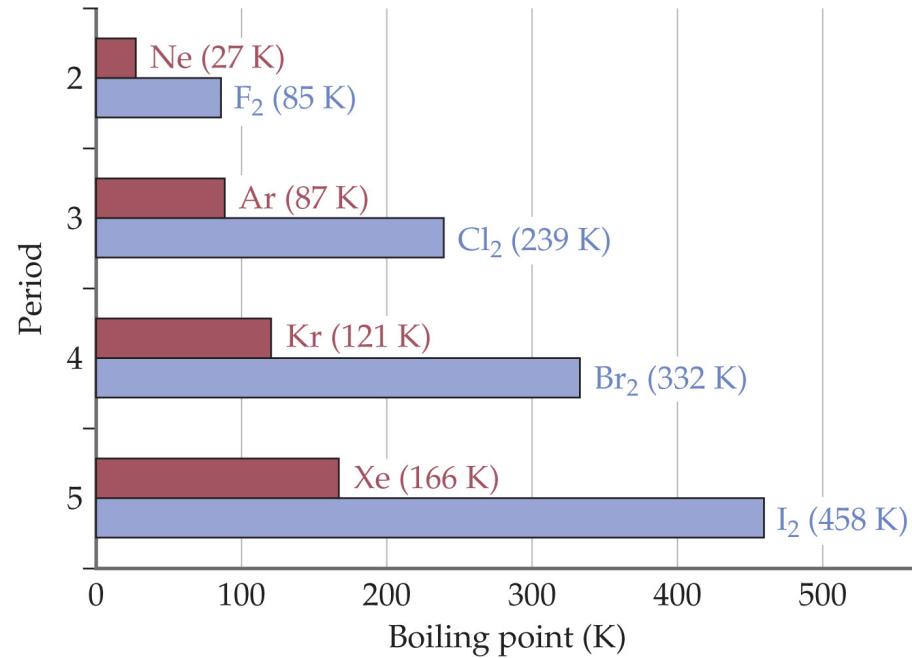
Spherical molecule—smaller surface area diminishes intermolecular contact and decreases dispersion force



Neopentane (C₅H₁₂)
bp = 282.7 K

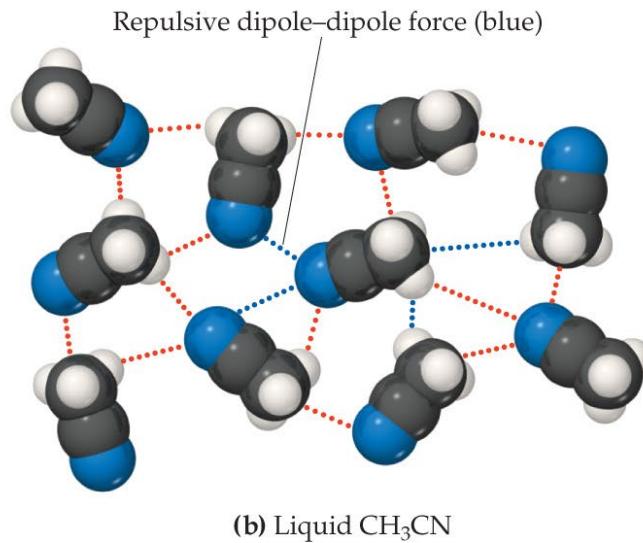
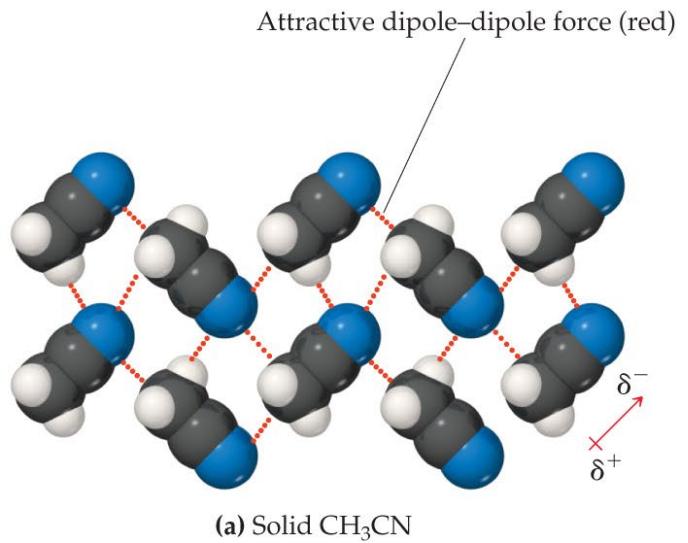
Polarizability & Boiling Point

- If something is **more difficult** to polarize, it has a *lower* boiling point.
- Remember: This means *less* intermolecular force (smaller molecule: lower molecular weight, fewer electrons).



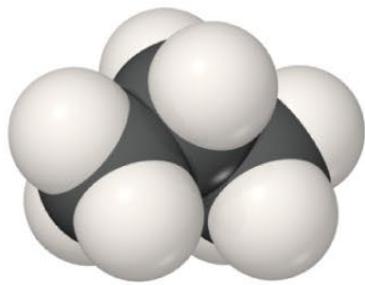
Dipole–Dipole Interactions

- Polar molecules have a more positive and a more negative end—a dipole (two poles, δ^+ and δ^-).
- The oppositely charged ends attract each other.

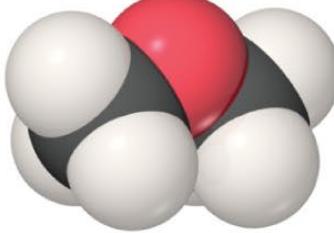


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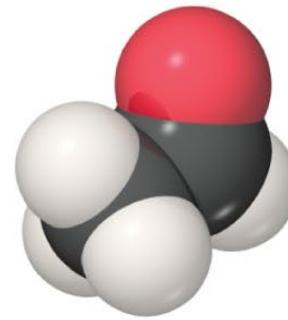
Dipole–Dipole Interactions



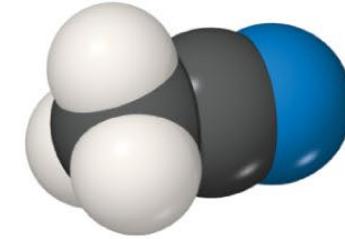
Propane
 $\text{CH}_3\text{CH}_2\text{CH}_3$
MW = 44 amu
 $\mu = 0.1 \text{ D}$
bp = 231 K



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

For molecules of approximately equal mass and size, the more polar the molecule, the higher its boiling point.

