

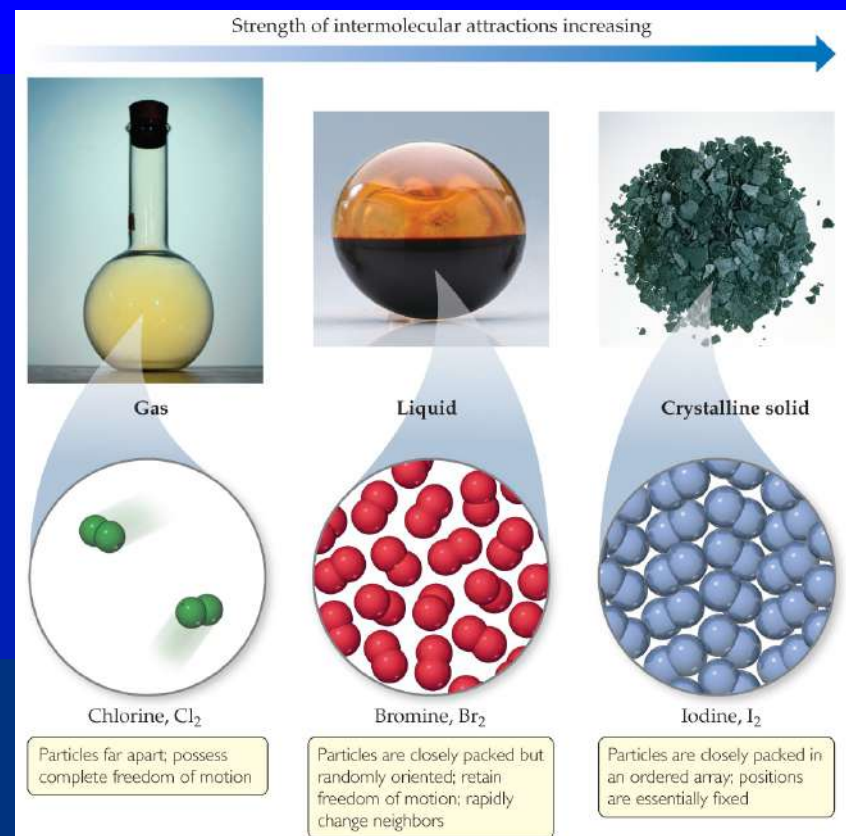
Chapter 11

Liquids and Intermolecular Forces

11.1 A Molecular Comparison of Gases, Liquids, and Solids

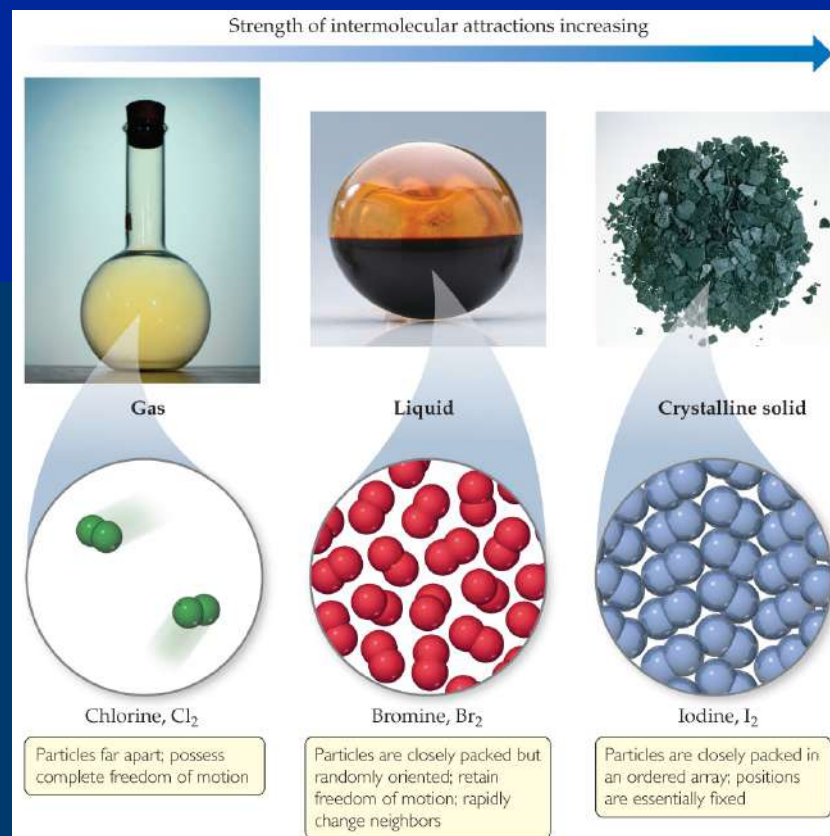
States of Matter

- 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*.



For a given substance, do you expect the density of the substance in its liquid state to be closer to the density in the gaseous state or in the solid state?

- a. It is closer to the density of a gas.
- b. It is closer to the density of a solid.
- c. Both are somewhat close to one another in density.
- d. They are significantly different in density.



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.

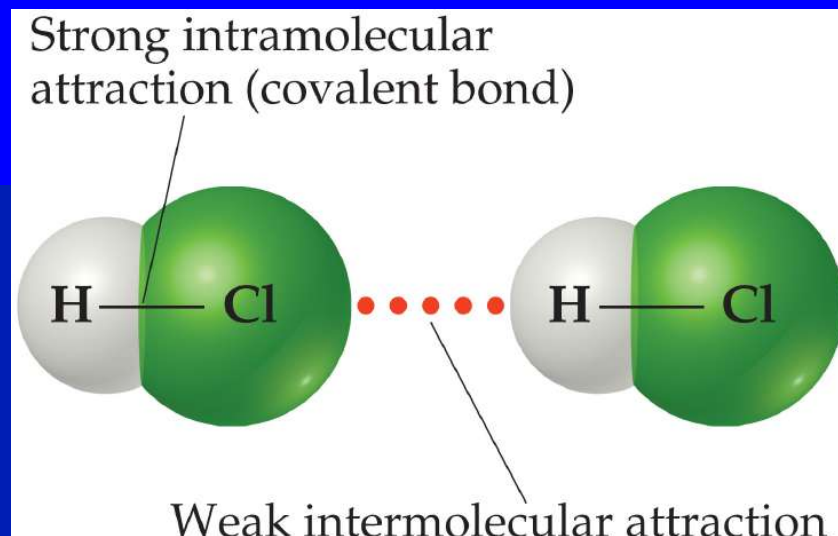
Table 11.2 Comparing Kinetic Energies and Energies of Attractions for States of Matter

Gas	Kinetic energies \gg energies of attraction
Liquid	Comparable kinetic energies and energies of attraction
Solid	Energies of attraction \gg kinetic energies

11.2

Intermolecular Forces

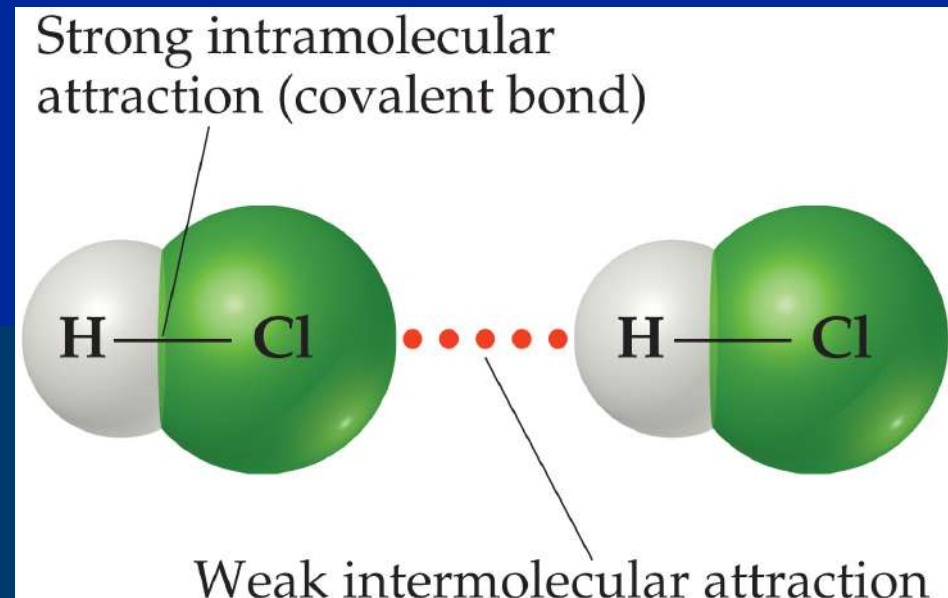
Intermolecular Forces



- 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.

How would you expect the H—Cl distance represented by the red dotted line to compare with the H—Cl distance within the HCl molecule?

- a. Smaller distance
- b. Larger distance
- c. Same distance



When water boils, what are the bubbles composed of?

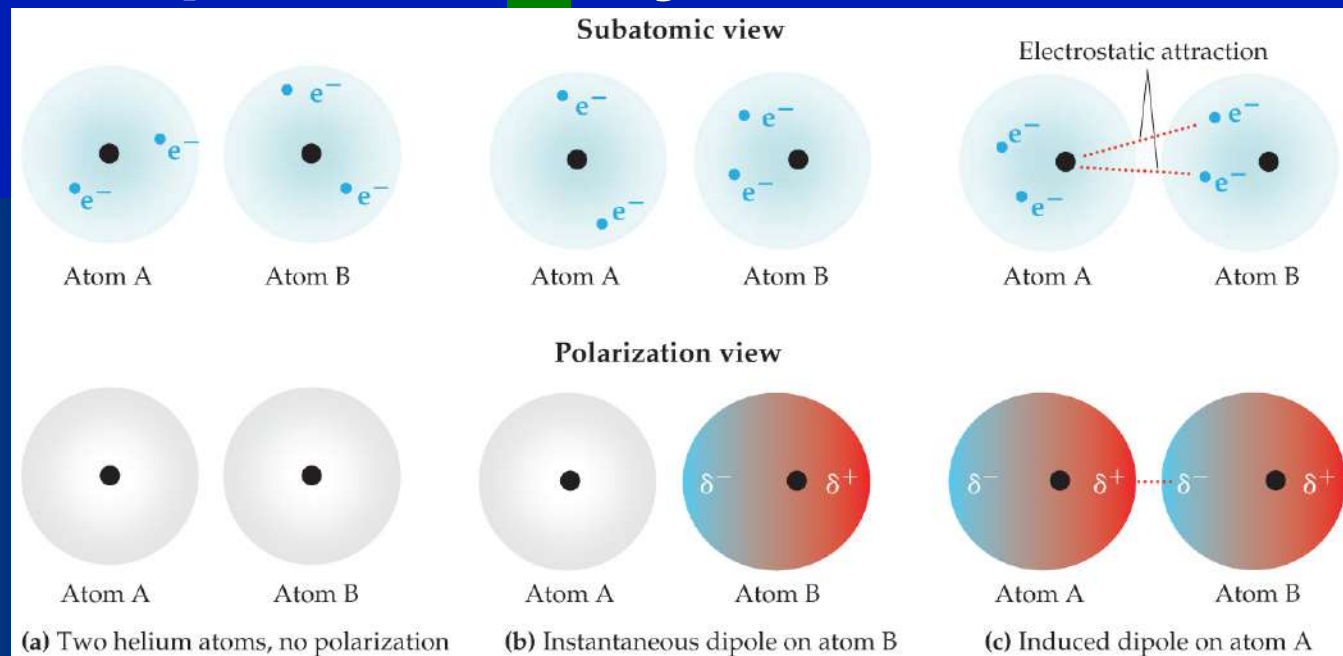
- a. Oxygen
- b. Water
- c. Carbon dioxide
- d. Other impurities

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**.



