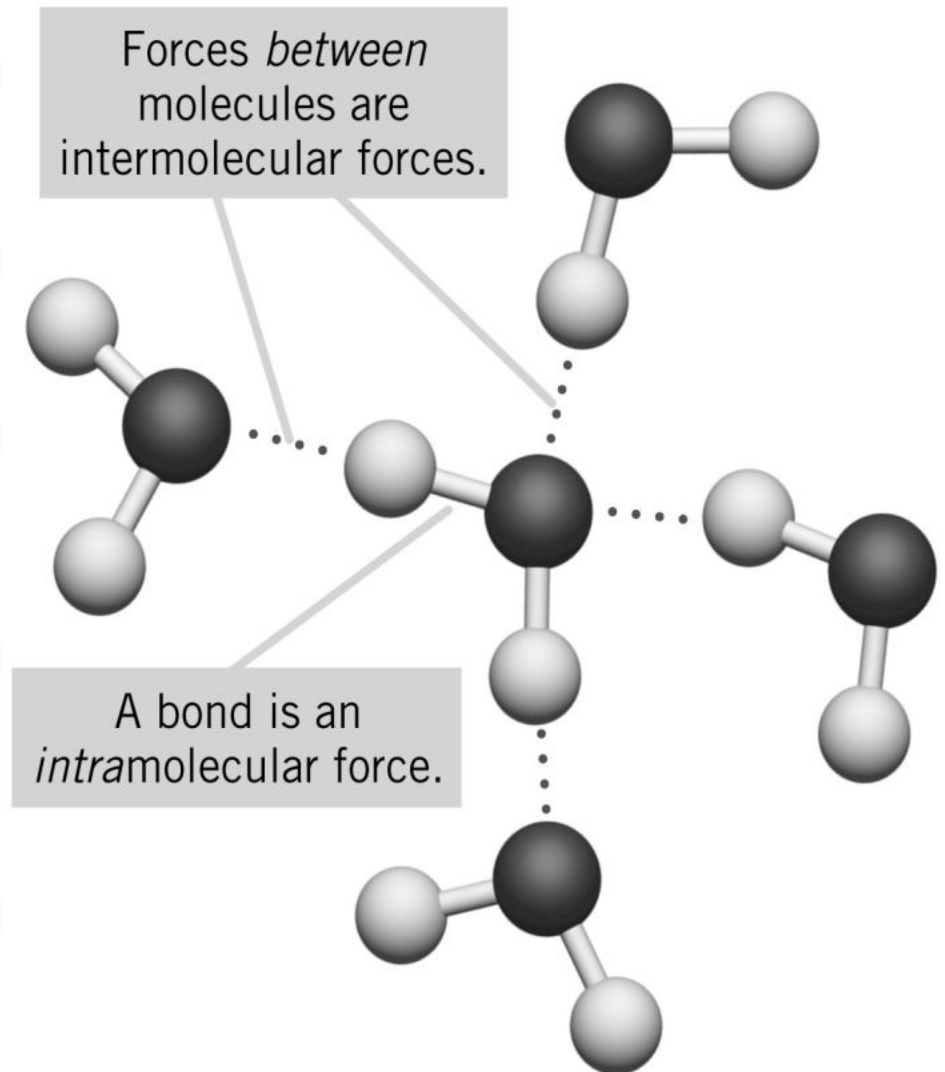


Professor K

Intermolecular forces

Inter vs. intra

- We've studied chemical bonds which are INTRAmolecular forces...
- We now explore the forces between molecules, or INTERmolecular forces which you might rightly assume to be weaker since they are over longer distances

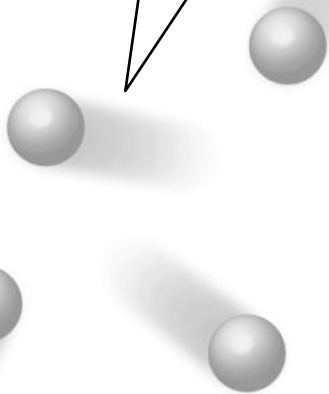


Inter vs. intra (cont'd)

- We did discuss the ideal gas law earlier, but what MAKES something a gas?
- Space between molecules determines state, but what determines the spacing?
- Intramolecular forces (bonds) govern molecular properties such as molecular shape/geometry around atoms and dipole moments.
- Intermolecular forces determine the macroscopic physical properties of liquids and solids such as melting points, freezing points, and other physical properties.

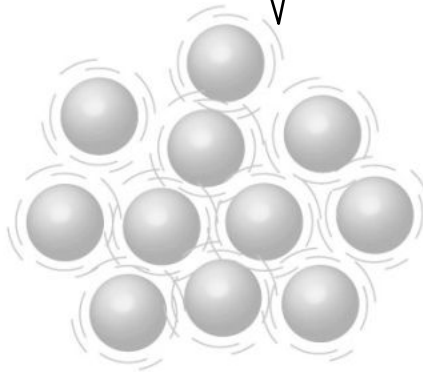
States of matter compared

Intermolecular forces are of little significance; why?



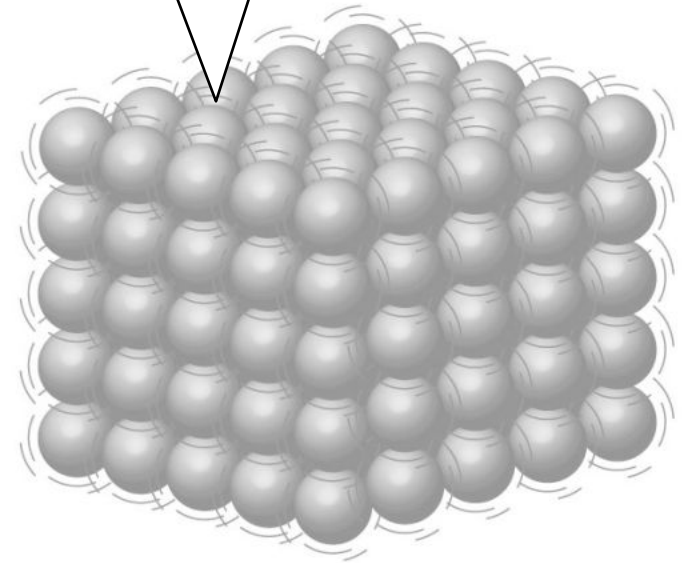
Gas

Intermolecular forces must be considered.



Liquid

Intermolecular forces are very important.



Solid

Vaporization

- Going from a liquid to a gas
- Requires energy (endothermic- ΔH_{vap} is a POSITIVE number since energy is being supplied to the system FROM the surroundings)
- Reverse is condensation, which gives off energy (exothermic- ΔH_{cond} is a NEGATIVE number since energy is coming OUT of the system into the surroundings)
- Enthalpy is a function of state: therefore, if a liquid is vaporized and the vapor condensed at constant temperature, the total ΔH must be zero:

$$\Delta H_{\text{vap}} + \Delta H_{\text{cond}} = 0$$

$$\Delta H_{\text{cond}} = -\Delta H_{\text{vap}}$$

- The vaporization-condensation cycle is the basis of refrigeration and air conditioning
- The study of energy changes involved in this phenomenon is called calorimetry

Table 11.1 Some Enthalpies (Heats) of Vaporization at 298 K^a

Liquid	ΔH_{vapn}, kJ/mol
Carbon disulfide, CS ₂	27.4
Carbon tetrachloride, CCl ₄	37.0
Methanol, CH ₃ OH	38.0
Octane, C ₈ H ₁₈	41.5
Ethanol, CH ₃ CH ₂ OH	43.3
Water, H ₂ O	44.0
Aniline, C ₆ H ₅ NH ₂	52.3

^a ΔH_{vapn} values are somewhat temperature-dependent.

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Example

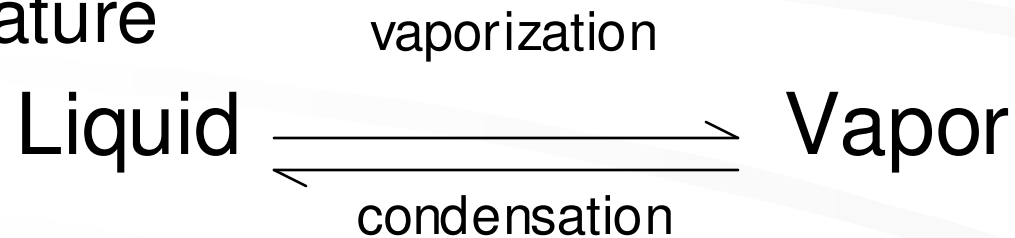
How much heat, in kilojoules, is required to vaporize 175 g methanol, CH_3OH , at 25 °C?

Example An Estimation Example

Without doing detailed calculations, determine which liquid in Table 11.1 requires the greatest quantity of heat for the vaporization of 1 kg of liquid.