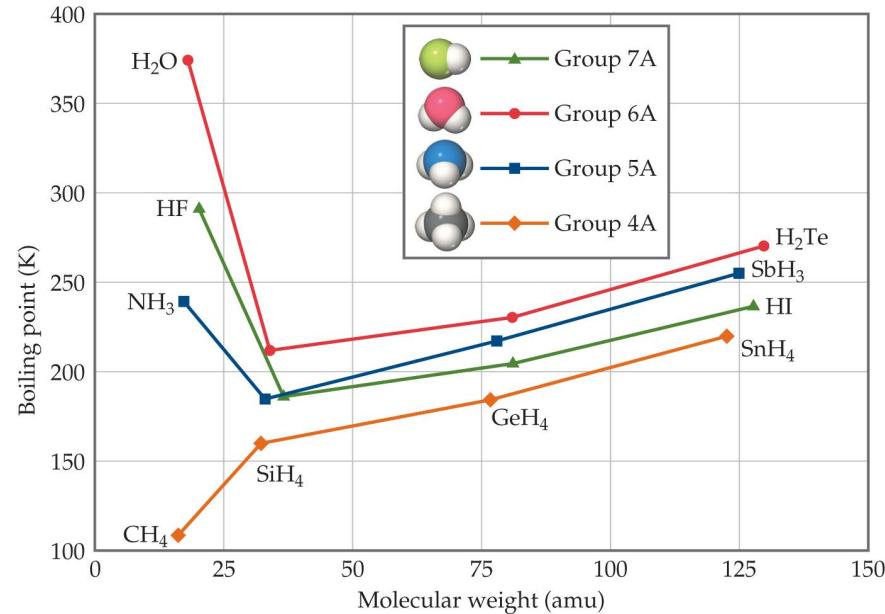
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Which Have a Greater Effect: Dipole–Dipole Interactions or Dispersion Forces?

- 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.

What Does This Graph Show Us?

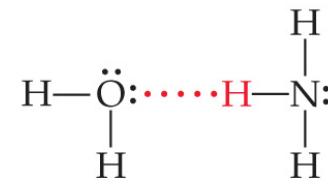
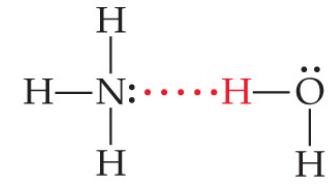
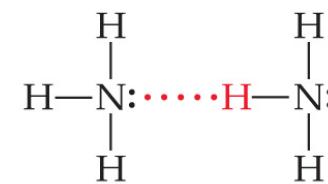
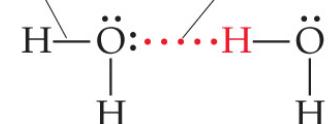
- In a group, the period 3/4/5 elements have higher boiling points as the group member gets larger.
- What happens with the period 2 elements? For group 4A, the trend is continued. What about for the other groups?



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**.
- A hydrogen bond is an attraction between a **hydrogen atom** attached to a highly **electronegative atom** and a nearby small electronegative atom in another molecule or chemical group.

Covalent bond,
intramolecular Hydrogen bond,
intermolecular



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In which of the following molecules is hydrogen bonding likely to be the most significant component of the total intermolecular forces?

- A) CH_4
- B) $\text{C}_5\text{H}_{11}\text{OH}$
- C) $\text{C}_6\text{H}_{13}\text{NH}_2$
- D) CH_3OH
- E) CO_2

The intermolecular force(s) responsible for the fact that CH₄ has the lowest boiling point in the set CH₄, SiH₄, GeH₄, SnH₄ is/are _____.

- A) hydrogen bonding
- B) dipole-dipole interactions
- C) London dispersion forces
- D) mainly hydrogen bonding but also dipole-dipole interactions
- E) mainly London-dispersion forces but also dipole-dipole interactions

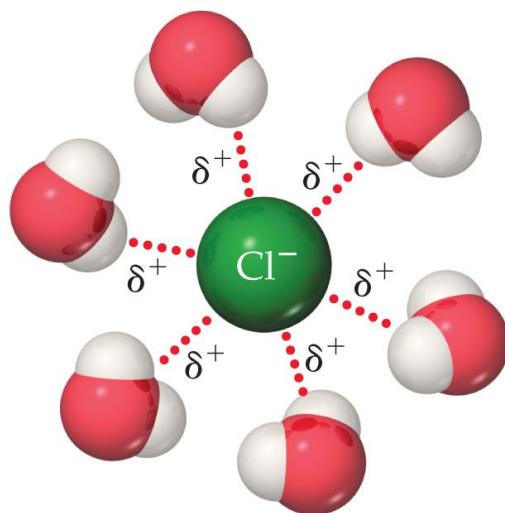
What Forms Hydrogen Bonds?

- Hydrogen bonding arises in part from the high electronegativity of nitrogen, oxygen, and fluorine.
- These atoms interact with a nearly bare nucleus (which contains one proton).

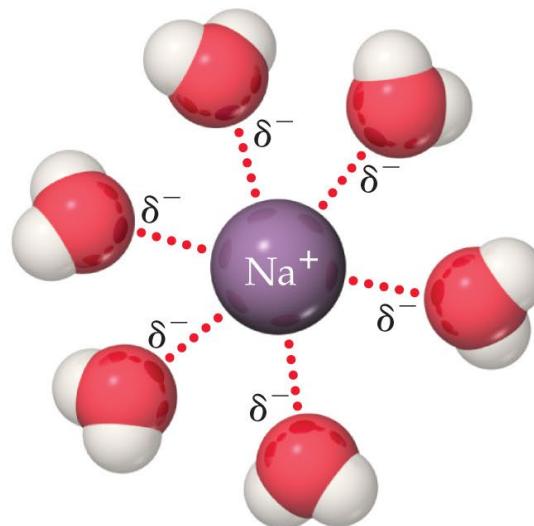


Ion–Dipole Interactions

- Ion–dipole interactions are found 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

Summarizing Intermolecular Forces

Go Figure

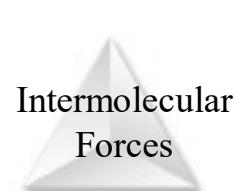
Can the energies of multiple dispersion forces between two molecules be larger than the energy of hydrogen bonding between the two molecules?