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 compact, less dispersion force)

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



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

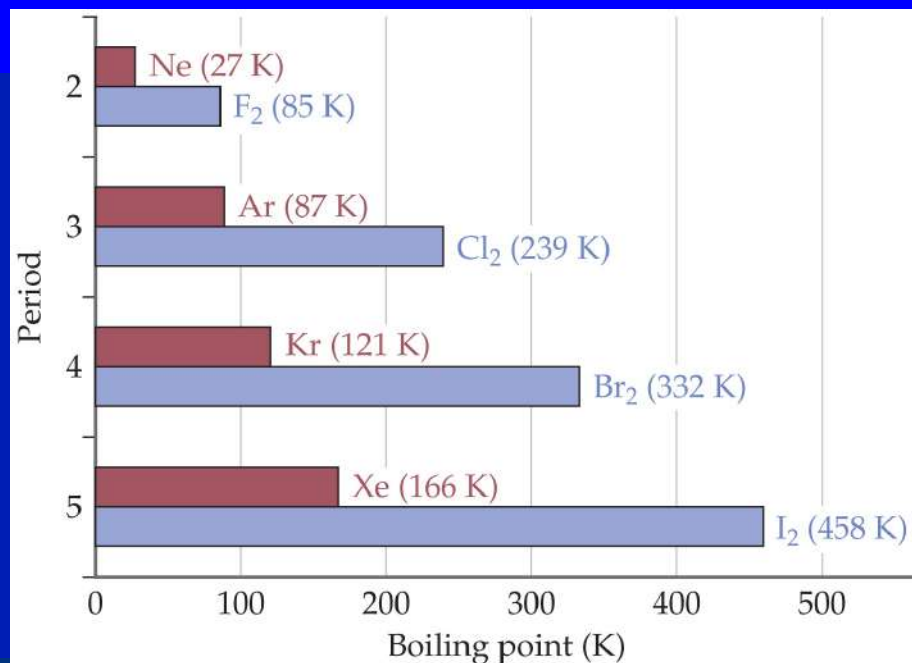
Spherical molecule—smaller surface area diminishes intermolecular contact and decreases dispersion force



Neopentane (C_5H_{12})
bp = 282.7 K

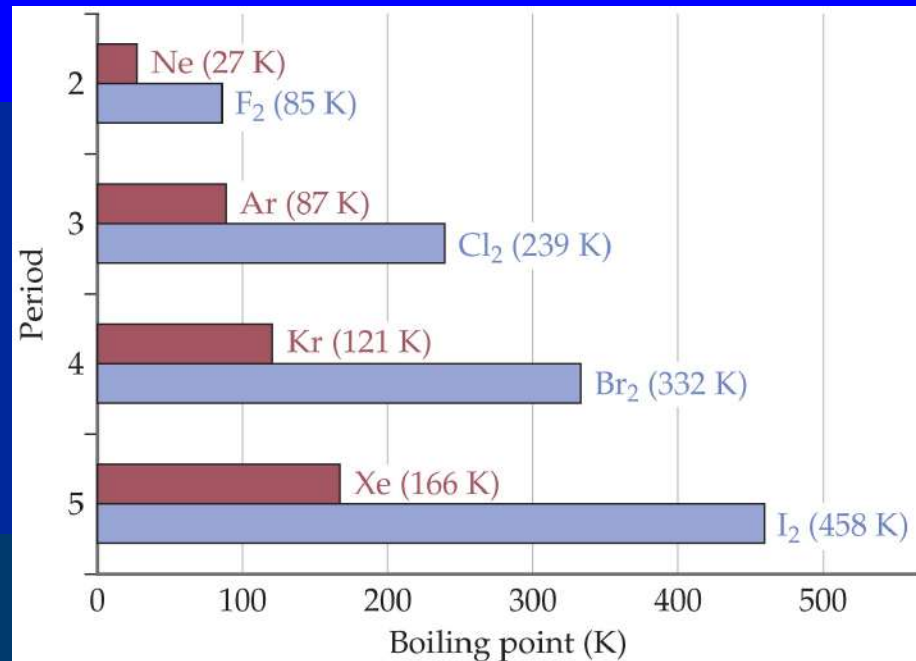
Polarizability & Boiling Point

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



Why is the boiling point of the halogen in each period greater than the noble gas?

- a. The halogen gas molecules are closer together than the noble gas molecules.
- b. The noble gas dispersion forces are greater.
- c. The halogen molecule dispersion forces are greater.
- d. The halogen molecule dipole forces are greater.

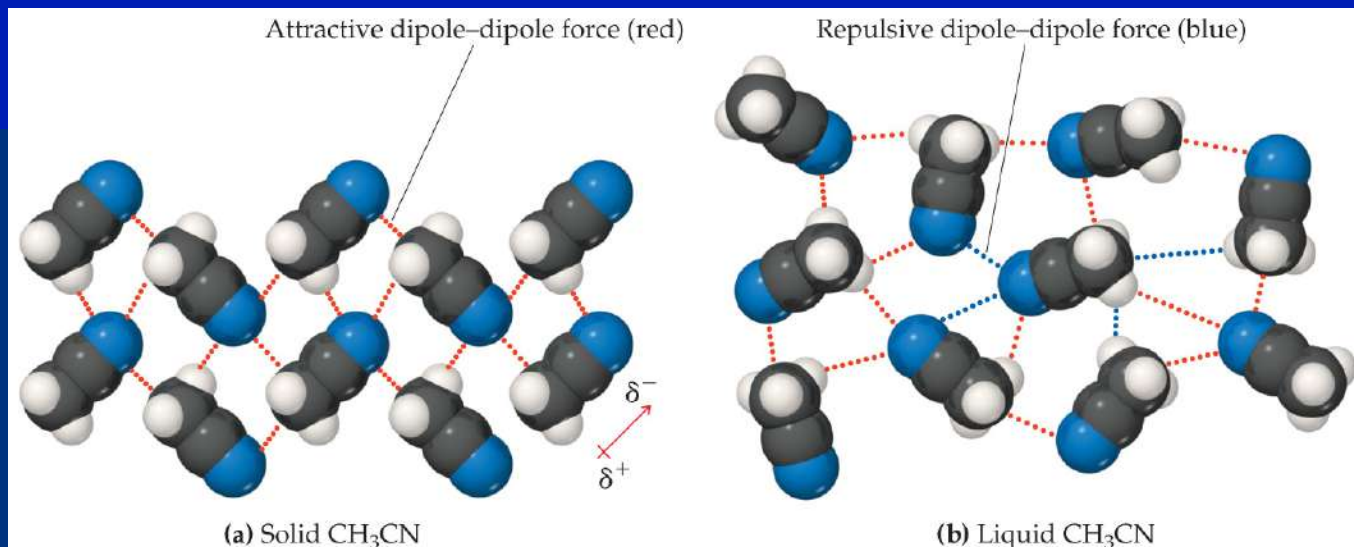


List the substances CCl_4 , CBr_4 , and CH_4 in order of increasing boiling point.

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

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.



Dipole–Dipole Interactions



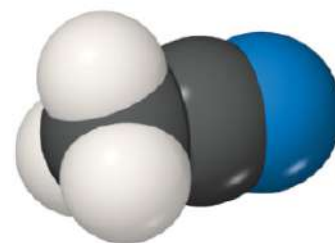
Propane
CH3CH2CH3
MW = 44 amu
 $\mu = 0.1$ D
bp = 231 K



Dimethyl ether
CH3OCH3
MW = 46 amu
 $\mu = 1.3$ D
bp = 248 K



Acetaldehyde
CH3CHO
MW = 44 amu
 $\mu = 2.7$ D
bp = 294 K



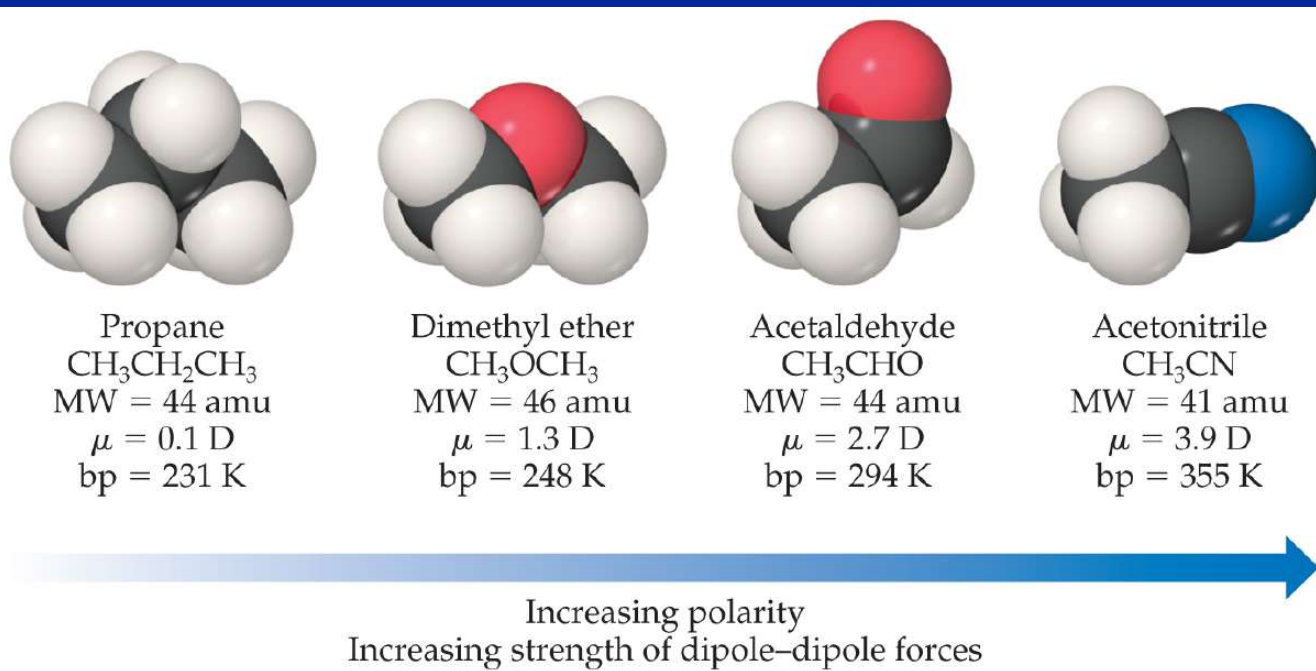
Acetonitrile
CH3CN
MW = 41 amu
 $\mu = 3.9$ D
bp = 355 K

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.

Moving from left to right, do the dispersion forces get stronger, get weaker, or stay roughly the same in the molecules shown here?