Vaporization (cont'd)

- Vapor pressure- the partial pressure exerted by the vapor when it is in DYNAMIC EQUILIBRIUM with a liquid at constant temperature



- BOILING point- occurs when vapor pressure = atmospheric pressure

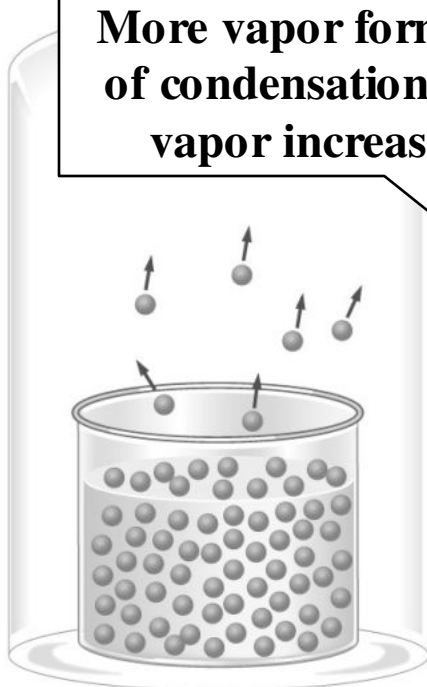
Liquid-vapor equilibrium

↑ Molecules undergoing vaporization

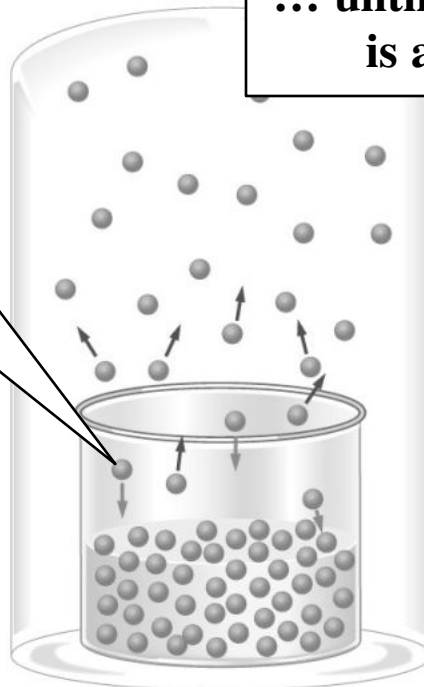
↓ Molecules undergoing condensation

More vapor forms; rate of condensation of that vapor increases ...

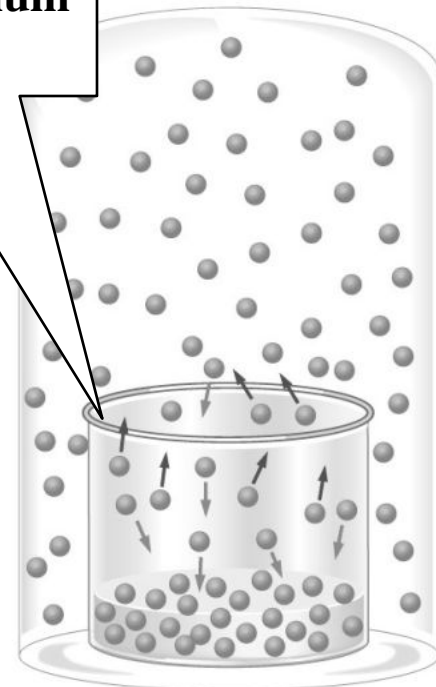
... until equilibrium is attained.



(a) Vaporization



(b) Vaporization rate > condensation rate



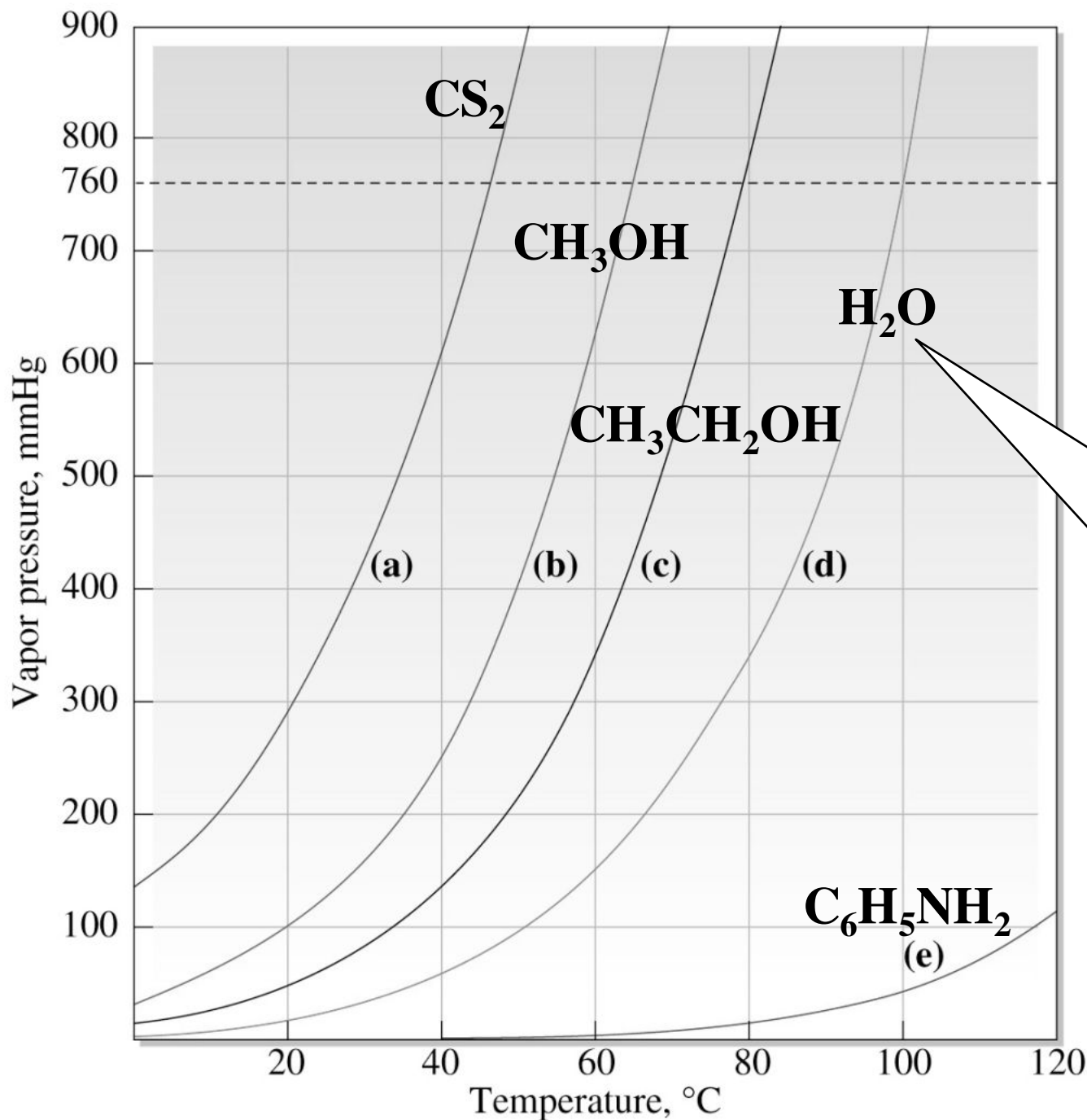
(c) Vaporization rate = condensation rate

Table 11.2 Vapor Pressure of Water at Various Temperatures

Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg	Temperature, °C	Pressure, mmHg
0.0	4.6	29.0	30.0	93.0	588.6
10.0	9.2	30.0	31.8	94.0	610.9
20.0	17.5	40.0	55.3	95.0	633.9
21.0	18.7	50.0	92.5	96.0	657.6
22.0	19.8	60.0	149.4	97.0	682.1
23.0	21.1	70.0	233.7	98.0	707.3
24.0	22.4	80.0	355.1	99.0	733.2
25.0	23.8	90.0	525.8	100.0	760.0
26.0	25.2	91.0	546.0	110.0	1074.6
27.0	26.7	92.0	567.0	120.0	1489.1
28.0	28.3				

Vapor pressure increases with temperature; why?

Vapor pressure curves



What is the vapor pressure of H₂O at 100 °C, according to this graph? What is the significance of that numeric value of vapor pressure?

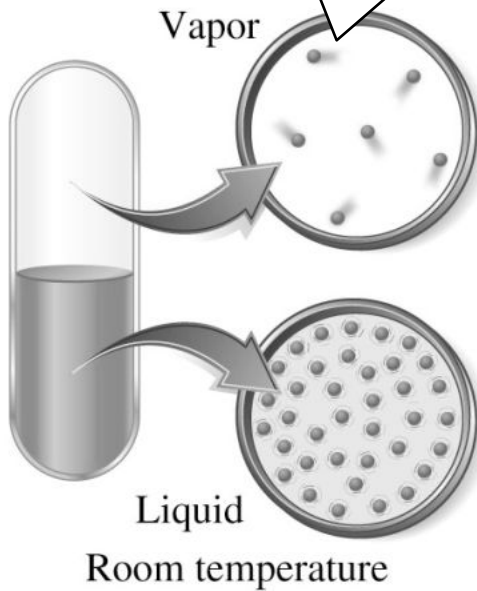
Which of the five compounds has the *strongest* intermolecular forces? How can you tell?

Boiling point and critical point

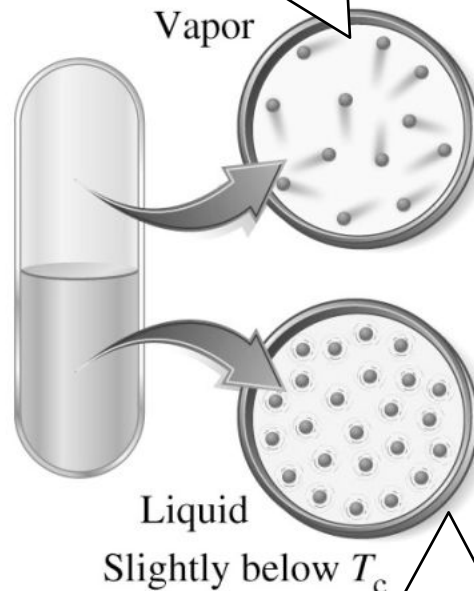
- ***Boiling point***: the temperature at which the vapor pressure of the liquid equals the external (atmospheric) pressure.
- ***Normal boiling point***: boiling point at 1 atm.
- ***Critical temperature*** (T_c): the highest temperature at which a liquid can exist.
- The ***critical pressure***, P_c , is the vapor pressure at the critical temperature.
- The condition corresponding to a temperature of T_c and a pressure of P_c is called the ***critical point***.