Type of intermolecular interaction	Atoms Examples: Ne, Ar	Nonpolar molecules Examples: BF ₃ , CH ₄	Polar molecules without OH, NH, or HF groups Examples: HCl, CH ₃ CN	Polar molecules containing OH, NH, or HF groups Examples: H ₂ O, NH ₃	Ionic solids dissolved in polar liquids Examples: NaCl in H ₂ O
Dispersion forces (0.1–30 kJ/mol)	✓	✓	✓	✓	✓
Dipole–dipole interactions (2–15 kJ/mol)			✓	✓	
Hydrogen bonding (10–40 kJ/mol)				✓	
Ion–dipole interactions (>50 kJ/mol)					✓

Figure 11.14 Checklist for determining intermolecular forces. Multiple types of intermolecular forces can be operating in a given substance or mixture. Note that dispersion forces occur in all substances.

Liquid Properties Affected by Intermolecular Forces

- boiling point and melting point
- viscosity
- surface tension
- capillary action



Viscosity 黏滯性

- 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.



SAE 40
higher number
higher viscosity
slower pouring

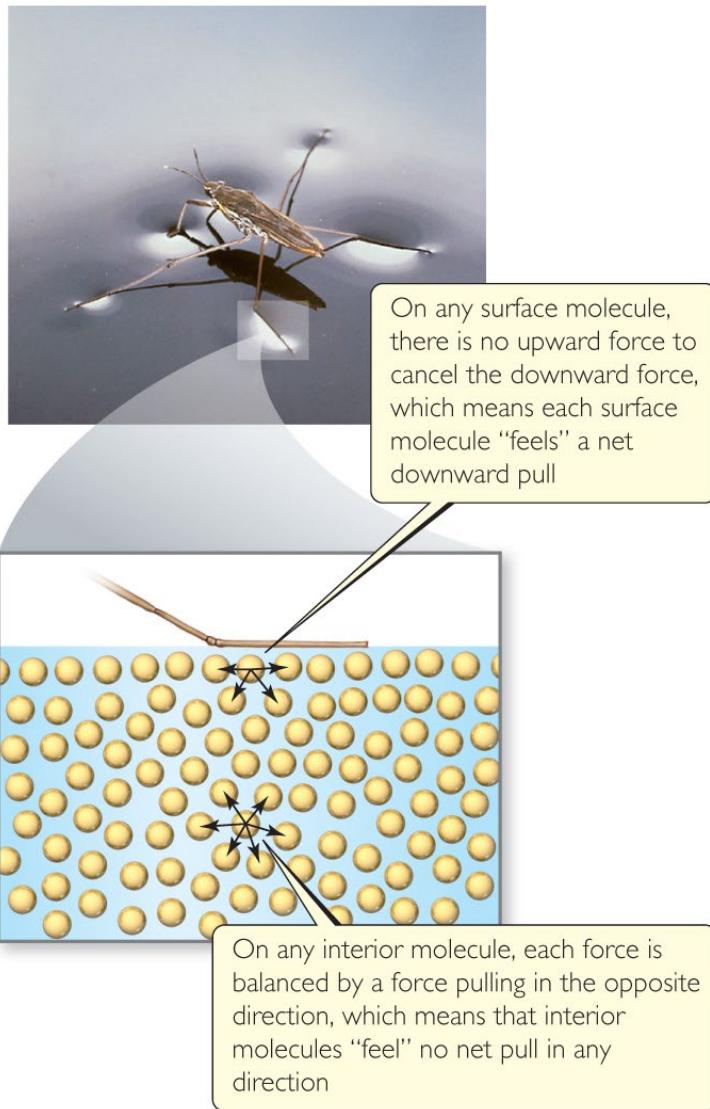
SAE 10
lower number
lower viscosity
faster pouring

Table 11.5 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}

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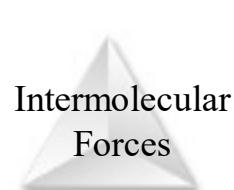
Surface Tension



- Water acts as if it has a “skin” on it due to extra inward forces on its surface. Those forces are called the **surface tension**.

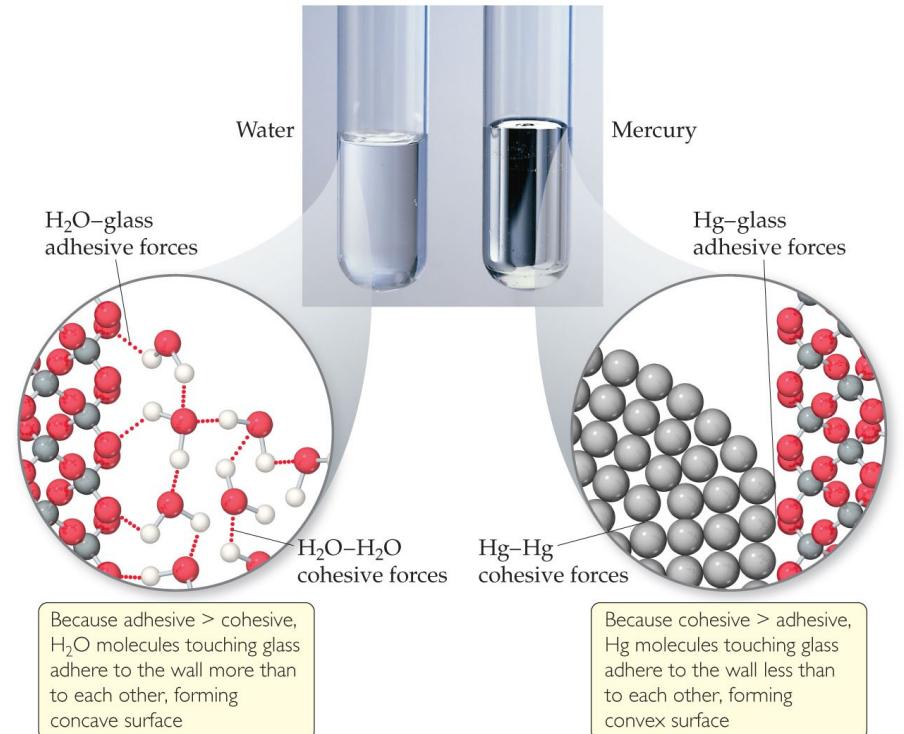
Cohesion and Adhesion

- Intermolecular forces that bind similar molecules to one another are called *cohesive forces*.
- Intermolecular forces that bind a substance to a surface are called *adhesive forces*.
- These forces are important in capillary action.



Capillary Action

- The rise of liquids up **narrow** tubes is called **capillary action**.
- Adhesive forces attract the liquid to the wall of the tube.
- Cohesive forces attract the liquid to itself.
- Water has stronger adhesive forces with glass; mercury has stronger cohesive forces with itself.