- a. Stronger
- b. Weaker
- c. About the same

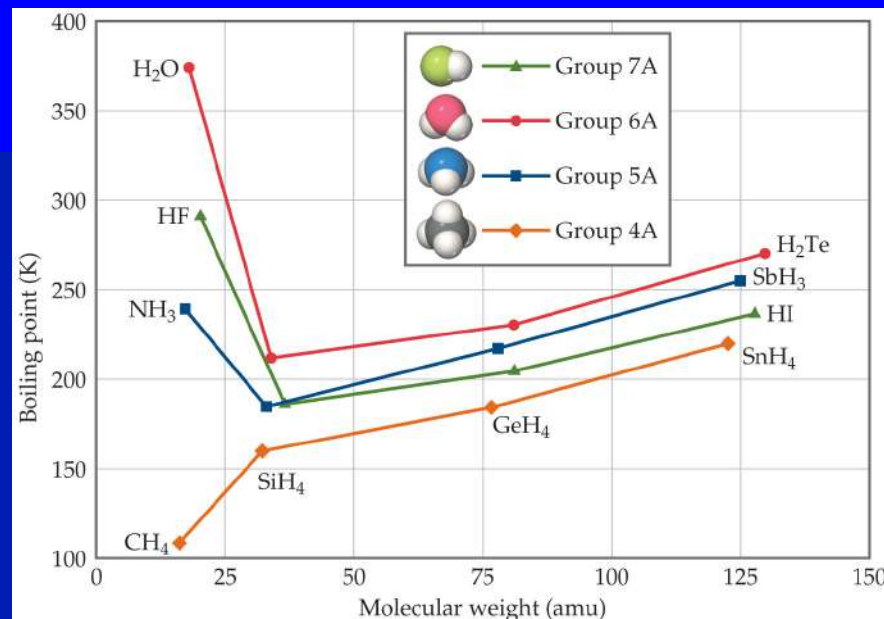


Which Have a Greater Effect: Dipole–Dipole Interactions or Dispersion Forces?

- 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.

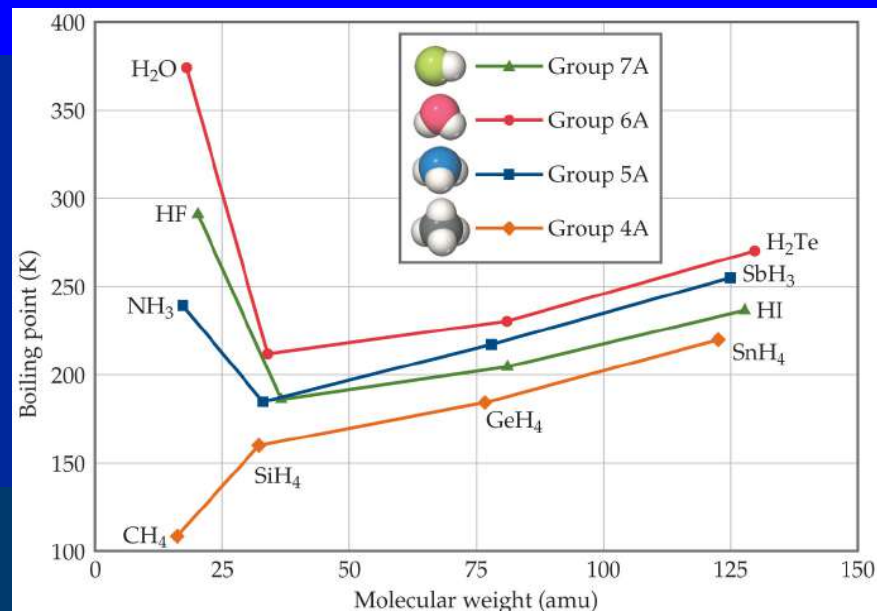
What Does This Graph Show Us?

- 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?



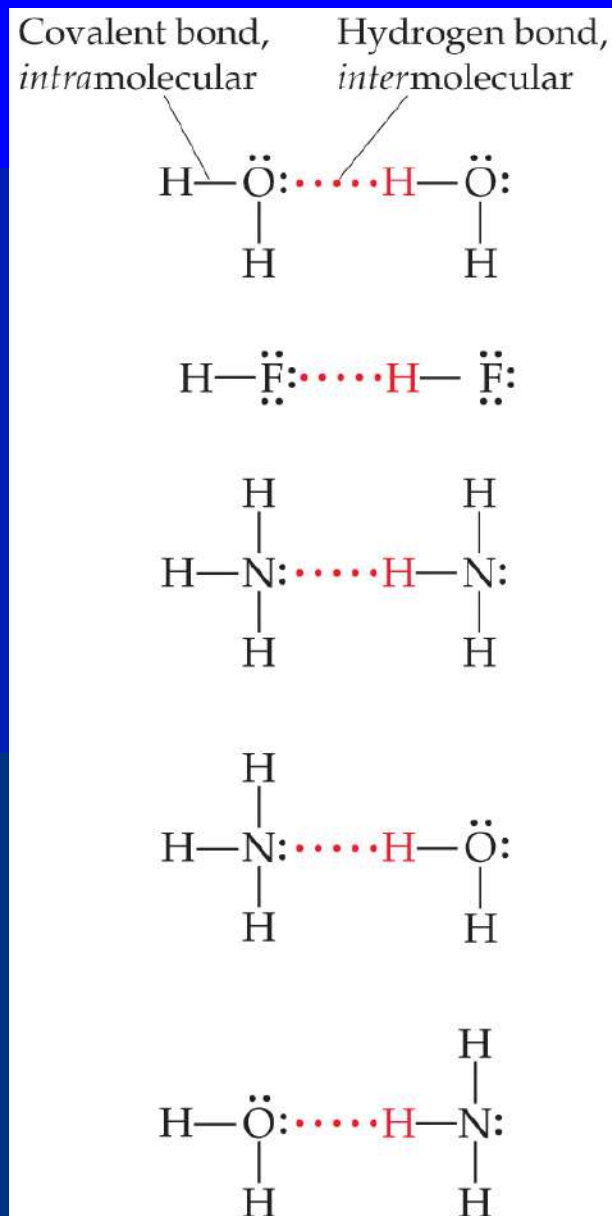
Why is the boiling point of SiH_4 higher than that of CH_4 ?

- a. SiH_4 is more polar than CH_4 .
- b. SiH_4 is smaller in size than CH_4 .
- c. SiH_4 has greater internal dispersion forces than in CH_4 .
- d. SiH_4 is ionic in structure and CH_4 is



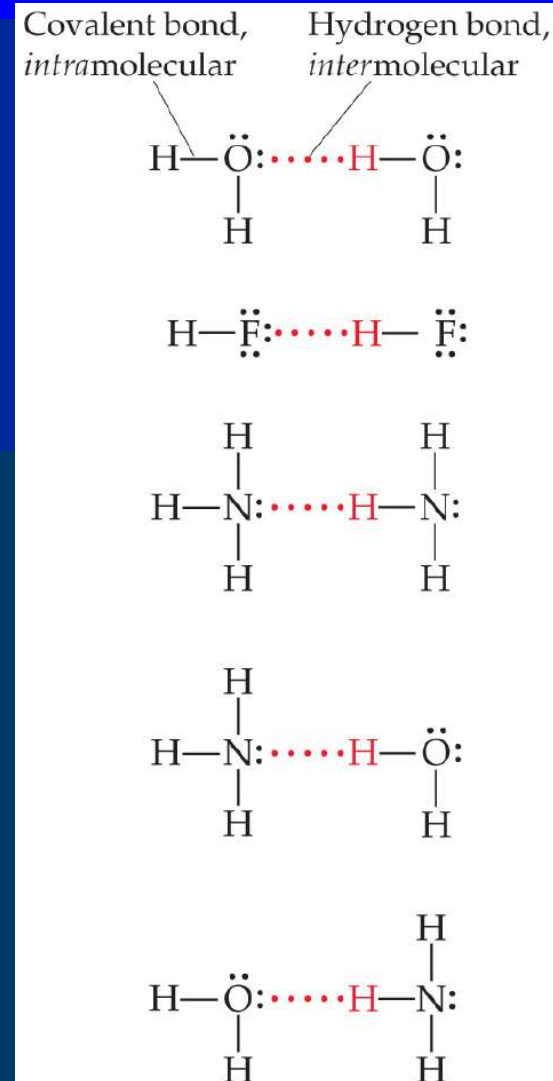
Hydrogen Bonding

- 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.



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

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



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).



Sample Exercise 11.1

In which of the following substances is hydrogen bonding likely to play an important role in determining physical properties?

methane (CH_4)

hydrazine (H_2NNH_2)

methyl fluoride (CH_3F)

hydrogen sulfide (H_2S)

Practice Exercise 1

Which of the following substances is most likely to be a liquid at room temperature?

- (a) Formaldehyde, H_2CO
- (b) fluoromethane, CH_3F
- (c) hydrogen cyanide, HCN
- (d) hydrogen peroxide, H_2O_2
- (e) hydrogen sulfide, H_2S

Practice Exercise 2

In which of these substances is significant hydrogen bonding possible:

methylene chloride (CH_2Cl_2)

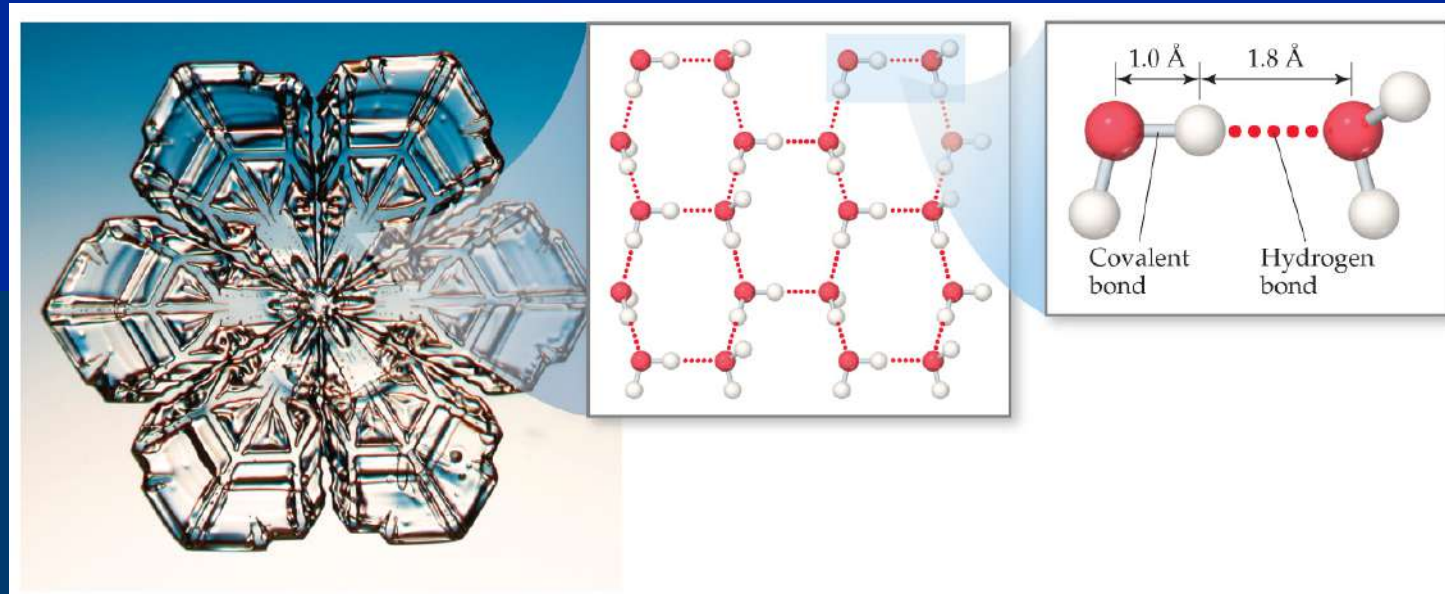
phosphine (PH_3)

chloramine (NH_2Cl)

acetone (CH_3COCH_3)