The critical point

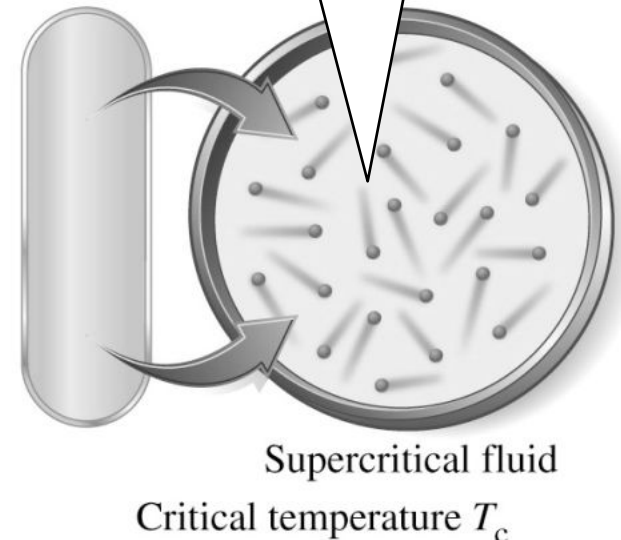
At room temperature there is relatively little vapor, and its density is low.



At higher temperature, there is more vapor, and its density increases ...



At T_c , the densities of liquid and vapor are equal; a single phase.



... while the density of the liquid *decreases*; molecular motion increases.

Table 11.3 Critical Temperature and Pressure of Various Substances

	T_c , K	P_c , atm
H ₂	33.0	12.8
N ₂	126.3	33.5
O ₂	154.8	50.1
CH ₄	190.6	45.4
CO ₂	304.2	72.9
C ₂ H ₆	305.4	48.2
HCl	324.6	81.5
C ₃ H ₈	369.8	41.9
NH ₃	405.6	111.3
SO ₂	430.6	77.9
H ₂ O	647.3	218.3

These four gases can't be liquefied at room temperature, no matter what pressure is applied; why not?

Phase changes

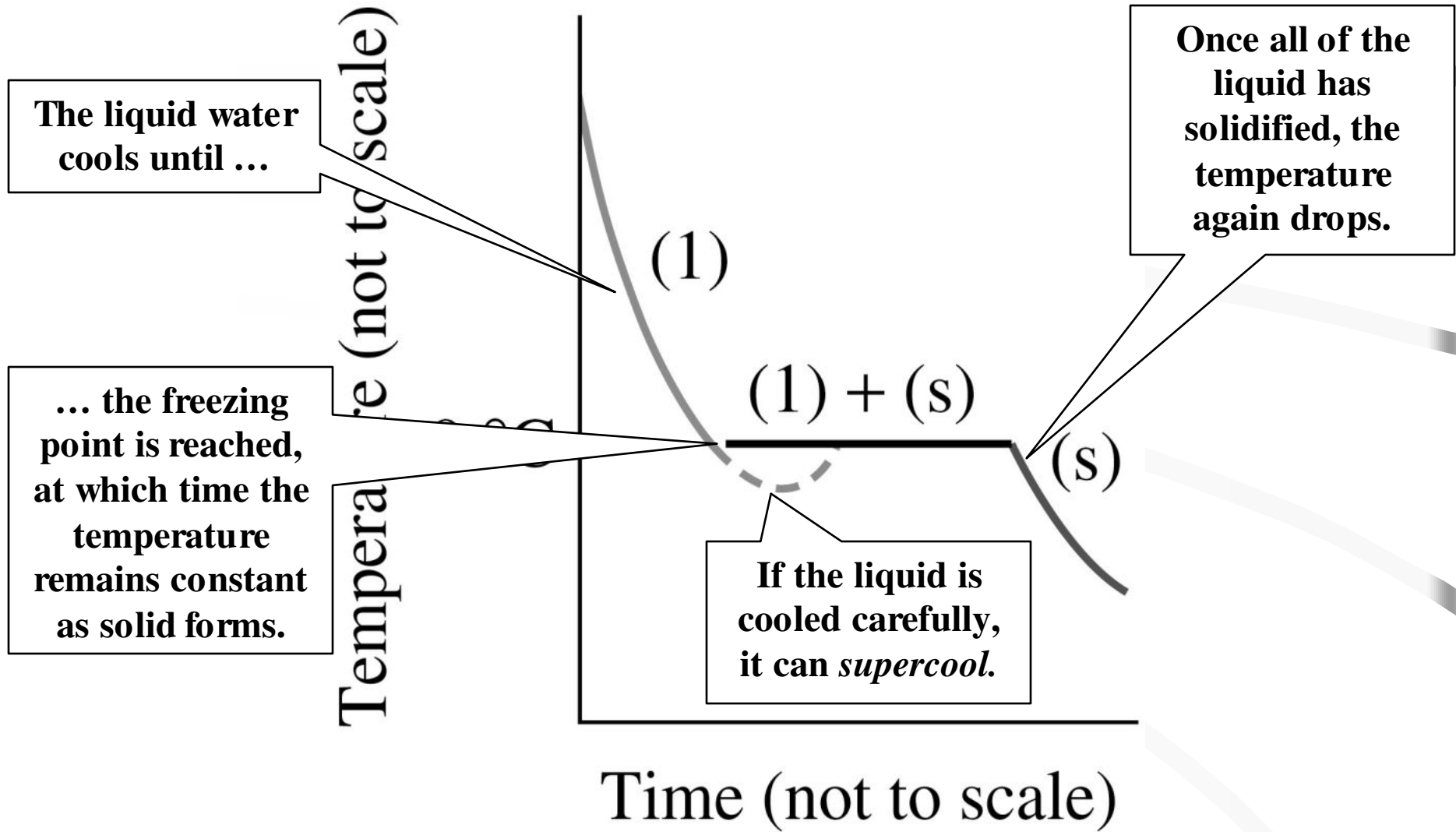
- **FUSION** is the reverse of **MELTING** which is the transition of a solid to a liquid, as you know
- *Melting point* and *freezing point* are the same temperature, just different direction (warming or cooling)
- **Enthalpy of fusion**, ΔH_{fus} , is the quantity of heat required to melt a set amount (one gram, one mole) of solid.
- *Sublimation*- going directly from solid to gas
- Examples? (should know 3 for SAT II)
- Remember the Jack Black/Ben Stiller movie *Envy*?
- **Enthalpy of sublimation**, ΔH_{sub} , is the sum of the enthalpies of fusion and vaporization.
- **TRIPLE POINT**: all three phases—solid, liquid, vapor—are in equilibrium.

Some enthalpies of fusion

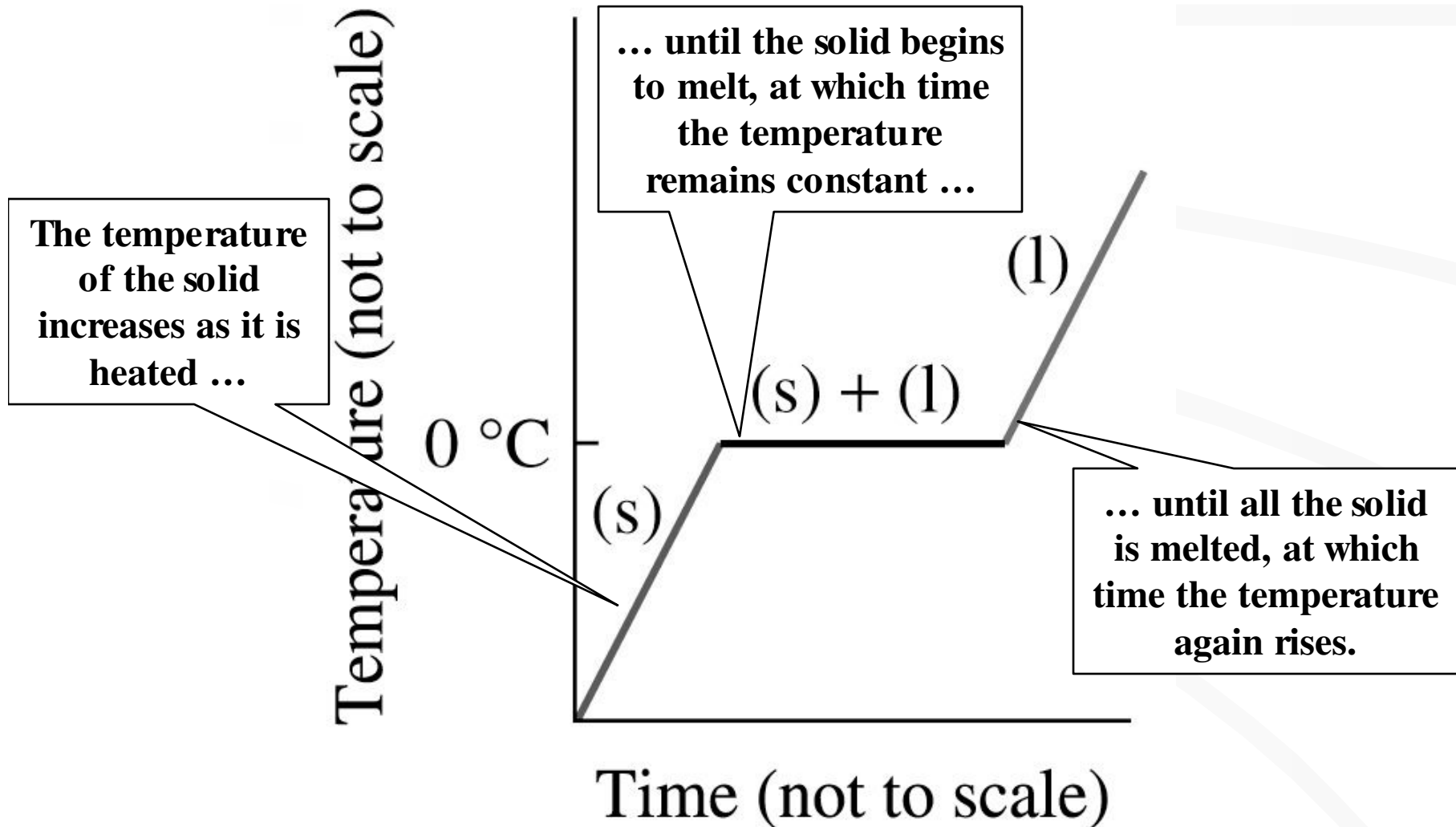
Table 11.4 Some Enthalpies (Heats) of Fusion