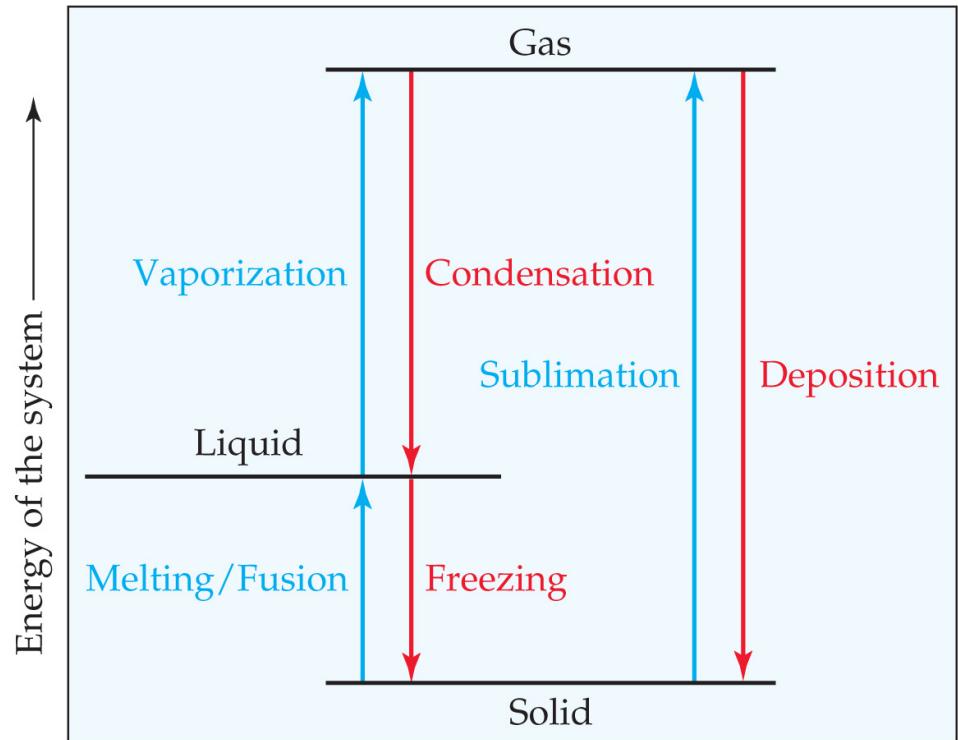


Self-cleaning property of lotus



Phase Changes

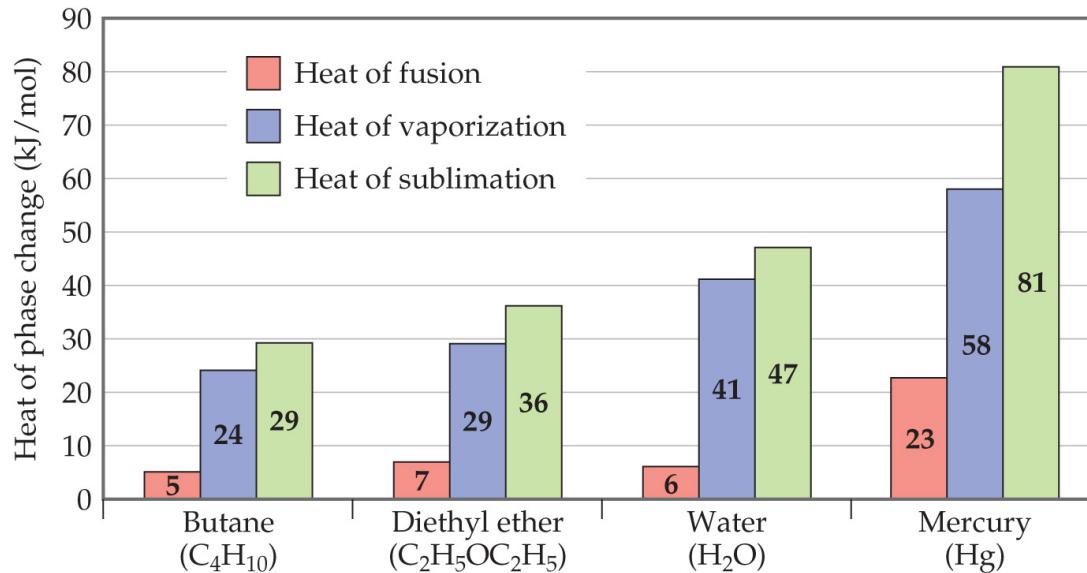
- Conversion from one state of matter to another is called a **phase change**.
- Energy is either added or released in a phase change.
- Phase changes: melting/freezing, vaporizing/condensing, subliming/depositing.



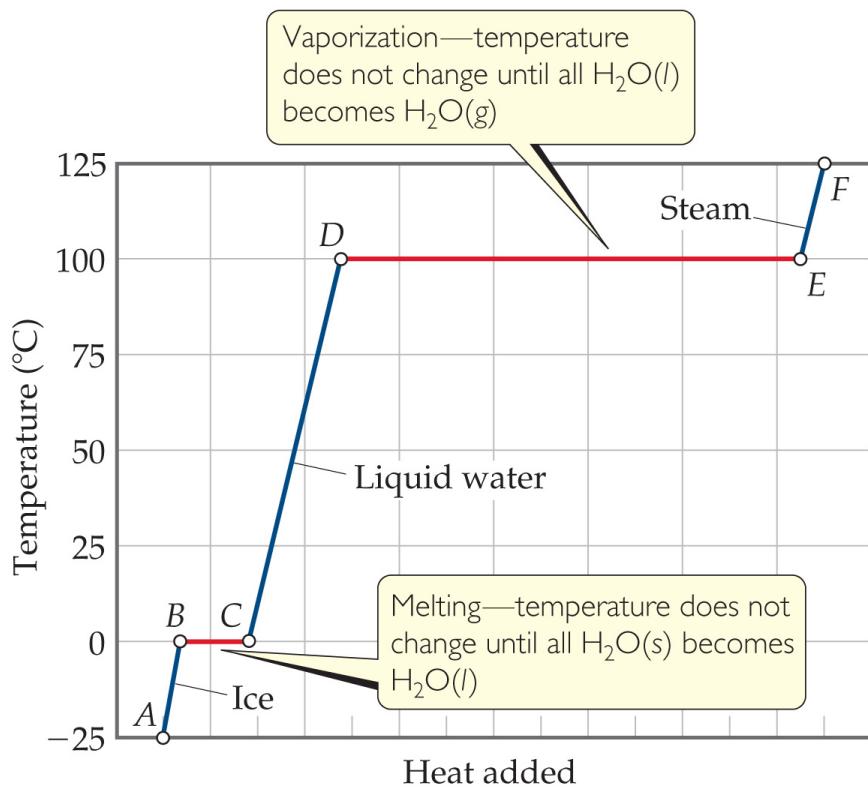
— Endothermic process (energy added to substance)
— Exothermic process (energy released from substance)

Energy Change & Change of State

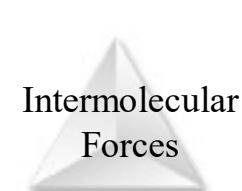
- The **heat of fusion** is the energy required to change a solid at its melting point to a liquid.
- The **heat of vaporization** is the energy required to change a liquid at its boiling point to a gas.
- The **heat of sublimation** is the energy required to change a solid directly to a gas.