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

- a. 90°
- b. 109°
- c. 120°
- d. 180°

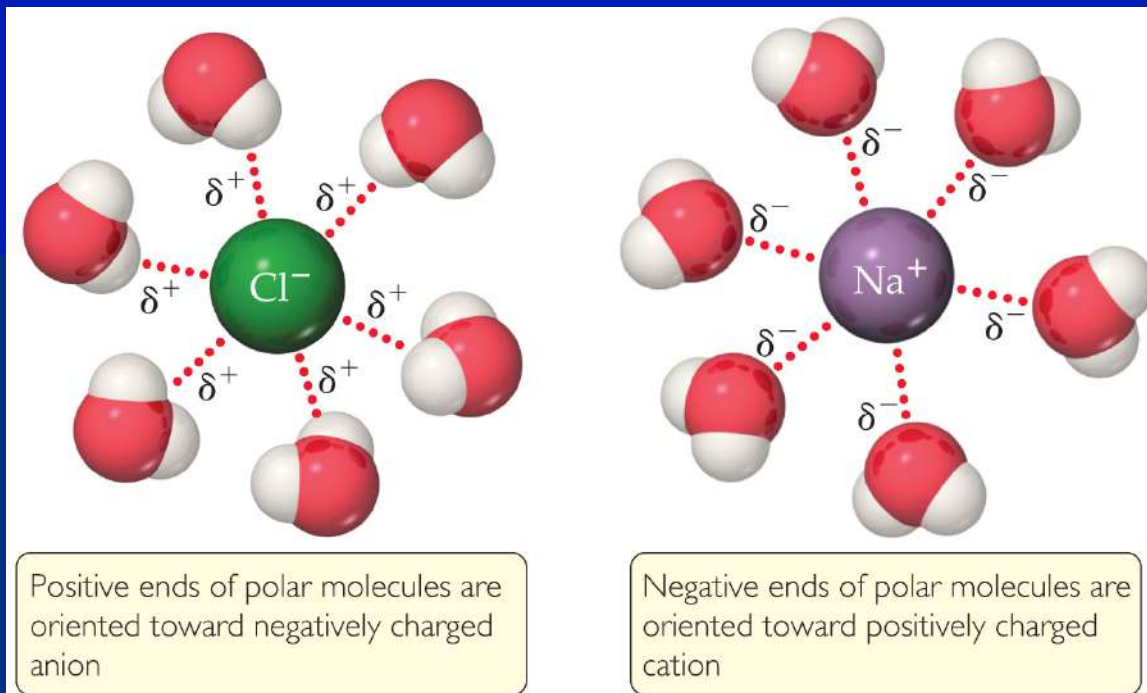


What major type of attractive interaction must be overcome for water to evaporate?

- a. Hydrogen bonding
- b. Dispersion forces
- c. Covalent bonds
- d. Dipole-dipole forces

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.

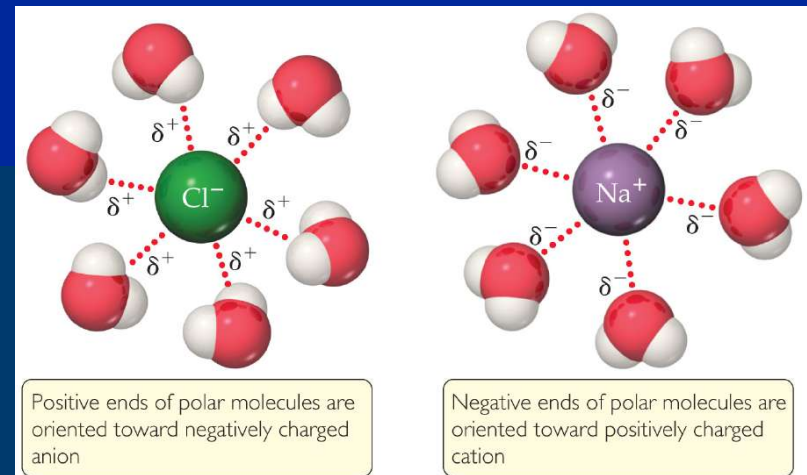


In which mixture do you expect to find ion dipole forces between solute and solvent? CH_3OH in water or $\text{Ca}(\text{NO}_3)_2$ in water.

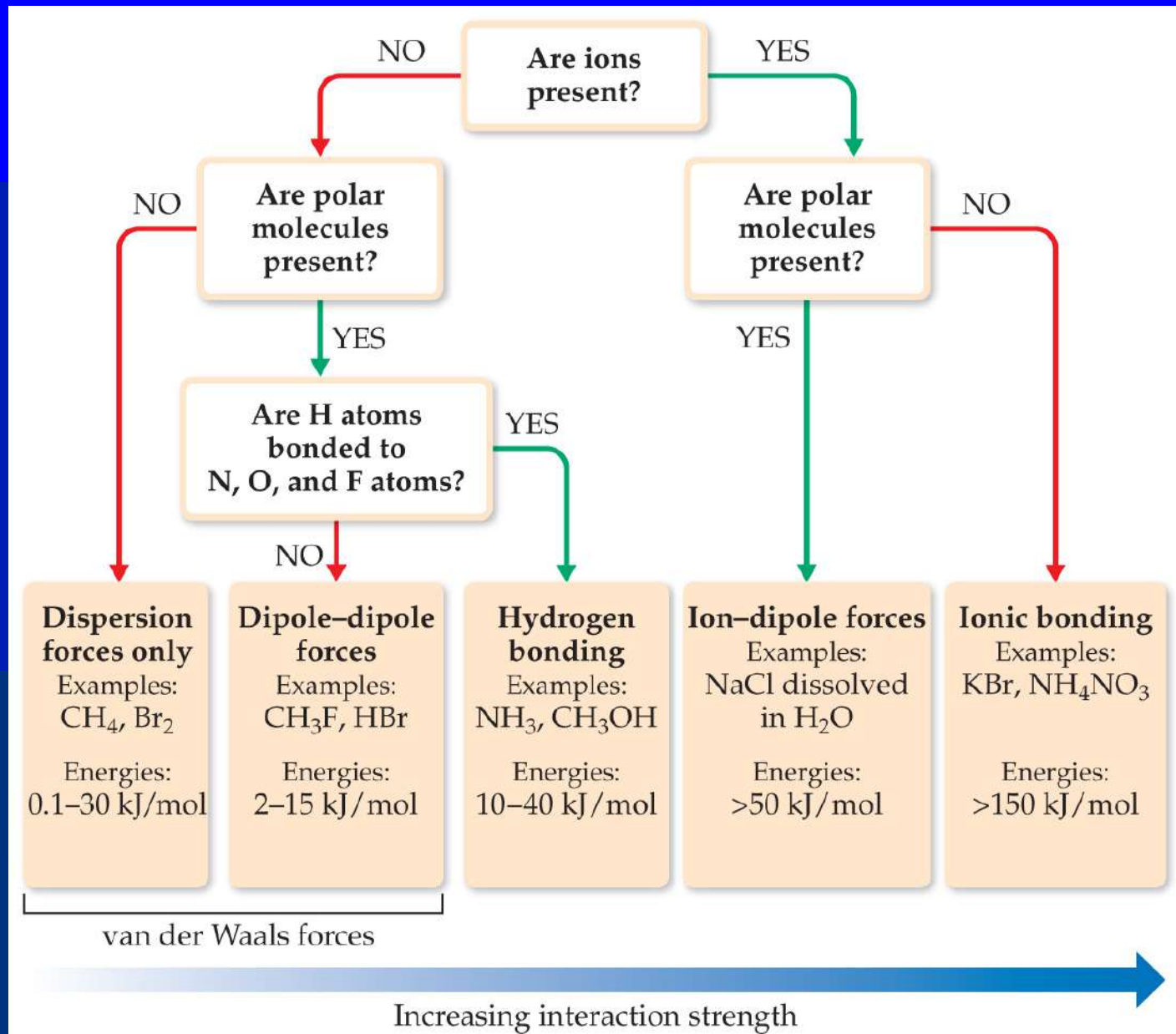
- a. CH_3OH in water, because CH_3OH is a strong electrolyte and forms ions.
- b. $\text{Ca}(\text{NO}_3)_2$ in water, because $\text{Ca}(\text{NO}_3)_2$ is a strong electrolyte and forms ions.
- c. CH_3OH in water, because CH_3OH is a weak electrolyte and forms ions.
- d. $\text{Ca}(\text{NO}_3)_2$ in water, because $\text{Ca}(\text{NO}_3)_2$ is a weak electrolyte and forms ions.

Why does the O side of H₂O point toward the Na⁺ ion?

- a. The H atoms repel the Na⁺ ion.
- b. The H atoms are attracted to other H₂O molecules.
- c. The angle of the HOH bond requires this orientation.
- d. The negatively charged O is attracted to the positive Na⁺.

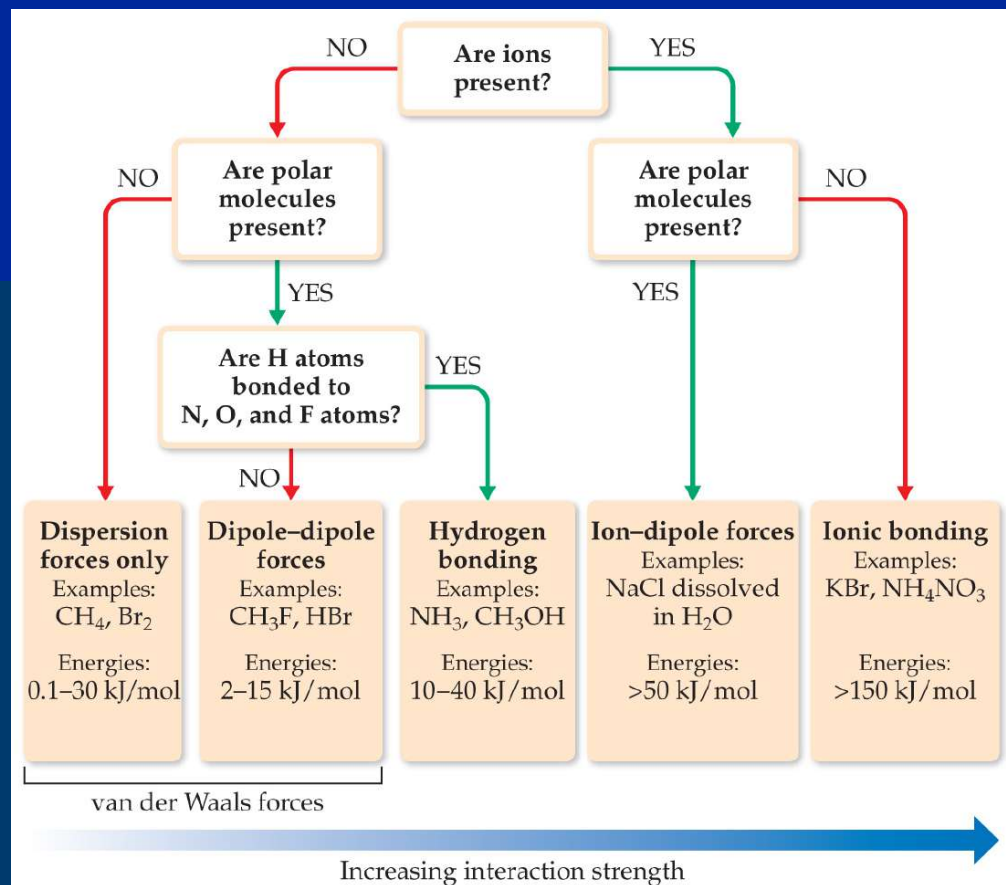


Summarizing Intermolecular Forces



At which point in this flowchart would a distinction be made between SiH_4 and SiH_2Br_2 ?