Substance	Melting Point, °C	ΔH_{fusion}, kJ/mol
Mercury, Hg	-38.9	2.30
Ethanol, CH ₃ CH ₂ OH	-114	5.01
Water, H ₂ O	0.0	6.01
Benzene, C ₆ H ₆	5.5	9.87
Silver, Ag	960.2	11.95
Iron, Fe	1537	15.19

Cooling curve for water

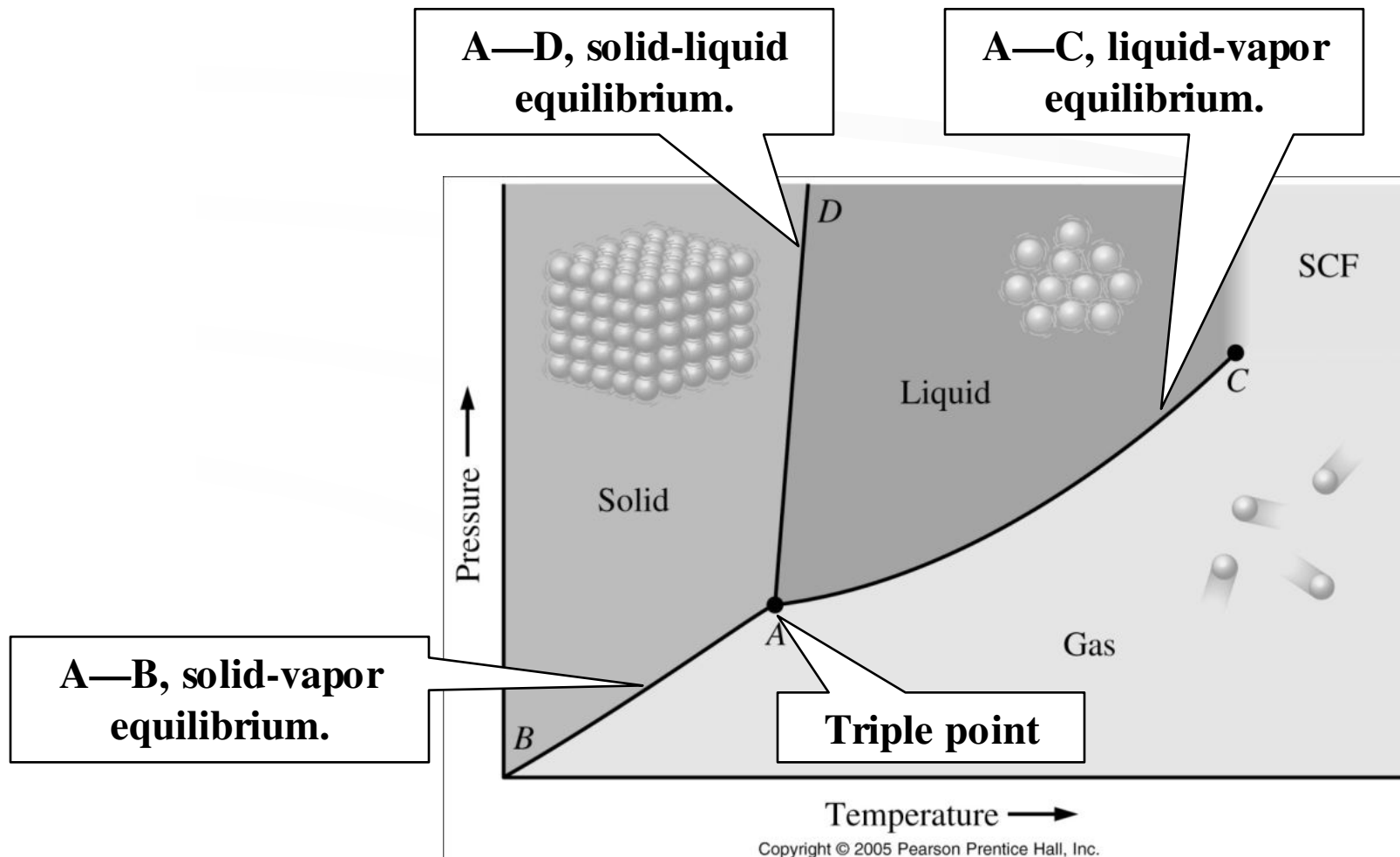


Heating curve for water

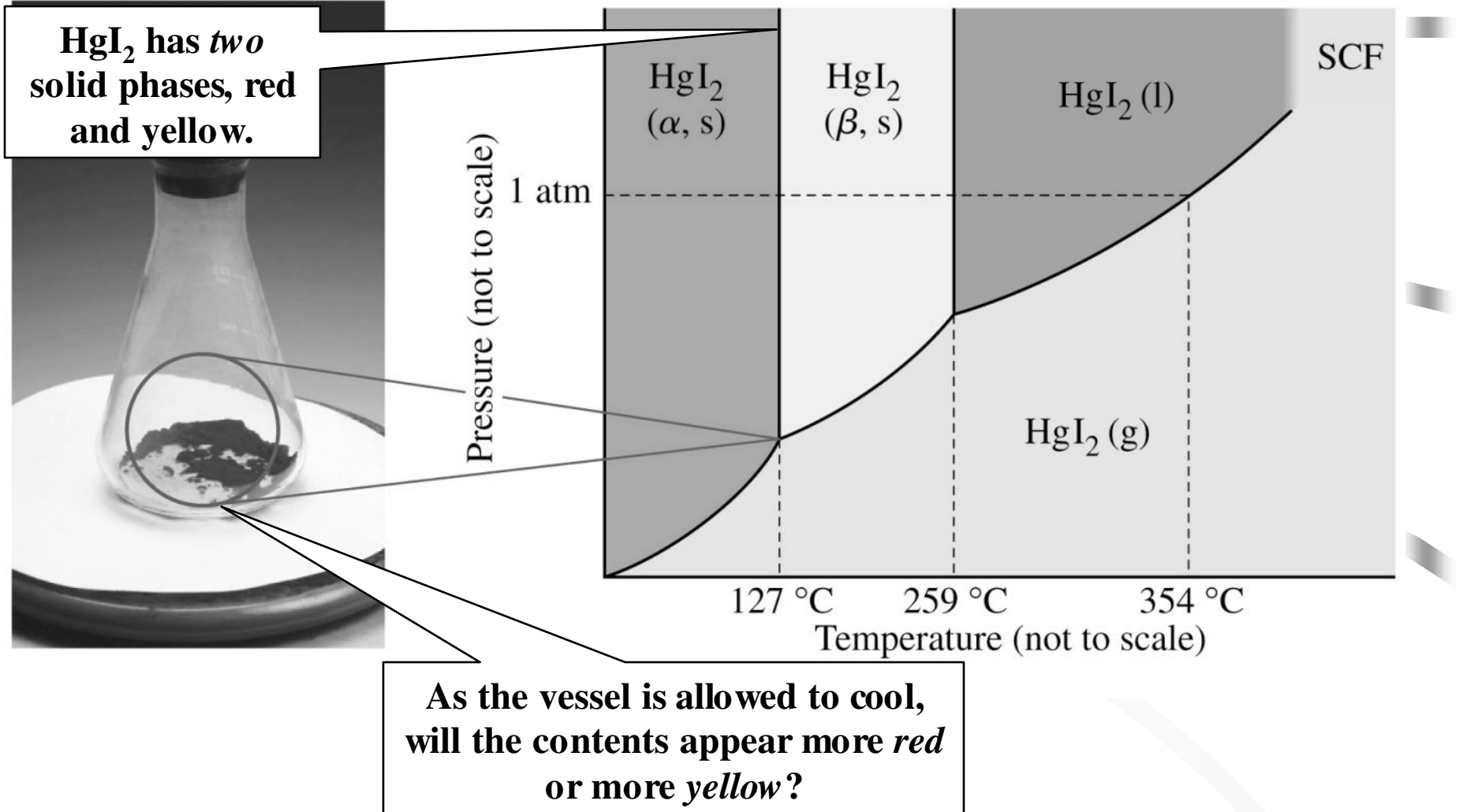


Phase diagram

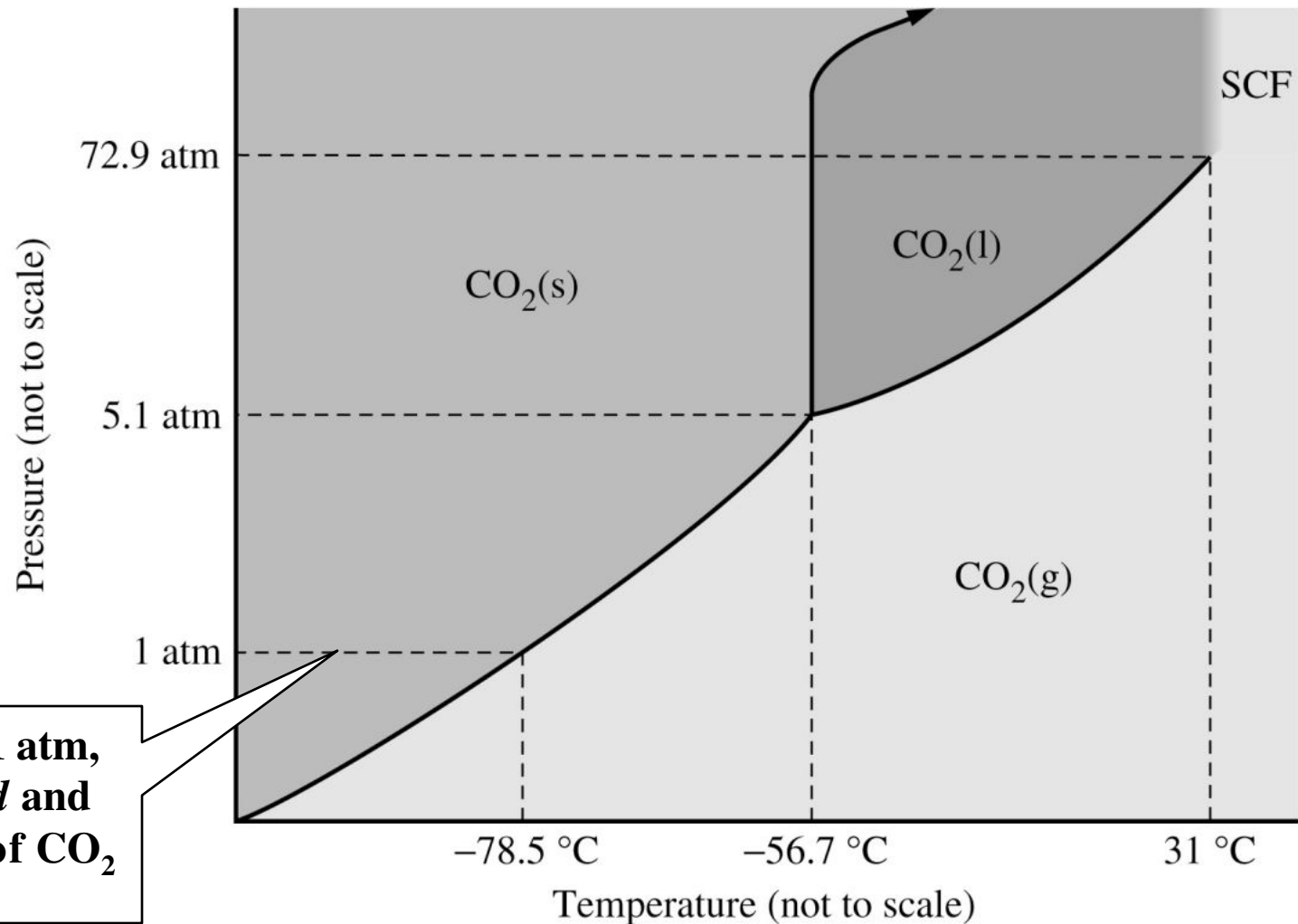
- Shows phases of a substance at various temperatures and pressures
- Polymorphs can exist in more than one form per phase (examples??)



Phase diagram for HgI_2

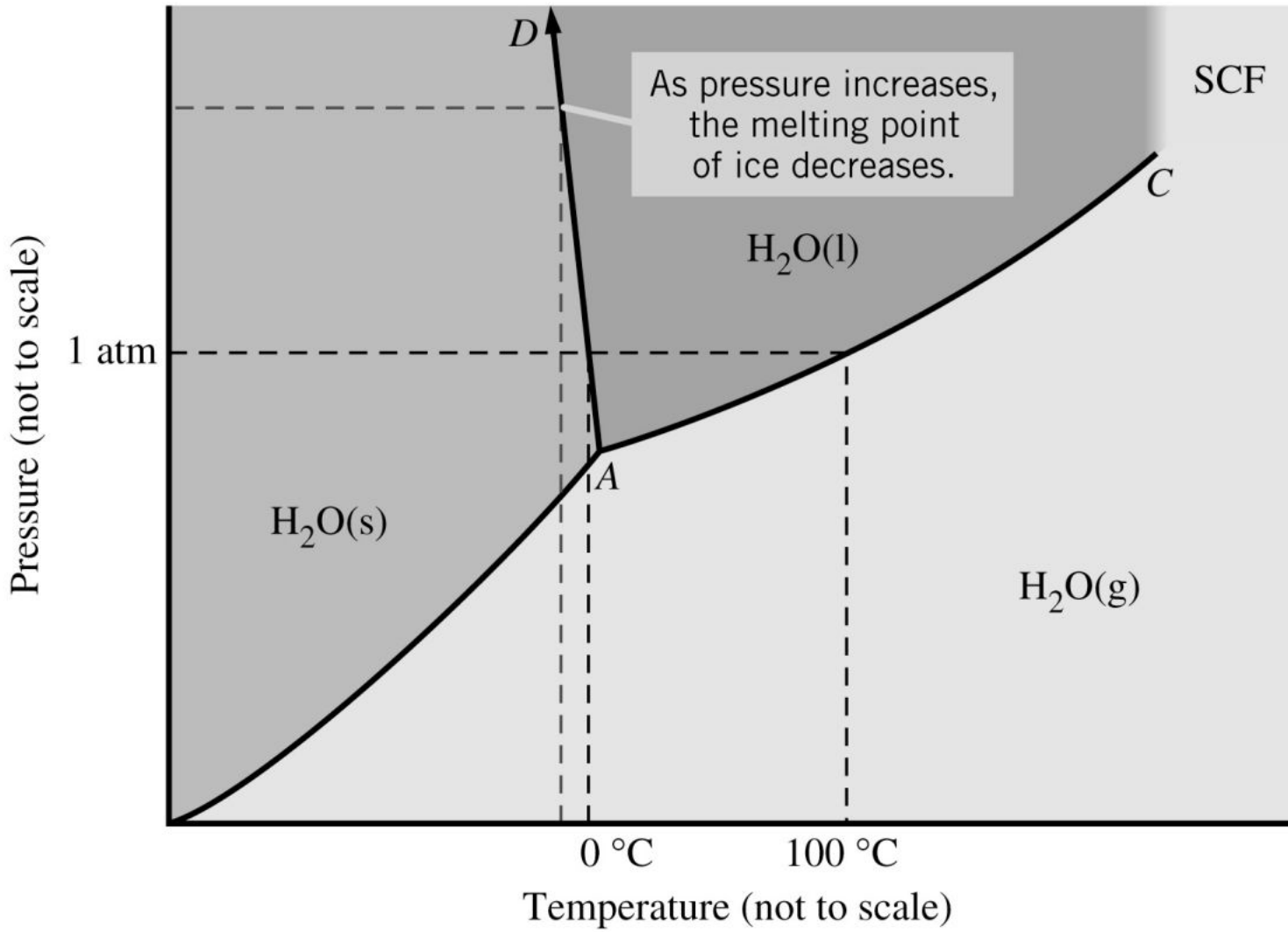


Phase diagram for CO₂



Note that at 1 atm, only the *solid* and *vapor* phases of CO₂ exist.

Phase diagram for H₂O



Van der Waals forces

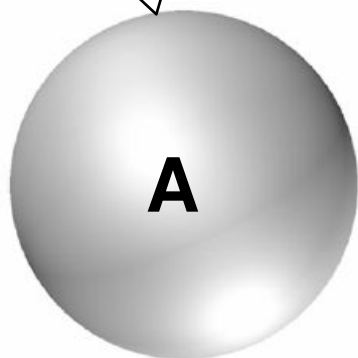
- Due to polarizability of electron clouds
- Dispersion forces (induced dipole-induced dipole forces)
- Dipole-dipole forces
- Ion-dipole forces