Heating Curves



- A plot of temperature vs. heat added is called a **heating curve**.
- Within a phase, heat is the product of specific heat, sample mass, and temperature change.
- **The temperature of the substance does not rise during a phase change.**
- For the phase changes, the product of mass and the heat of fusion of vaporization is heat.



Supercritical Fluids

- Gases liquefies when pressure is applied.
- The highest temperature at which a distinct liquid phase can form is called **critical temperature**.

The pressure needed to compress the liquid at critical temperature is called **critical pressure**.

- The state beyond critical temperature and critical pressure is called a **supercritical fluid**.

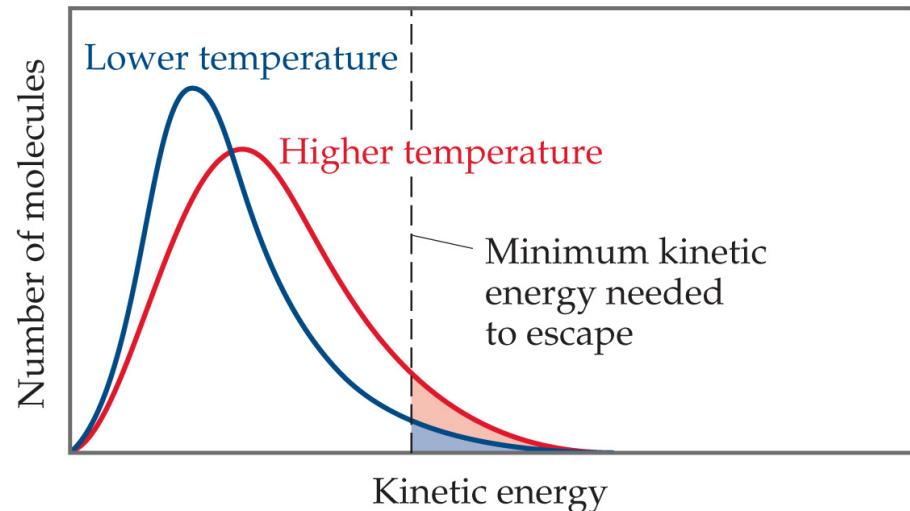
The liquid and gas phases of supercritical fluid are indistinguishable from each other.

Table 11.6 Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen, N ₂	126.1	33.5
Argon, Ar	150.9	48.0
Oxygen, O ₂	154.4	49.7
Methane, CH ₄	190.0	45.4
Carbon dioxide, CO ₂	304.3	73.0
Phosphine, PH ₃	324.4	64.5
Propane, CH ₃ CH ₂ CH ₃	370.0	42.0
Hydrogen sulfide, H ₂ S	373.5	88.9
Ammonia, NH ₃	405.6	111.5
Water, H ₂ O	647.6	217.7

Vapor Pressure

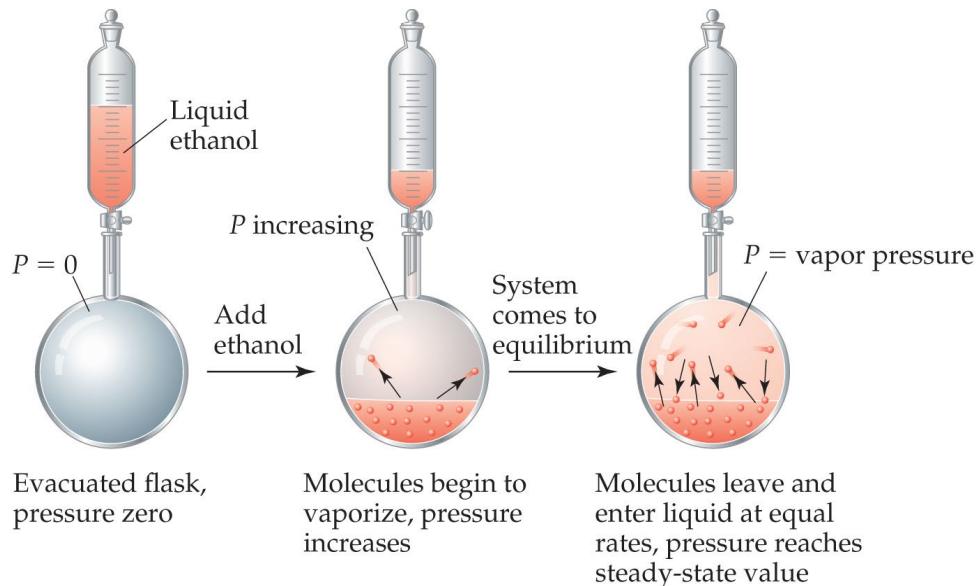
- At any temperature, some liquid molecules have enough energy to escape the surface and become a gas.
- As the temperature rises, the fraction of molecules that have enough energy to break free increases.