- a. The presence of ions
- b. The presence of polar molecules
- c. H atoms bonded to N, O, and F
- d. The flow chart would not differentiate between them.



Practice

- which has highest boiling pt?

- HF, HCl, or HBr?

- Identify the most important intermolecular forces :

- BaSO₄

- H₂S

ionic

- Xe

dipole-dipole

- C₂H₆

H-bonding

- P₄

London Dispersion

- H₂O

- CsI

Which has stronger IMF's?

■ CO_2 or OCS

■ SF_2 or SF_6

■ PF_3 or PF_5

■ SO_3 or SO_2

Sample Exercise 11.2

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

Practice Exercise 2

(a) Identify the intermolecular attractions present in the following substances, and
(b) select the substance with the highest boiling point: CH_3CH_3 , CH_3OH , and $\text{CH}_3\text{CH}_2\text{OH}$.

Practice Exercise 1

List the substances Ar, Cl₂, CH₄, and CH₃COOH in order of increasing strength of intermolecular attractions.



11.3 Select Properties of Liquids

Liquid Properties Affected by Intermolecular Forces

- boiling point (previously discussed) and melting point
- viscosity
- surface tension
- capillary action

Viscosity

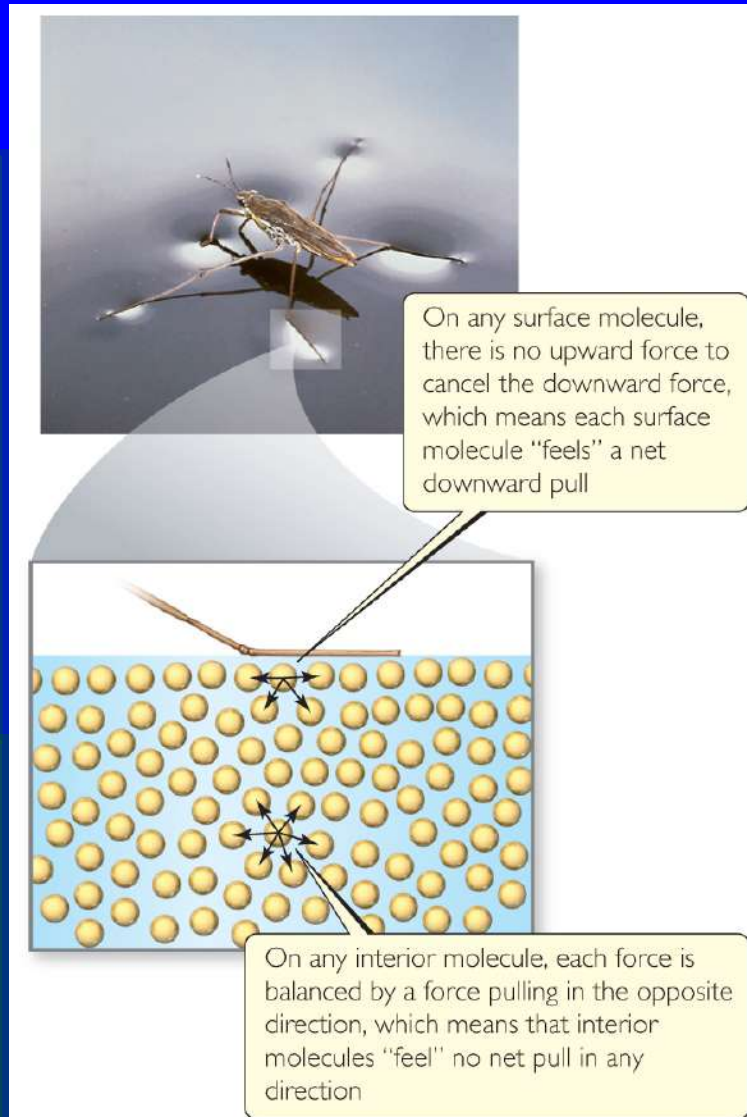
- Resistance of a liquid to flow is called **viscosity**.
- It is related to the ease with which molecules can move past each other.
- Viscosity increases with stronger intermolecular forces and decreases with higher temperature.



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}

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**.

How do viscosity and surface tension change?

(a) as temperature increases

(b) as intermolecular forces of attraction become stronger

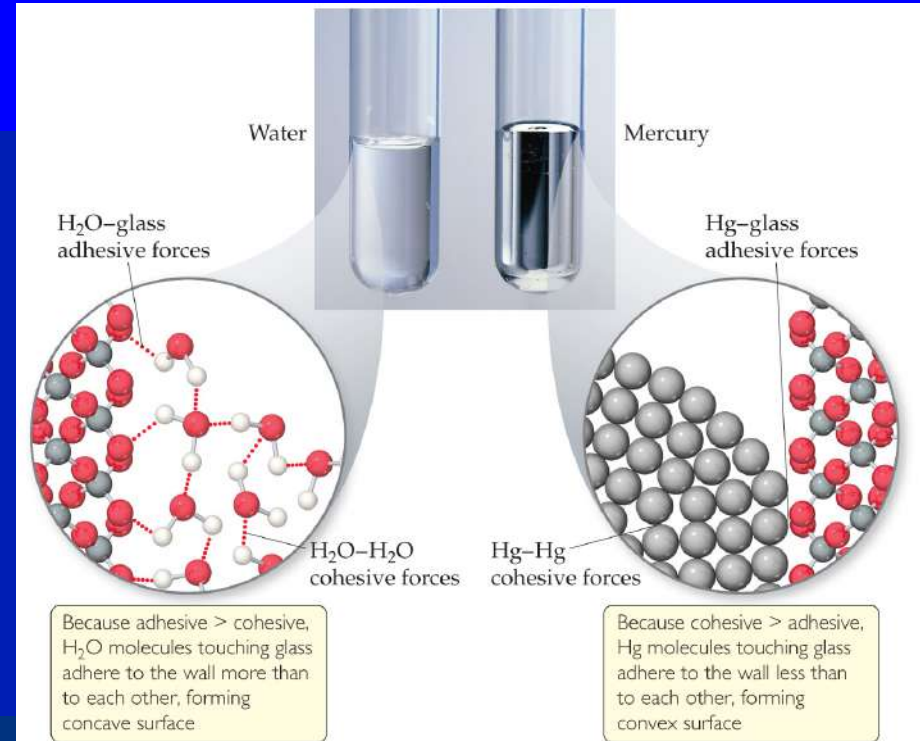
- a. Viscosity increases as intermolecular forces increase while surface tension decreases. Both viscosity and surface tension increase with increasing temperature.
- b. Viscosity decreases as intermolecular forces increase while surface tension increases. Both viscosity and surface tension increase 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.

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.



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

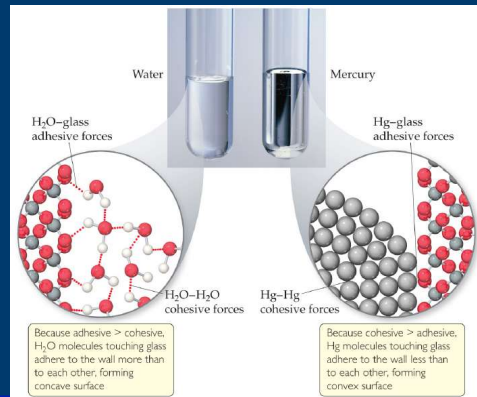
Shape of Water Meniscus Shape of Hg Meniscus