Dispersion forces

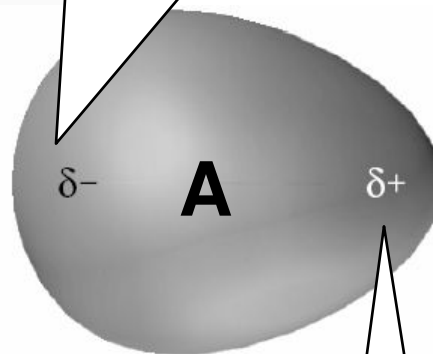
- ... exist between any two particles.
- Also called *London* forces (after Fritz London, who offered a theoretical explanation of these forces in 1928).
- Dispersion forces arise because the electron cloud is not perfectly uniform.
- Tiny, momentary dipole moments can exist even in nonpolar molecules.
- aka “induced dipole-induced dipole” interactions

Dispersion forces illustrated

At a given instant, electron density, even in a nonpolar molecule like this one, is not perfectly uniform.



The region of (momentary) higher electron density attains a small (-) charge ...

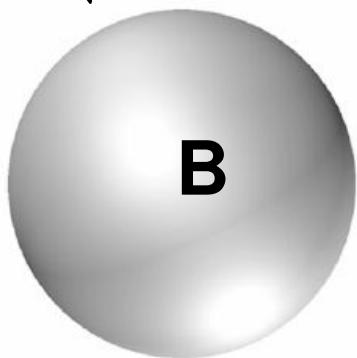


... the other end of the molecule is slightly (+).

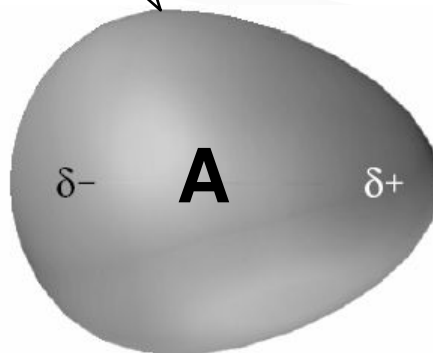
Dispersion forces illustrated

(cont'd)

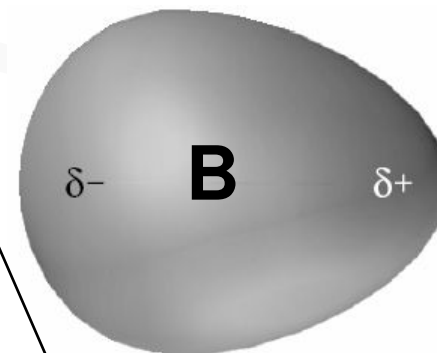
When another
nonpolar molecule
approaches ...