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

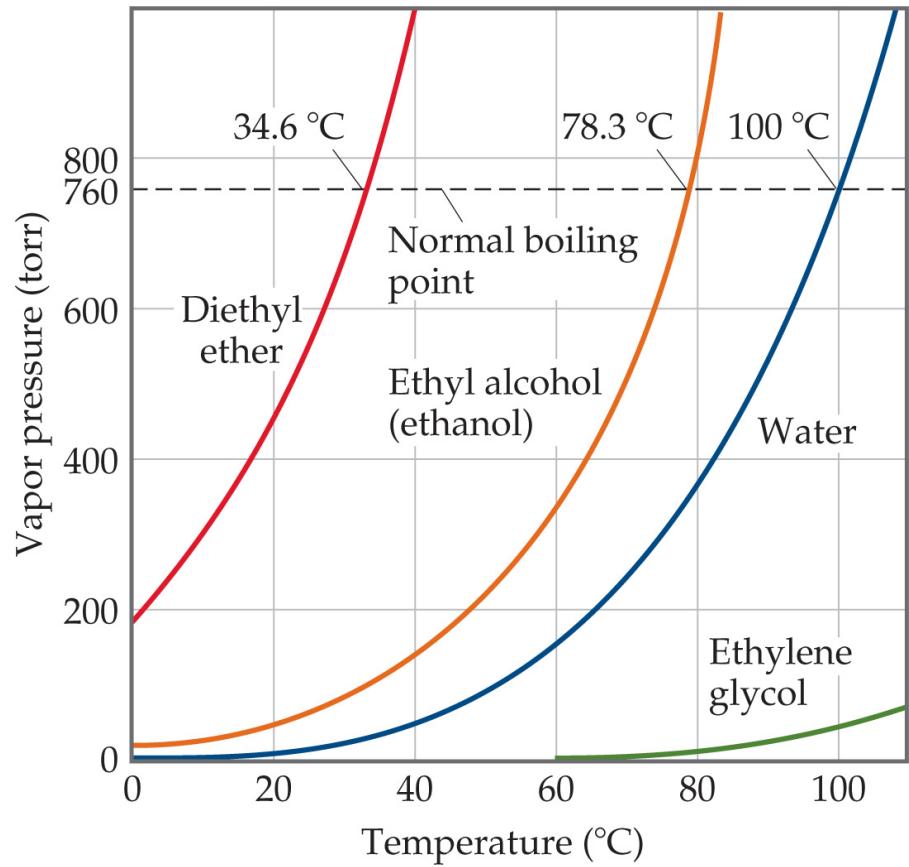


- As more molecules escape the liquid, the pressure they exert increases.
- The liquid and vapor reach a state of **dynamic equilibrium**: liquid molecules **evaporate and vapor molecules condense at the same rate**.

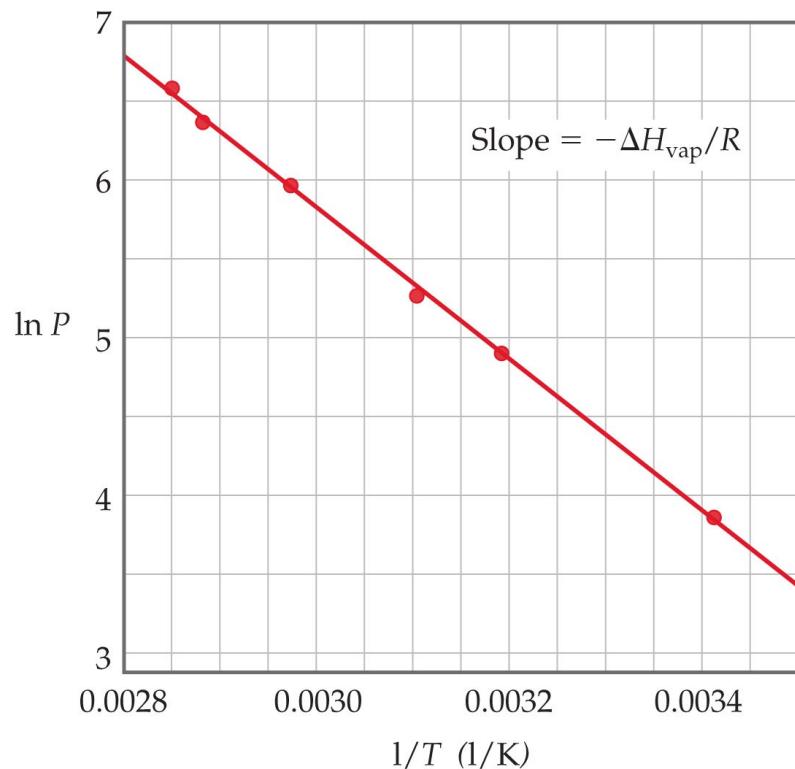
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Vapor Pressure

- 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

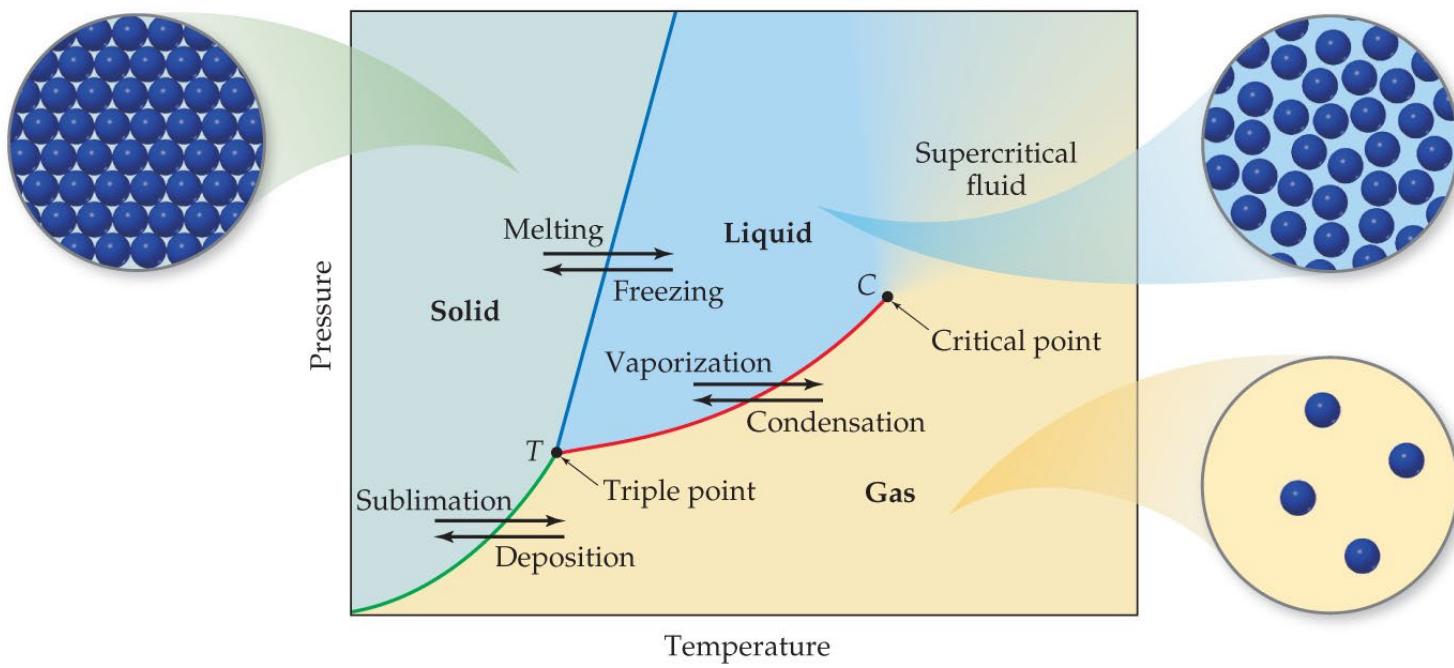


- The natural log of the vapor pressure of a liquid is inversely proportional to its temperature.
- This relationship is quantified in the **Clausius–Clapeyron equation**.