a. Yes, inverted U Yes, downward U

b. No change Yes, downward U

c. No change No change

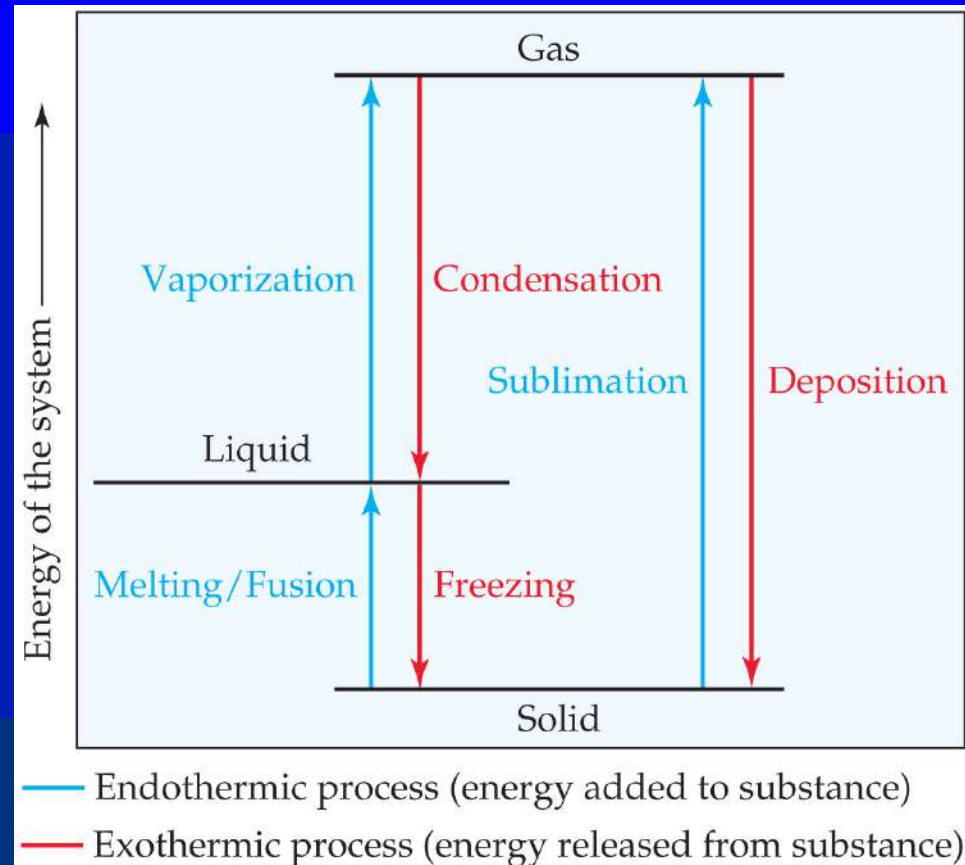
d. Inverted U No change



11.4 Phase Changes

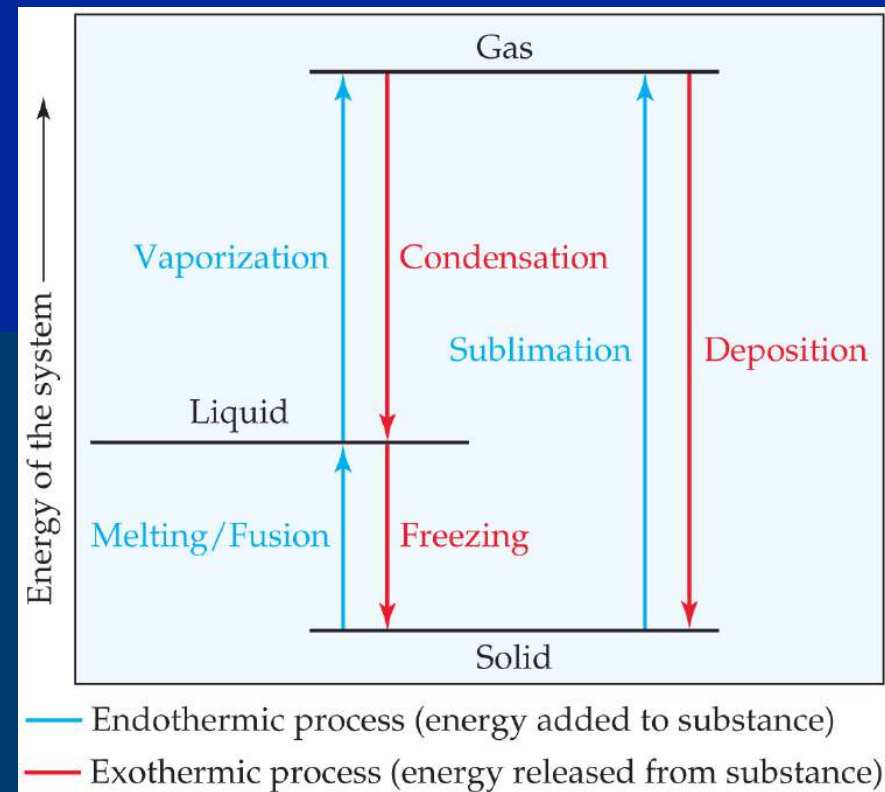
Phase Changes

- 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.



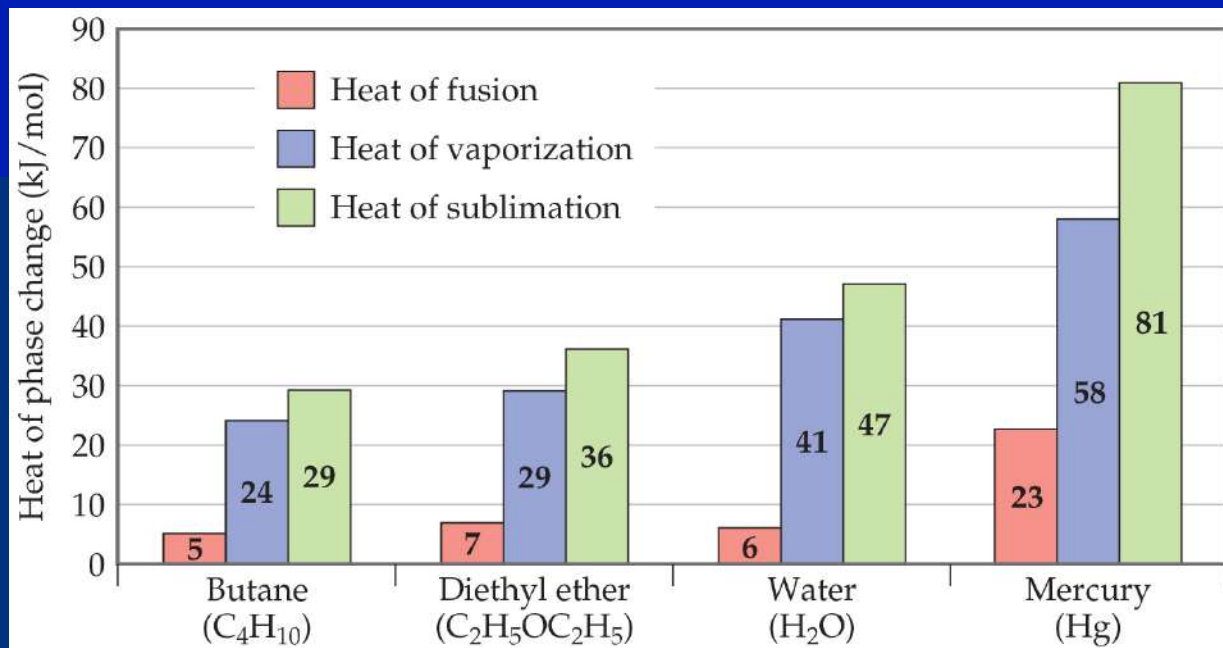
How is energy evolved in deposition related to those for condensation and freezing?

- a. Its magnitude is the difference between condensation and freezing.
- b. Its magnitude is opposite of the sum of condensation and freezing.
- c. Its magnitude is equal to the sum of condensation and freezing.
- d. Cannot tell from the figure



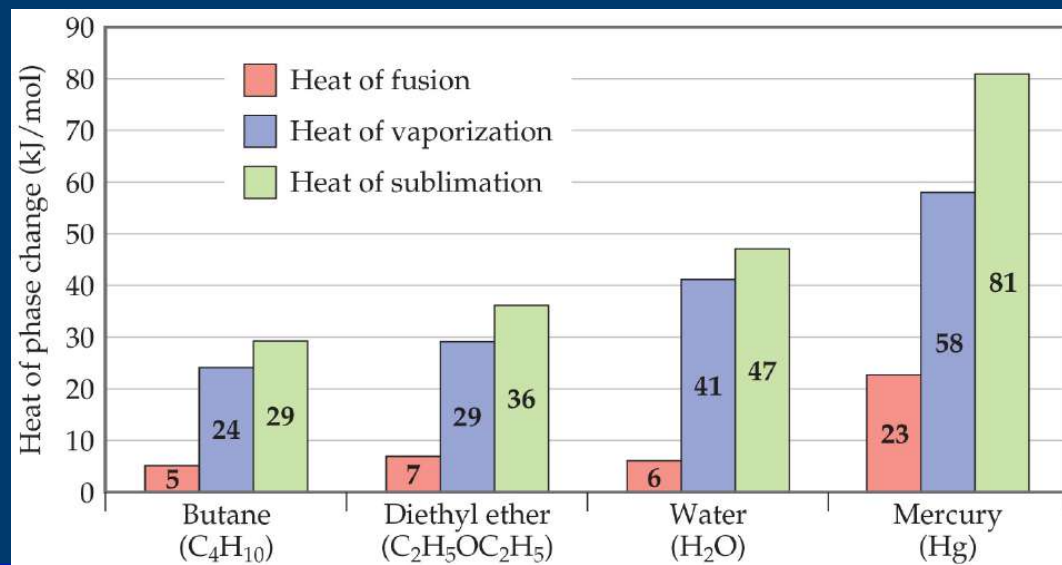
Energy Change & Change of State

- 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.



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?

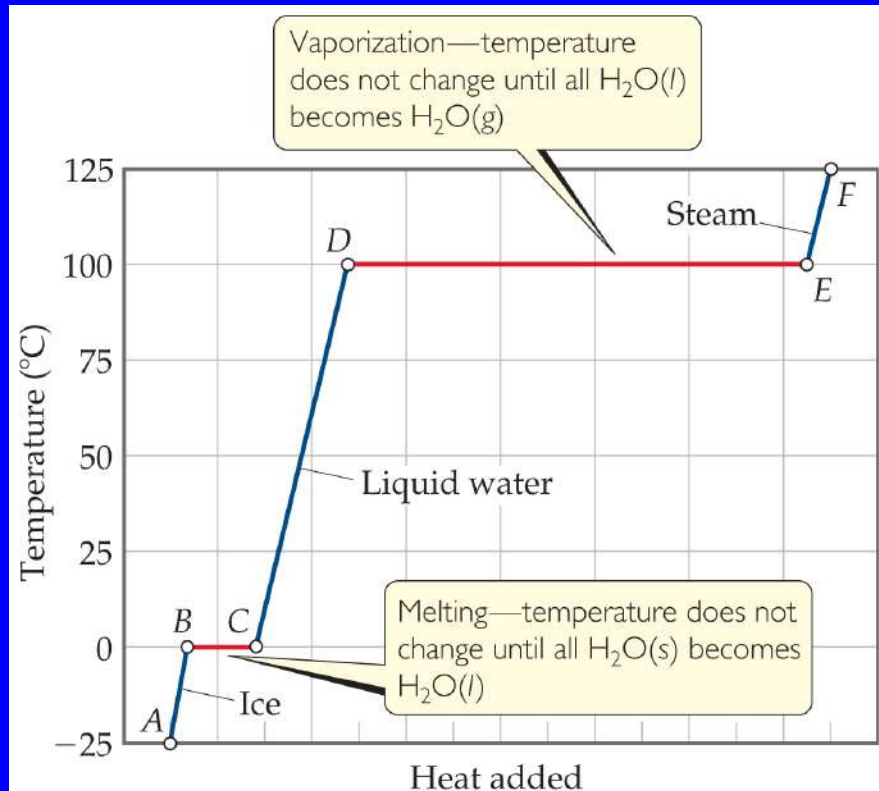
- a. No, because we are not dealing with state functions.
- b. No, because we need heat from melting.
- c. Yes, $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$
- d. Yes, $\Delta H_{sub} = \Delta H_{fus} - \Delta H_{vap}$



What is the name of the phase change that occurs when ice left at room temperature changes to liquid water? Is this change exothermic or endothermic?

- a. Melting (or fusion) and endothermic
- b. Melting (or fusion) and exothermic
- c. Freezing and endothermic
- d. Freezing and exothermic

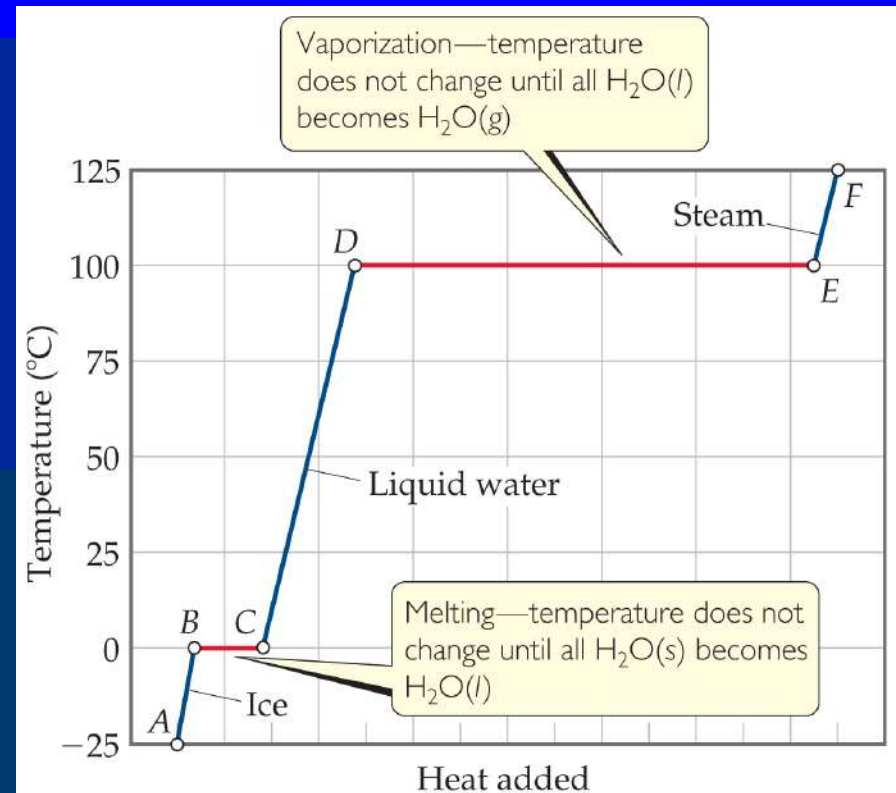
Heating Curves



- 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 or vaporization is heat.