... molecule A
induces a tiny
dipole moment ...



... in
molecule B.



Opposite charges _____.

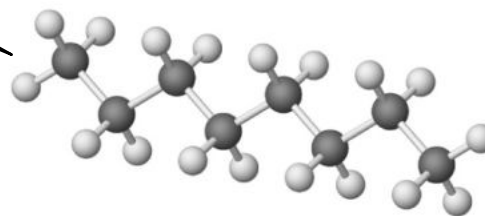
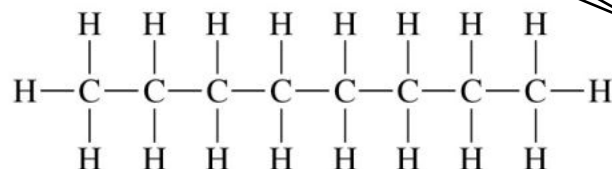
Strength of dispersion forces

- Dispersion force strength depends on ***polarizability***: the ease with which the electron cloud is distorted by an external electrical field.
- The *greater* the polarizability of molecules, the *stronger* the dispersion forces between them.
- Polarizability in turn depends on molecular size and shape.
- Heavier molecule => more electrons => a more- polarizable molecule.
- As to molecular shape ...

Molecular shape and polarizability

... higher boiling point.

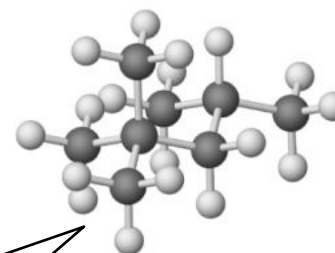
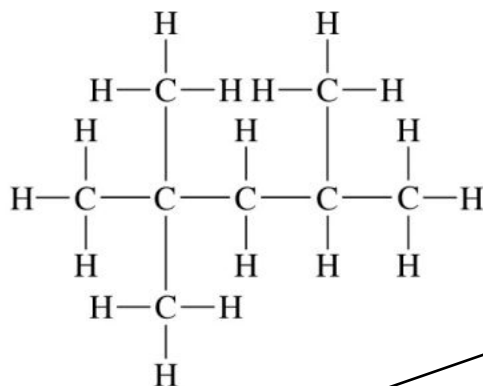
(a) Octane
 $\text{CH}_3(\text{CH}_2)_6\text{CH}_3$
melting point $-56.8\text{ }^\circ\text{C}$
boiling point $125.7\text{ }^\circ\text{C}$



Long skinny molecule ...

... can have greater separation of charge along its length. Stronger forces of attraction, meaning ...

(b) (Isooctane)
2,2,4-Trimethylpentane
 $\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}(\text{CH}_3)_2$
melting point $-104.7\text{ }^\circ\text{C}$
boiling point $99.2\text{ }^\circ\text{C}$



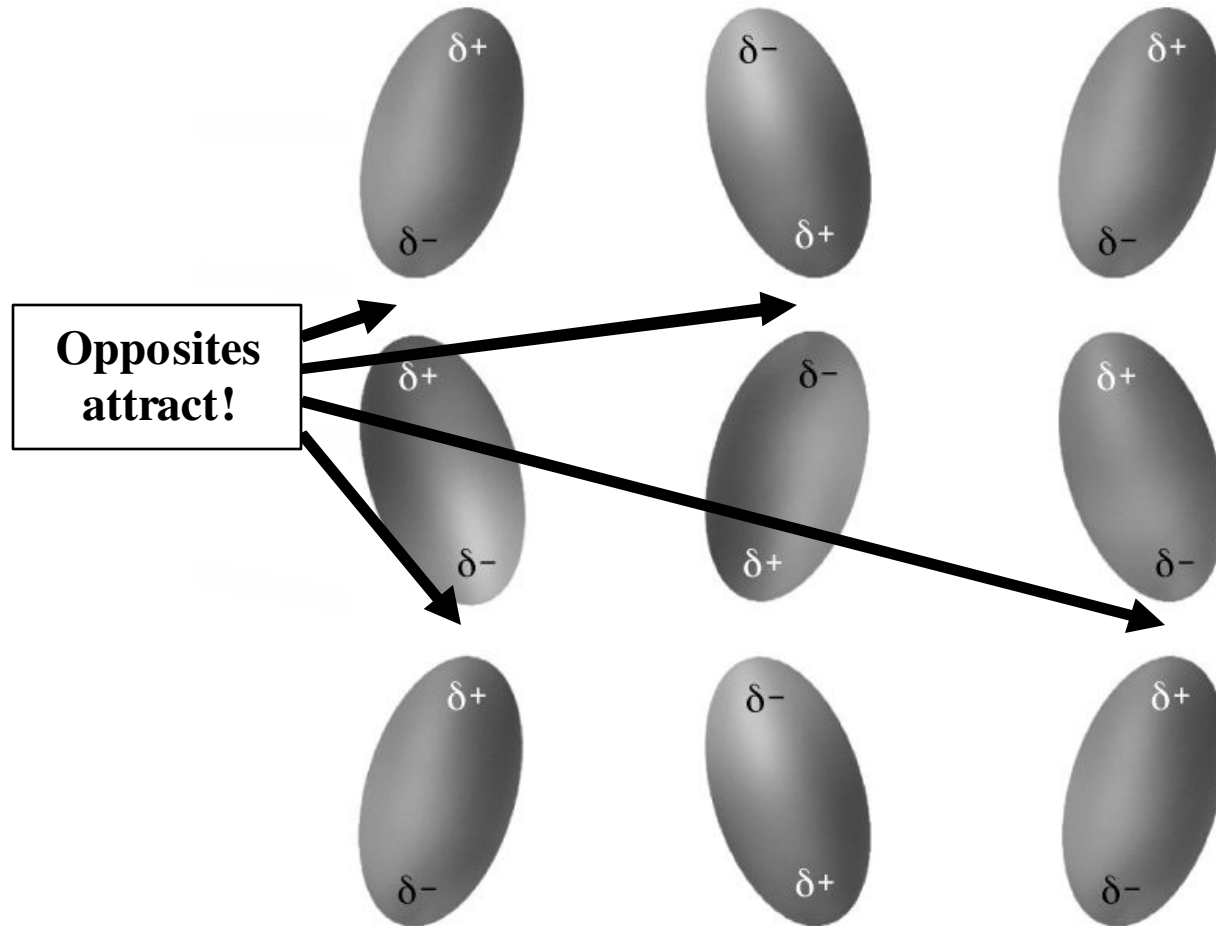
... giving weaker dispersion forces and a lower boiling point.

In the compact isomer, less possible separation of charge ...

Dipole–dipole forces

- A polar molecule has a positively charged “end” ($\delta+$) and a negatively charged “end” ($\delta-$).
- When molecules come close to one another, repulsions occur between like-charged regions of dipoles. Opposite charges tend to attract one another.
- The more polar a molecule, the more pronounced is the effect of dipole–dipole forces on physical properties.

Dipole–dipole interactions



Predicting physical properties of molecular substances

- Intermolecular forces become stronger with increasing molar mass and elongation of molecules. In comparing nonpolar substances, molar mass and molecular shape are the *essential* factors.
- Dipole–dipole and dipole-induced dipole forces are found in polar substances. The more polar the substance, the greater the intermolecular force is expected to be.
- Because they occur in *all* substances, dispersion forces must always be considered. Often they dominate.

Example

Arrange the following substances in the expected order of increasing boiling point: carbon tetrabromide, CBr_4 ; butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$; fluorine, F_2 ; acetaldehyde, CH_3CHO .

Hydrogen bonds

- A **hydrogen “bond”** is an intermolecular force in which:
 - a hydrogen atom that is covalently bonded to a (small, electronegative) nonmetal atom (generally N, O, F) in one molecule ...
 - is simultaneously attracted to a (small, electronegative) nonmetal atom of a neighboring molecule (generally lone pairs of N, O, F).

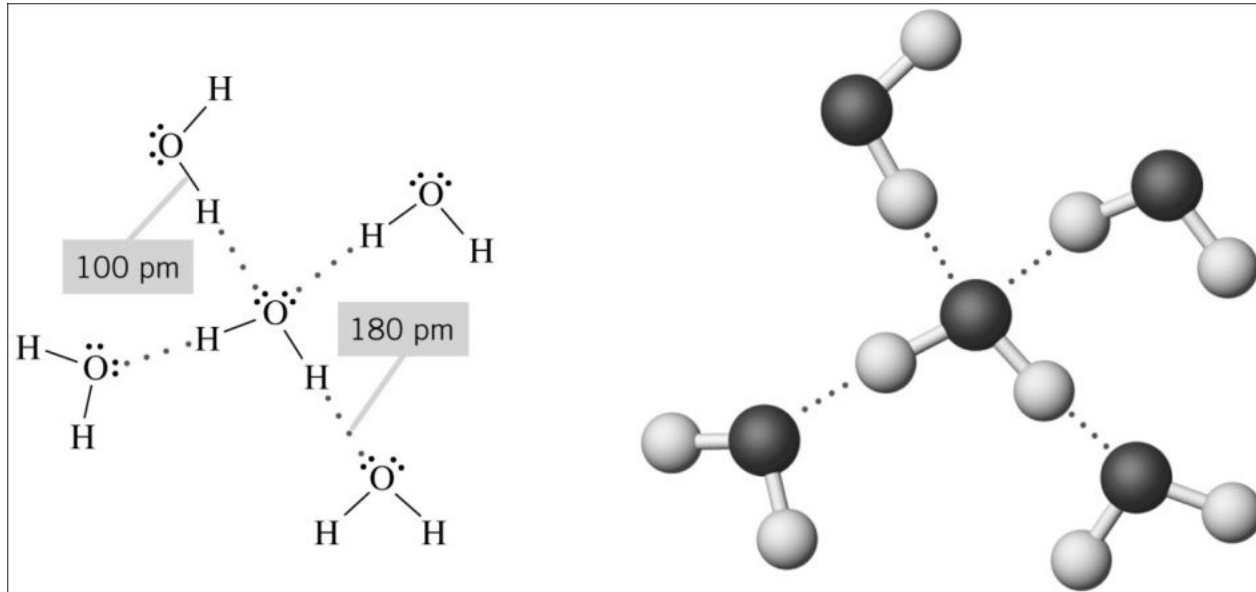


When Y and Z are small and highly electronegative (N, O, F) ...