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

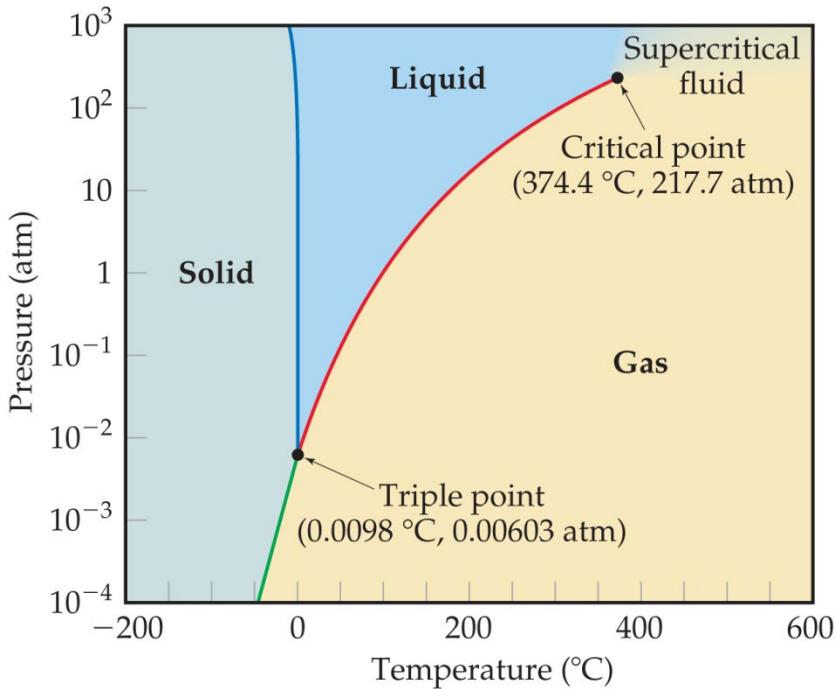
Phase Diagram

- A **phase diagram** is a graph of pressure vs. temperature for a substance. It shows
 - melting, boiling, and sublimation points at different pressures.
 - the triple point and critical point.



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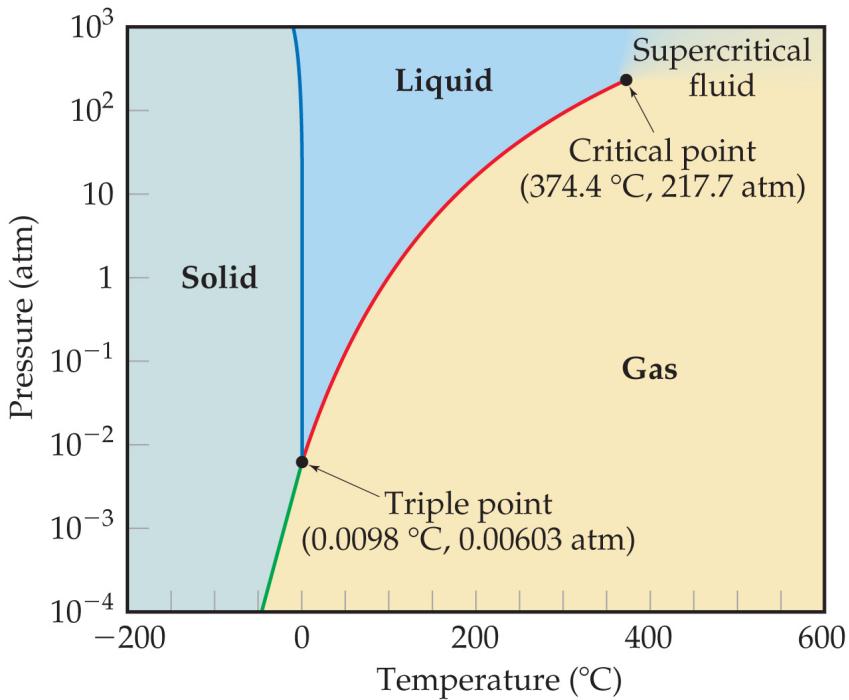
Phase Diagram of Water