What process is occurring between points C and D?

- a. Melting
- b. Vaporization
- c. Heating the solid
- d. Heating the liquid



Sample Exercise 11.3

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

Practice Exercise 1

What information about water is needed to calculate the enthalpy change for converting 1 mol $\text{H}_2\text{O}(g)$ at $100\text{ }^\circ\text{C}$ to $\text{H}_2\text{O}(l)$ at $80\text{ }^\circ\text{C}$?

- (a) Heat of fusion
- (b) heat of vaporization
- (c) heat of vaporization and specific heat of $\text{H}_2\text{O}(g)$
- (d) heat of vaporization and specific heat of $\text{H}_2\text{O}(l)$
- (e) heat of fusion and specific heat of $\text{H}_2\text{O}(l)$.

Practice Exercise 2

- What is the enthalpy change during the process in which 100.0 g of water at 50.0°C is cooled to ice at -30.0°C ?

Supercritical Fluids

- Gases liquefies when pressure is applied.
- The temperature beyond which a gas *cannot* be compressed is called its **critical temperature**. The pressure needed to compress the liquid at critical temperature is called **critical pressure**.
- The state beyond this temperature is called a **supercritical fluid**.

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

Why are the critical temperature and pressure for H₂O so much higher than those for H₂S, a related substance?

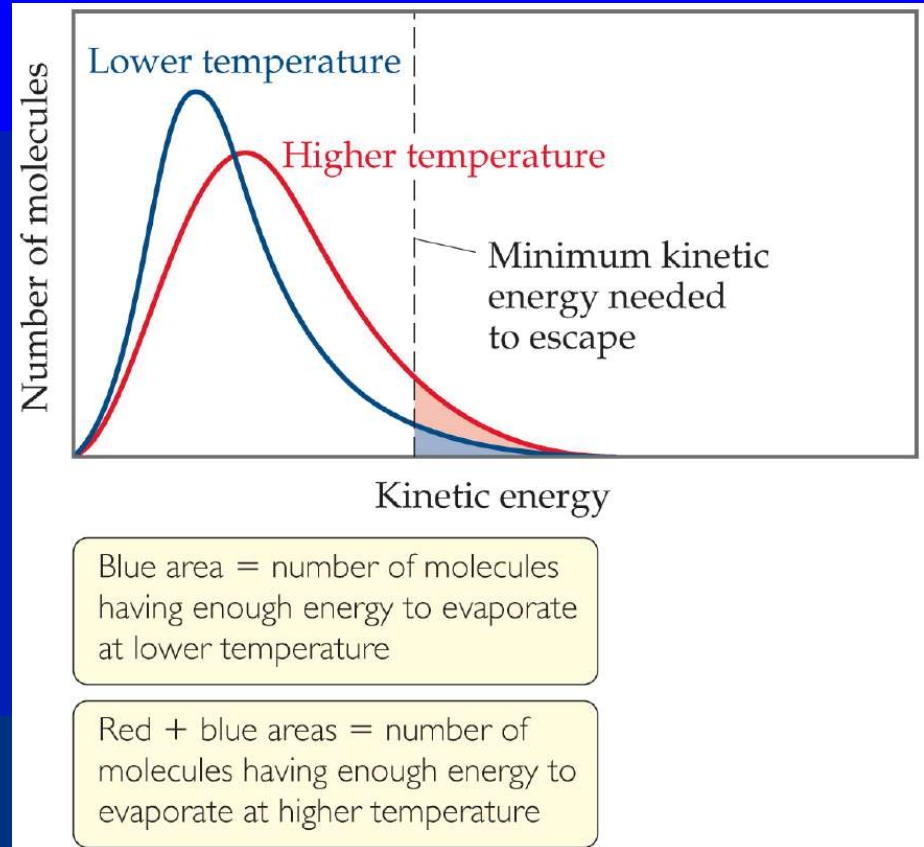
- a. The mass difference between H₂S and H₂O
- b. H₂S makes strong hydrogen bonds.
- c. H₂O makes strong hydrogen bonds.

Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen, N ₂	126.1	33.5
Argon, Ar	150.9	48.0
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11.5 Vapor Pressure

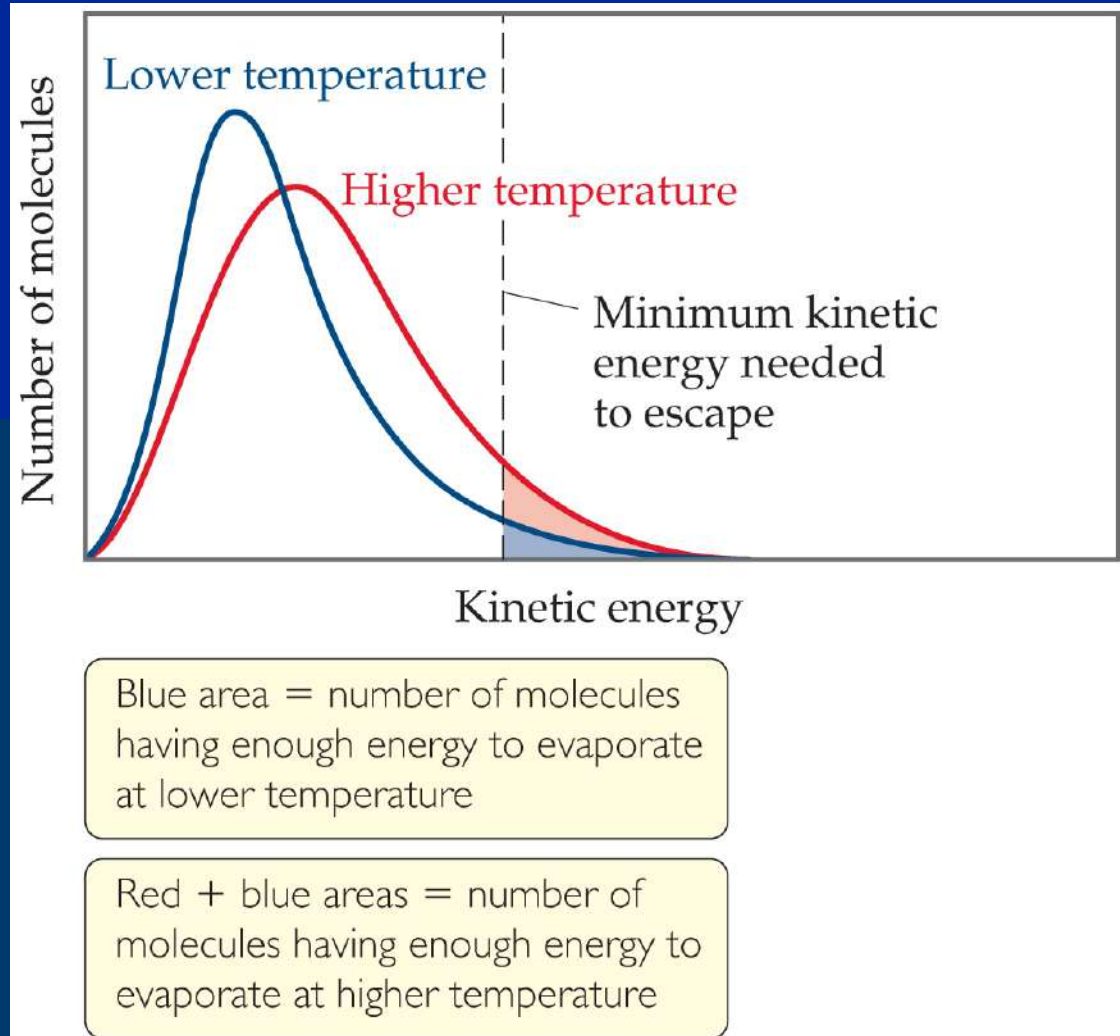
Vapor Pressure

- 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.

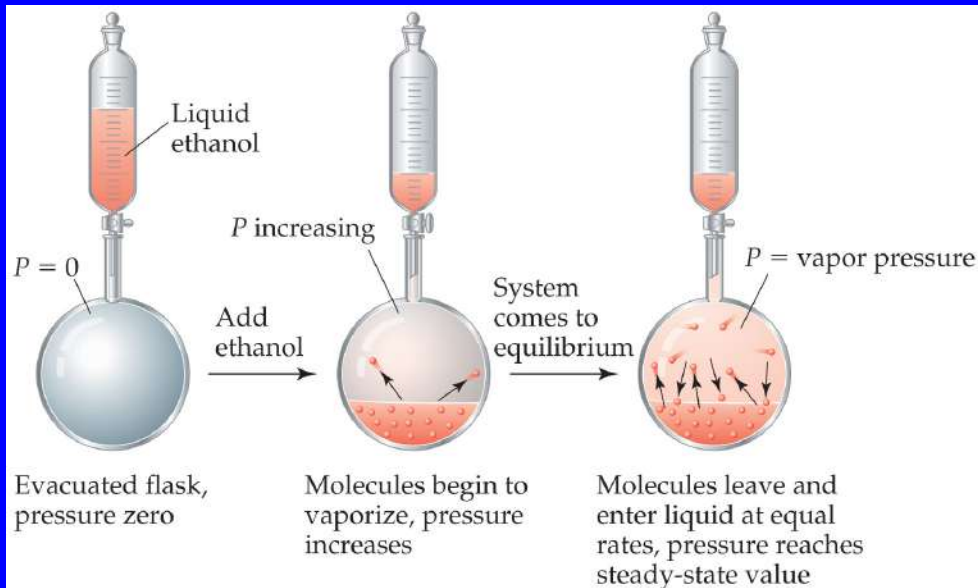


As the temperature increases, does the rate of molecules escaping into the gas phase increase or decrease?