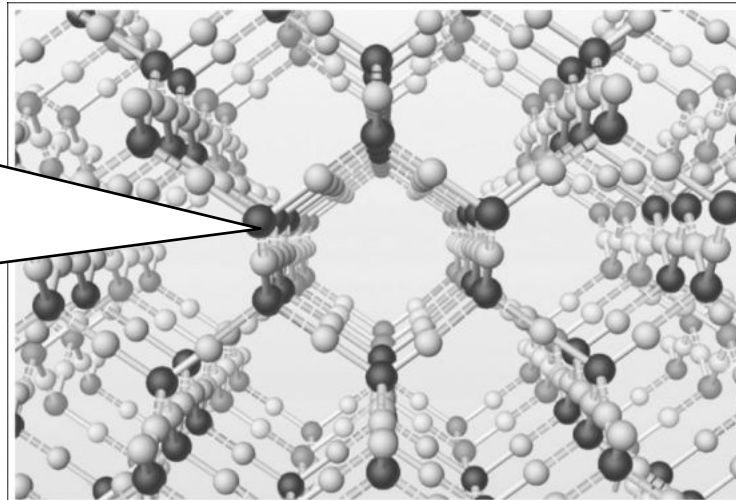
... this force is called a **hydrogen bond**; a special, **strong** type of dipole-dipole force.

Hydrogen bonds in water

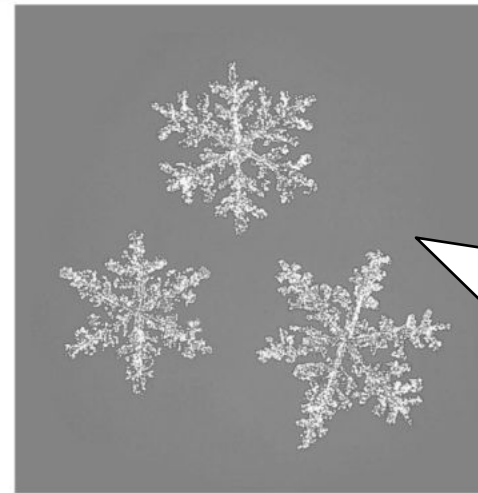
- Why does ice float?



Hydrogen bonding arranges the water molecules into an open hexagonal pattern.



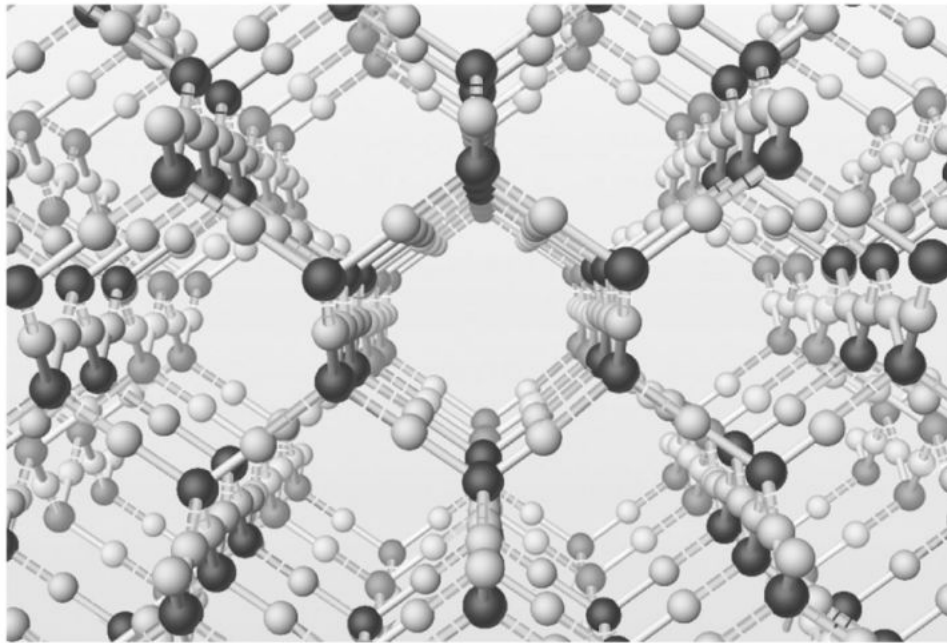
(a)



(b)

“Hexagonal” is reflected in the crystal structure. “Open” means reduced density of the solid (vs. liquid).

Hydrogen bonding in ice



(a)



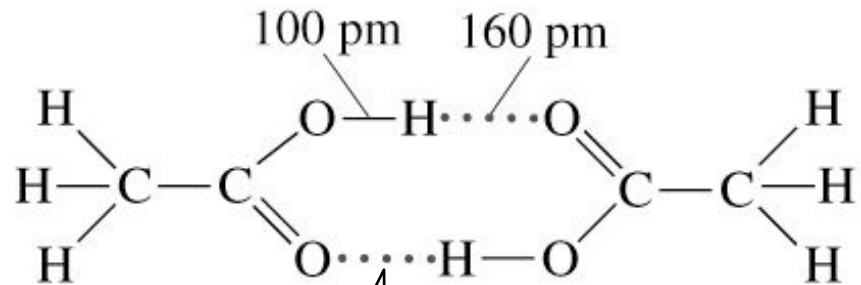
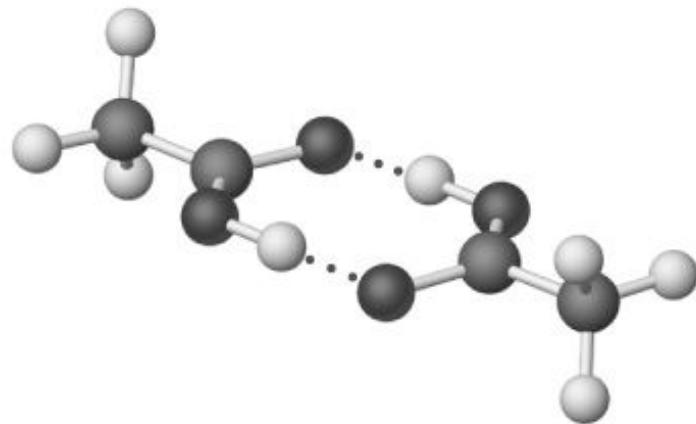
(b)

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Hydrogen bonding arranges the water molecules into an open hexagonal pattern.

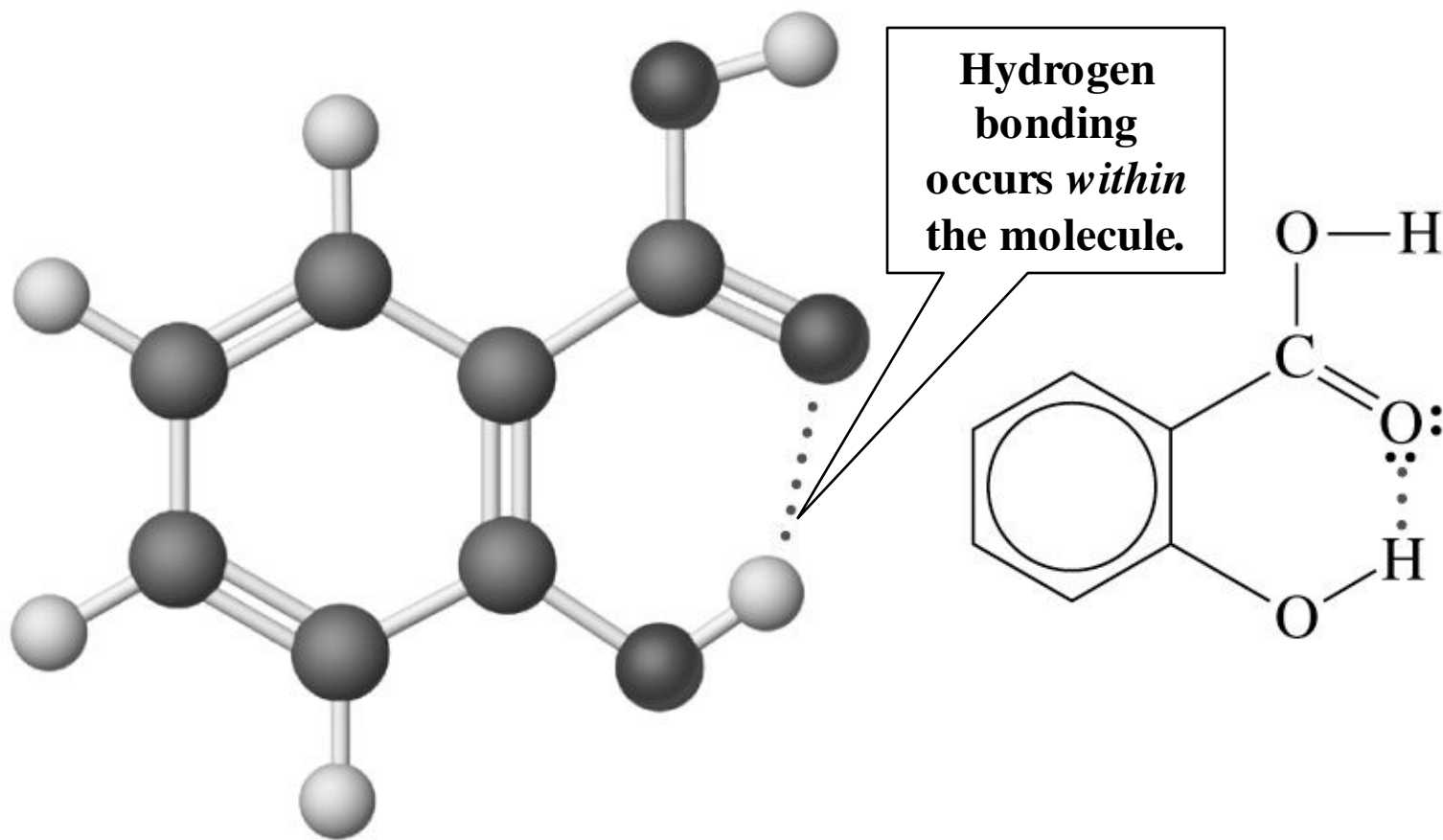
“Hexagonal” is reflected in the crystal structure. “Open” means reduced density of the solid (vs. liquid).