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

Supercritical property happens in between gas and liquid

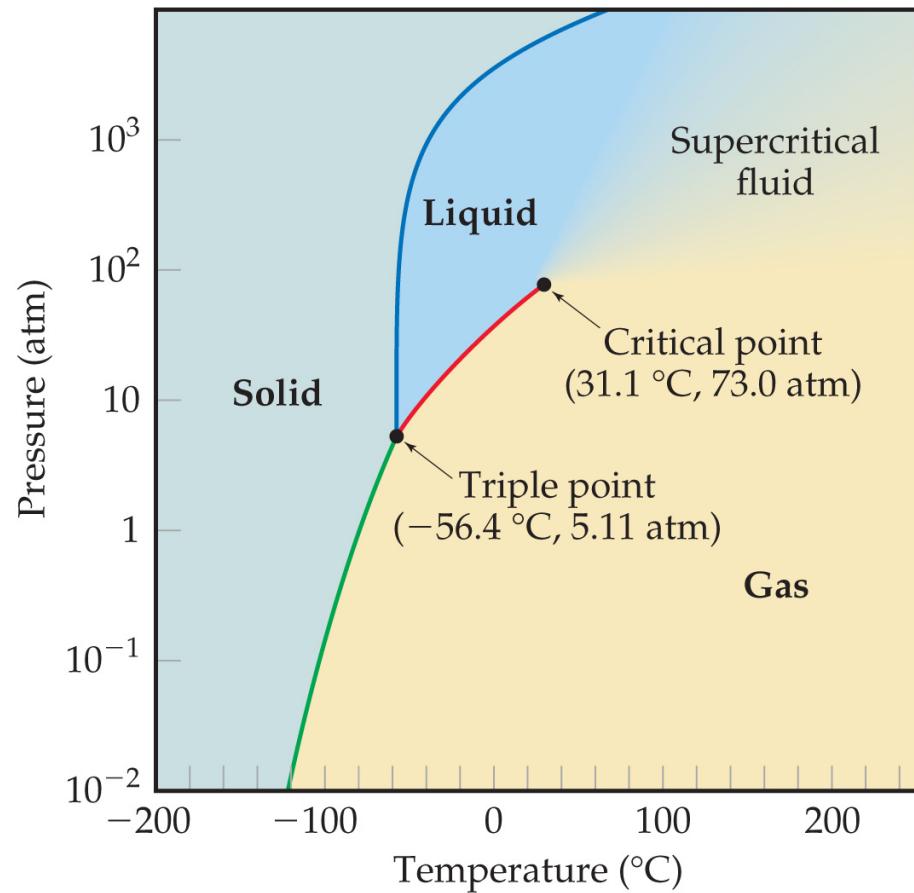
Phase Diagram of Water



- Unusual feature for water:
 - The slope of the solid–liquid line is negative.
 - ✓ This means that as the pressure is increased, the melting point decreases.

Phase Diagram of Carbon Dioxide

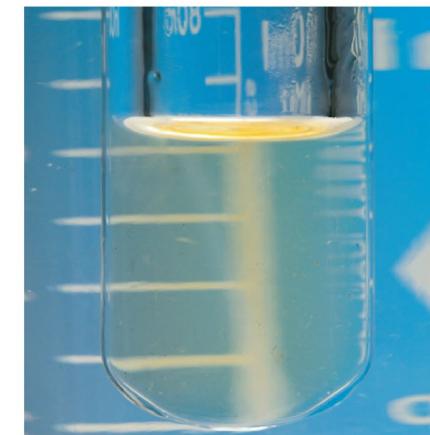
- Unusual features for carbon dioxide:
 - cannot exist in the liquid state at pressures below 5.11 atm (triple point)
 - ✓ CO_2 sublimes at normal pressures.



Liquid Crystals



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



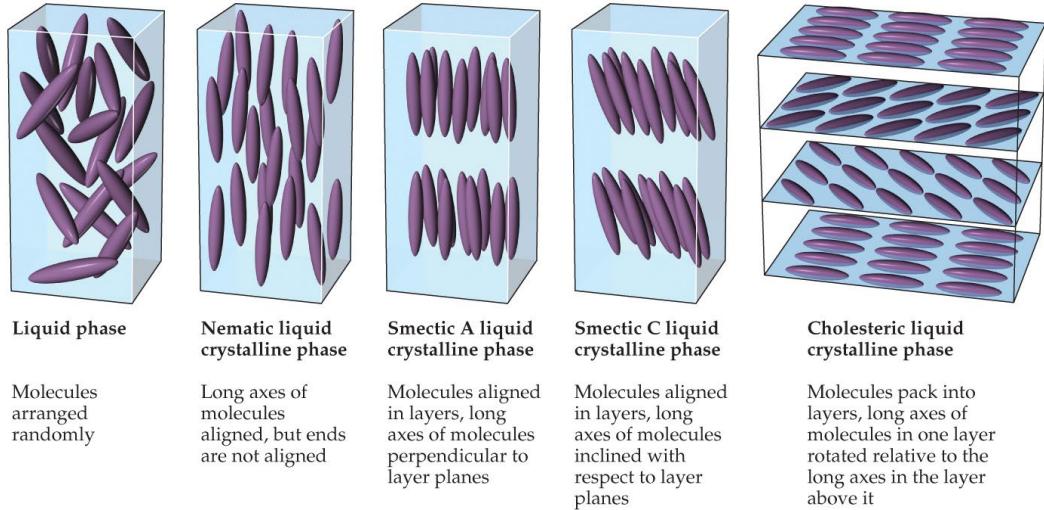
$T > 179\text{ }^{\circ}\text{C}$
Liquid phase

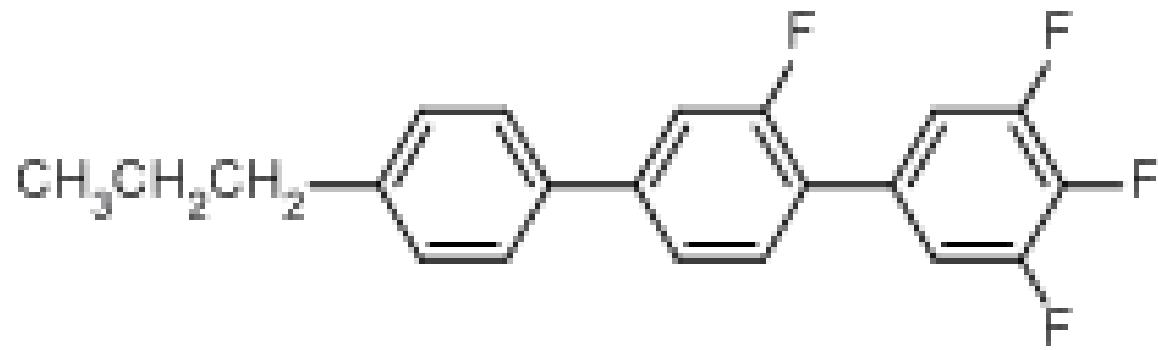
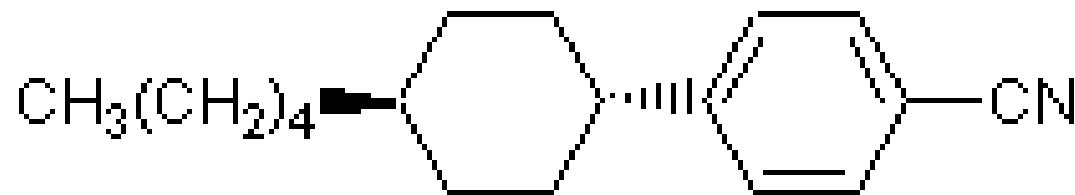
- Some substances do not go directly from the solid state to the liquid state.
- In this intermediate state, liquid crystals have some traits of solids and some of liquids.
- Molecules in liquid crystals have some degree of order.

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Liquid Crystals

- In **nematic liquid crystals**, molecules are only ordered in one dimension, along the long axis.
- In **smectic liquid crystals**, molecules are ordered in two dimensions, along the long axis and in layers.
- In **cholesteric liquid crystals**, nematic-like crystals are layered at angles to each other.





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