- a. Increases
- b. Decreases



Vapor Pressure



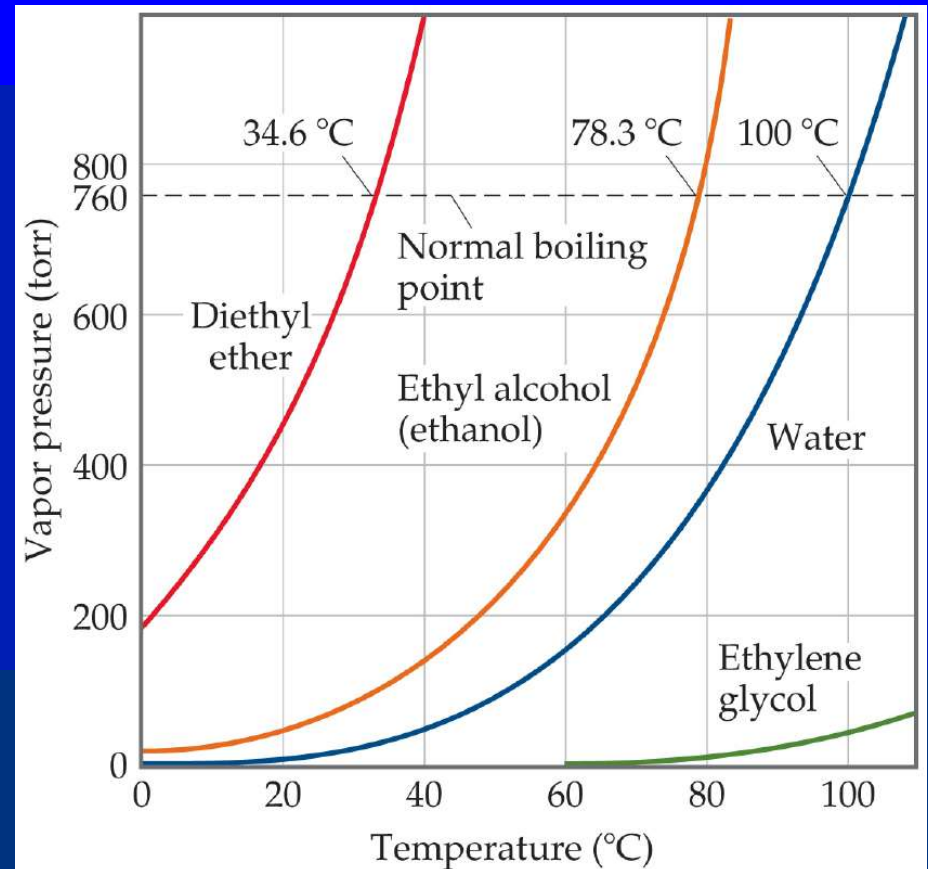
- As more molecules escape the liquid, the pressure they exert increases.
- The liquid and vapor reach a state of dynamic equilibrium: liquid molecules evaporate and vapor molecules condense *at the same rate*.

Which compound do you think is more volatile at 25 °C: CCl₄ or CBr₄?

- a. CBr₄, because dispersion forces between its molecules are greater than in CCl₄.
- b. CBr₄, because polar forces between its molecules are smaller than in CCl₄.
- c. CCl₄, because polar forces between its molecules are greater than in CBr₄.
- d. CCl₄, because dispersion forces between its molecules are smaller than in CBr₄.

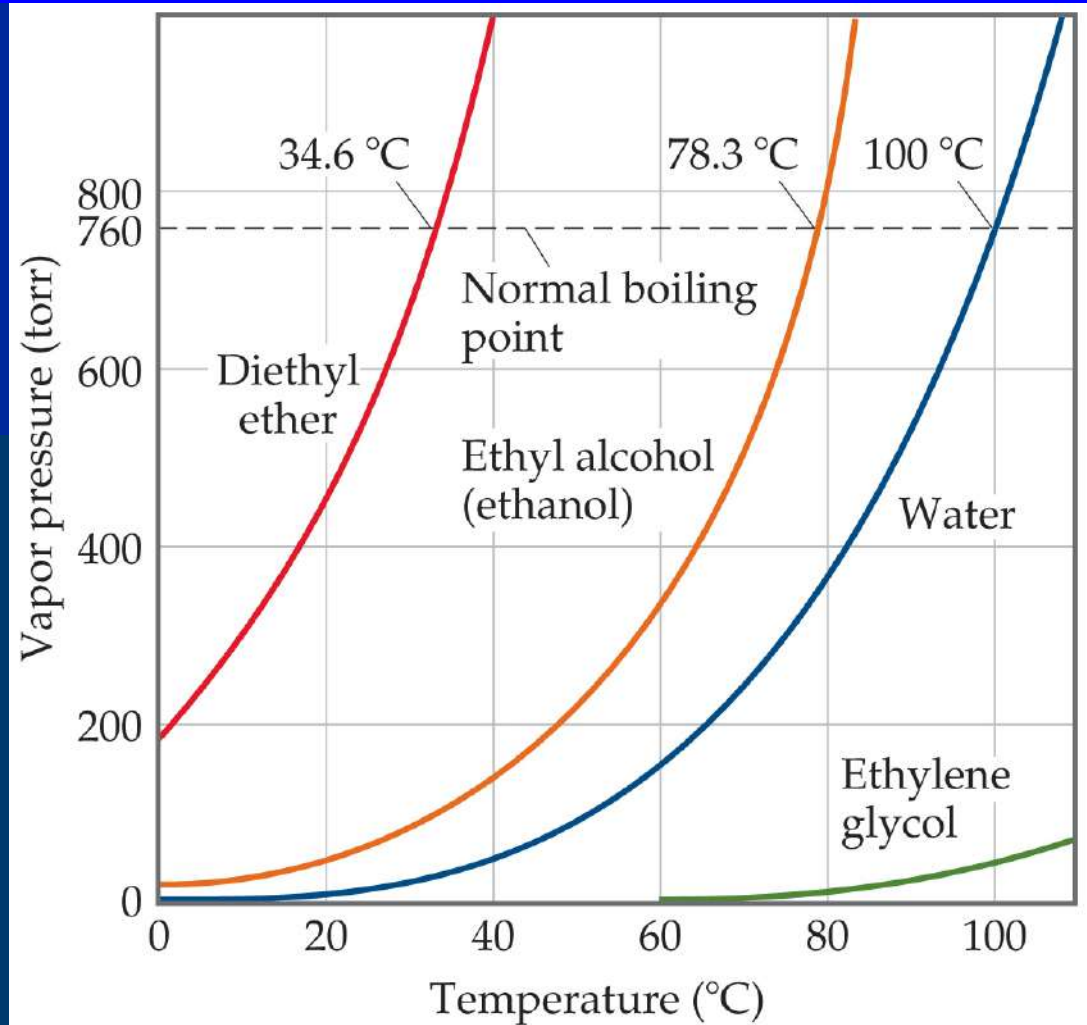
Vapor Pressure

- 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.

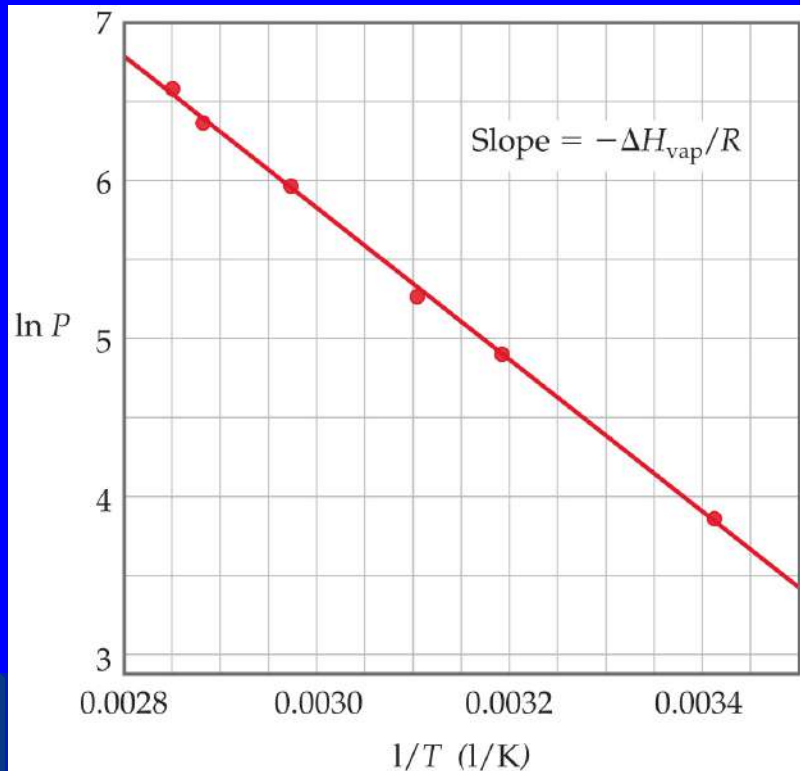


What is the vapor pressure of ethylene glycol at its normal boiling point?

- a. 260 torr
- b. 460 torr
- c. 660 torr
- d. 760 torr



Vapor Pressure

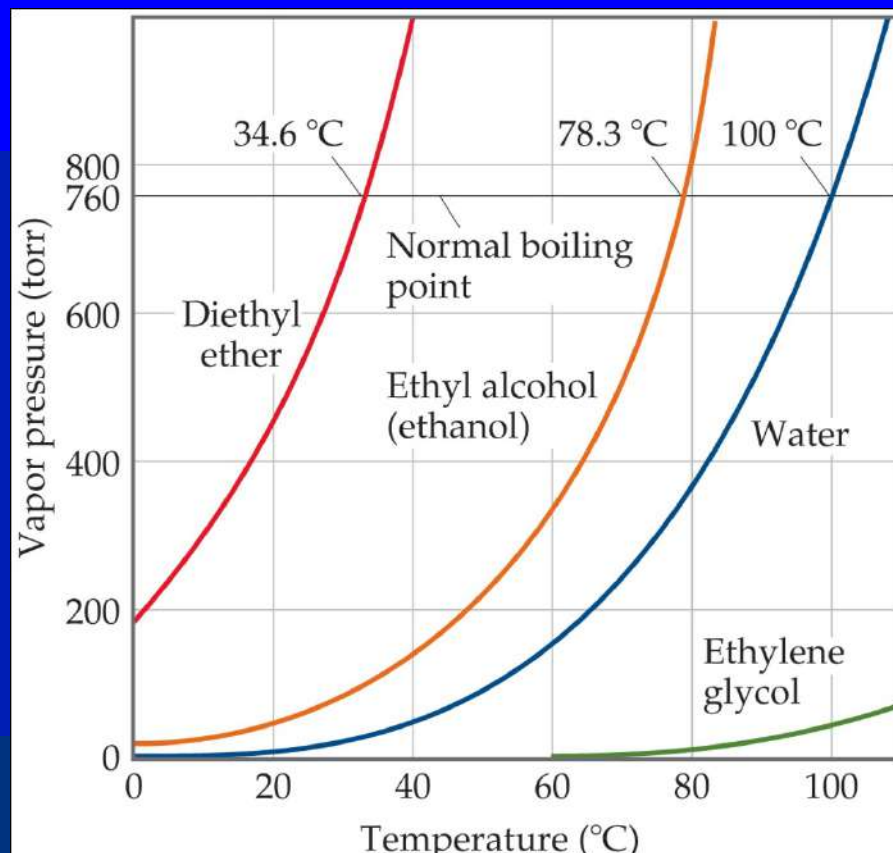


- The natural log of the vapor pressure of a liquid is inversely proportional to its temperature.
- This relationship is quantified in the **Clausius–Clapeyron** equation.

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

Sample Exercise 11.4

- 1) Use Figure 11.25 to estimate the boiling point of diethyl ether under an external pressure of 0.80 atm.
- 2) At what external pressure will ethanol have a boiling point of 60°C?



Practice Exercise 1

In the mountains, water in an open container will boil when

- (a) its critical temperature exceeds room temperature
- (b) its vapor pressure equals atmospheric pressure
- (c) its temperature is $100\text{ }^{\circ}\text{C}$
- (d) enough energy is supplied to break covalent bonds
- (e) none of these is correct

Integrative Exercise

- CS_2 has a melting point of -110.8°C and a boiling point of 46.3°C . Its density at 20°C is 1.26 g/cm^3 . It is highly flammable.
 - A) What is the compound's name?
 - B) List the intermolecular forces that CS_2 molecules would have with each other.
 - C) Write a balanced equation for the combustion of this substance.
 - D) The critical temperature and pressure for CS_2 are 552 K and 78 atm. Compare these values with those of CO_2 (304.3 K and 73 atm) and discuss the origin of their differences.