Hydrogen bonding in acetic acid



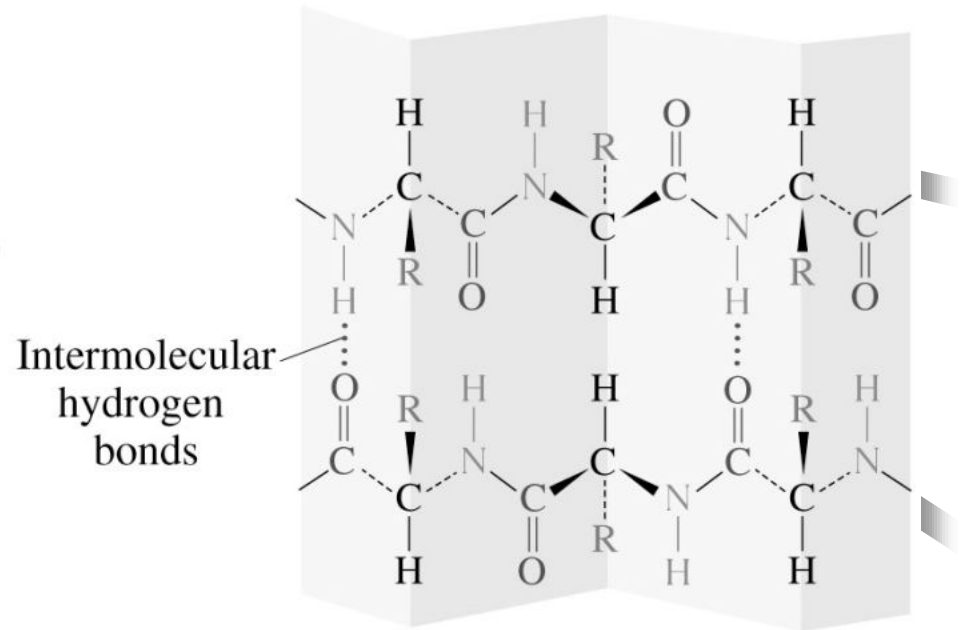
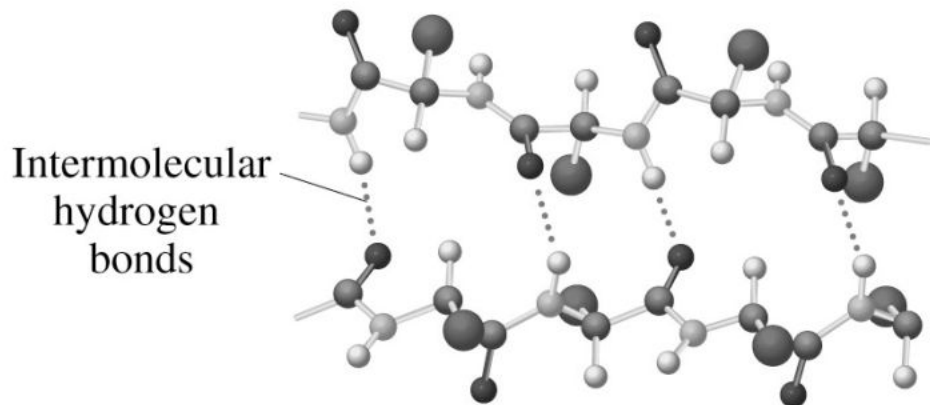
**Hydrogen bonding
occurs *between*
molecules.**

Hydrogen bonding in salicylic acid (aka?)



Intermolecular hydrogen bonds

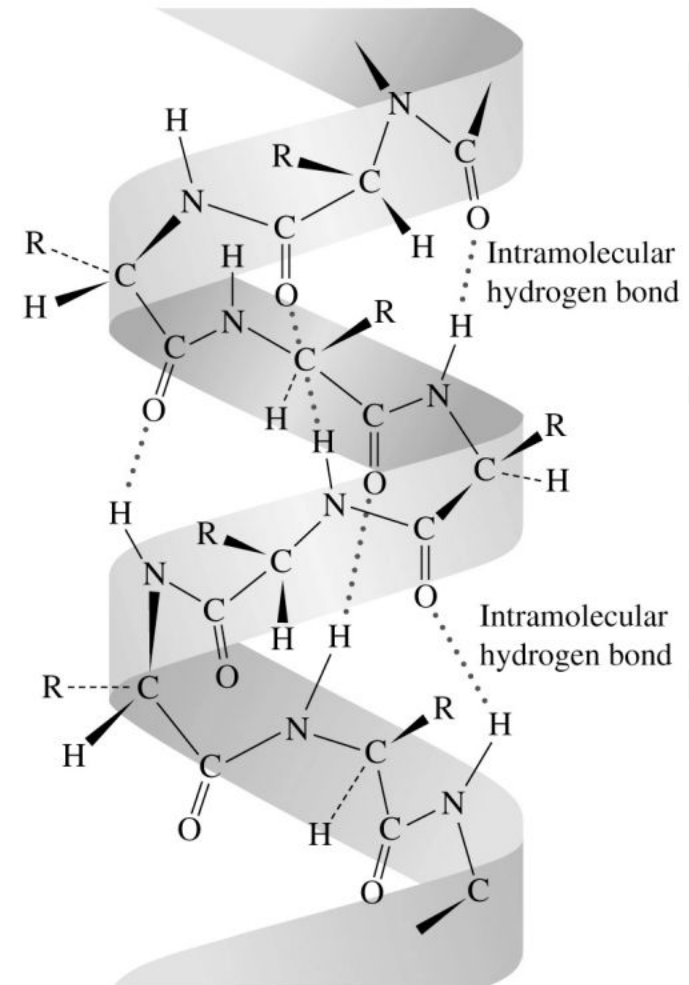
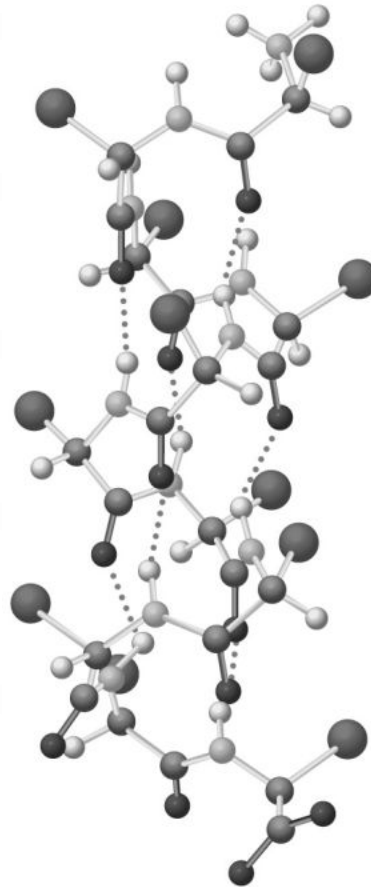
- Can you think of other examples?



Intermolecular hydrogen bonds give proteins their secondary shape, forcing the protein molecules into particular orientations, like a folded sheet ...

Intramolecular H-bonds (cont'd)

... while intramolecular hydrogen bonds can cause proteins to take a helical shape.



(b)

Example

In which of these substances is hydrogen bonding an important intermolecular force: N_2 , HI , HF , CH_3CHO , and CH_3OH ? Explain.

Homology

- A series of compounds whose formulas and structures vary in a regular manner also have ***properties*** that vary in a predictable manner.
- This principle is called ***homology***.
- Example: both densities and boiling points of the straight-chain alkanes increase in a continuous and regular fashion with increasing numbers of carbon atoms in the chain... a homologous series.
- Trends result from the regular increase in molar mass, which produces a fairly regular increase in the strength of dispersion forces.
- Different from an element which can exist in more than one basic structure known as an *allotrope*.

An Estimation Example

The boiling points of the straight-chain alkanes pentane, hexane, heptane, and octane are 36.1, 68.7, 98.4, and 125.7 °C, respectively. Estimate the boiling point of the straight-chain alkane decane.

Liquid crystals

- The thrust of your instructor's thesis
- Not quite solid, not quite liquid....a true 5th phase of matter

Crystals

- A solid substance with a regular shape and plane surfaces with sharp edges that intersect at fixed angles.
- Made up of a small number of atoms, ions, or molecules in a repeating unit.
- The repeating unit in the *crystal lattice* is the *formula unit*.

Other stuff

- Surface tension (this is how Rain-X[©] works)- OMIT
- Viscosity- OMIT
- Network covalent solids- example: C₆₀ which is another allotrope of carbon
- Ionic bonds- just common sense- strength of interaction increases as charges increase and distance decreases- OMIT
- Crystals- OMIT