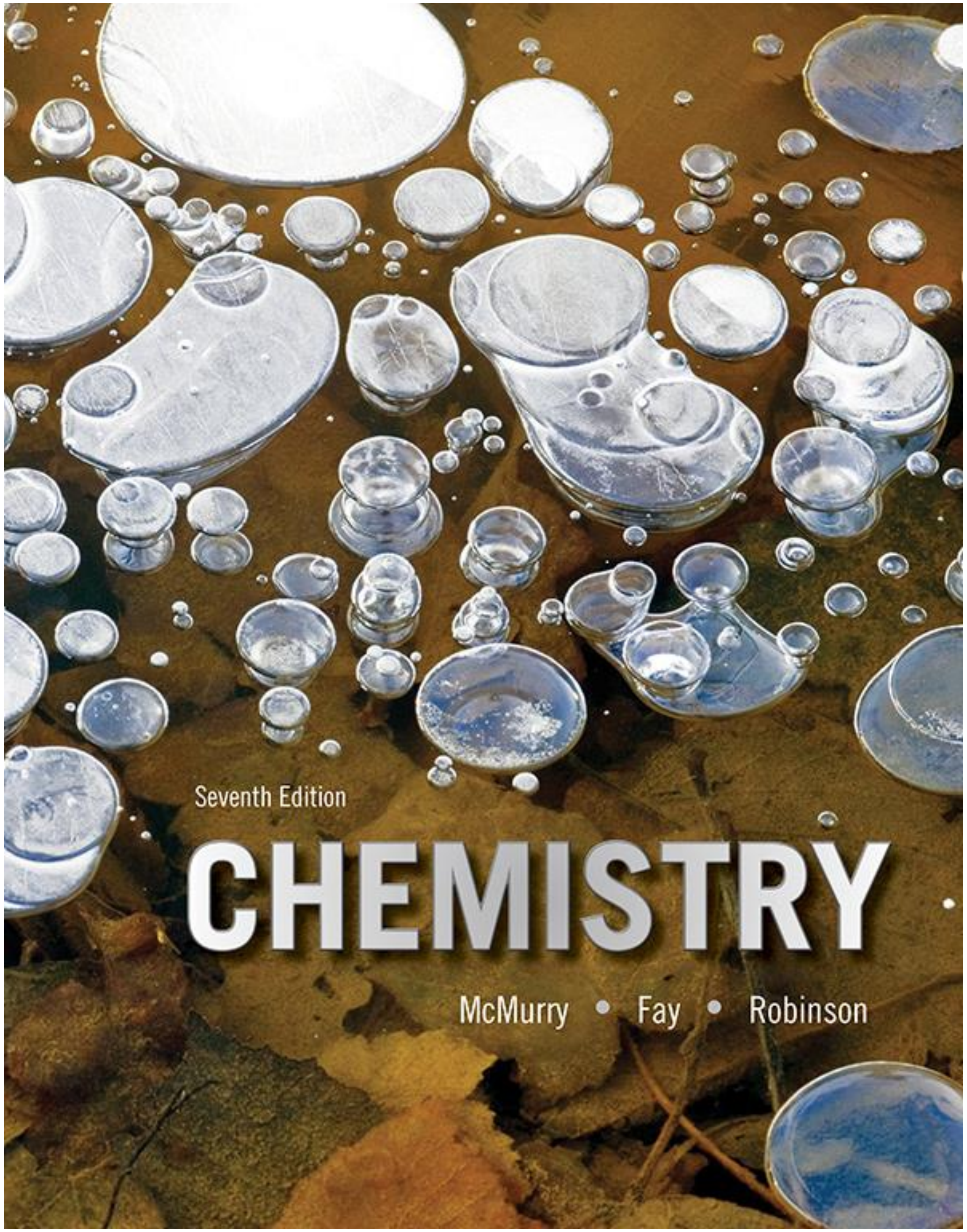


Lecture Presentation

Chapter 11
Liquids, Solids, and Phase Changes

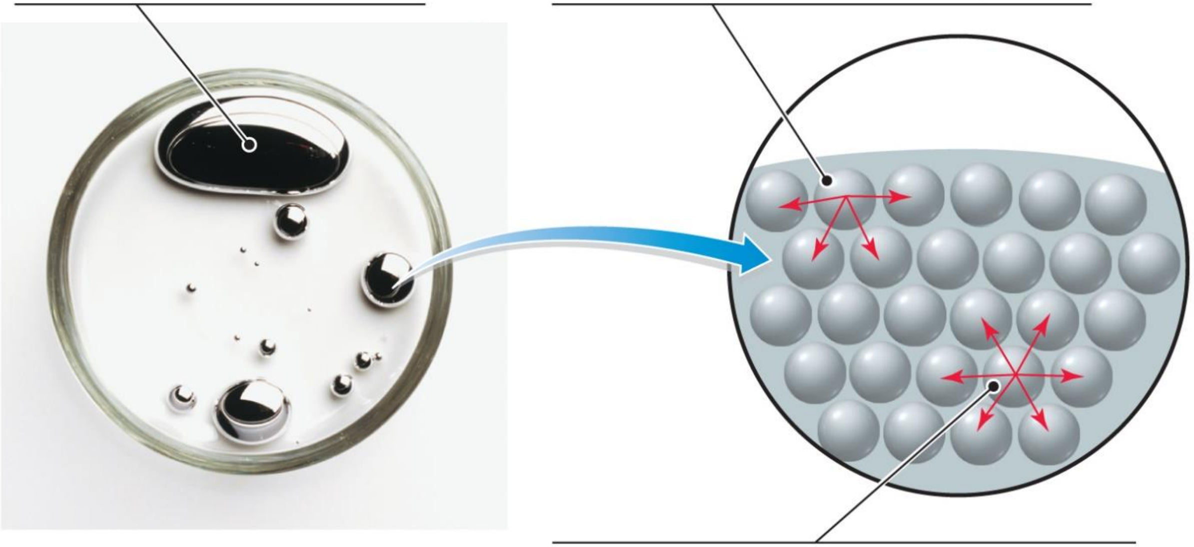
11.1, 11.2, 11.3, 11.4, 11.15, 11.17, 11.26, 11.30, 11.32, 11.40, 11.42, 11.60, 11.82, 11.116

John E. McMurry
Robert C. Fay

Properties of Liquids

Viscosity: The measure of a liquid’s resistance to flow (higher intermolecular force, higher viscosity)

Surface Tension: The resistance of a liquid to spread out and increase its surface area (forms beads) (higher intermolecular force, higher surface tension)



Surface tension causes these drops of liquid mercury to form beads.

Molecules or atoms on the **surface** feel attractive forces on only one side and are thus drawn in toward the liquid.

Molecules or atoms in the **middle** of a liquid are attracted equally in all directions.

Properties of Liquids

low intermolecular force –
low viscosity, low surface tension

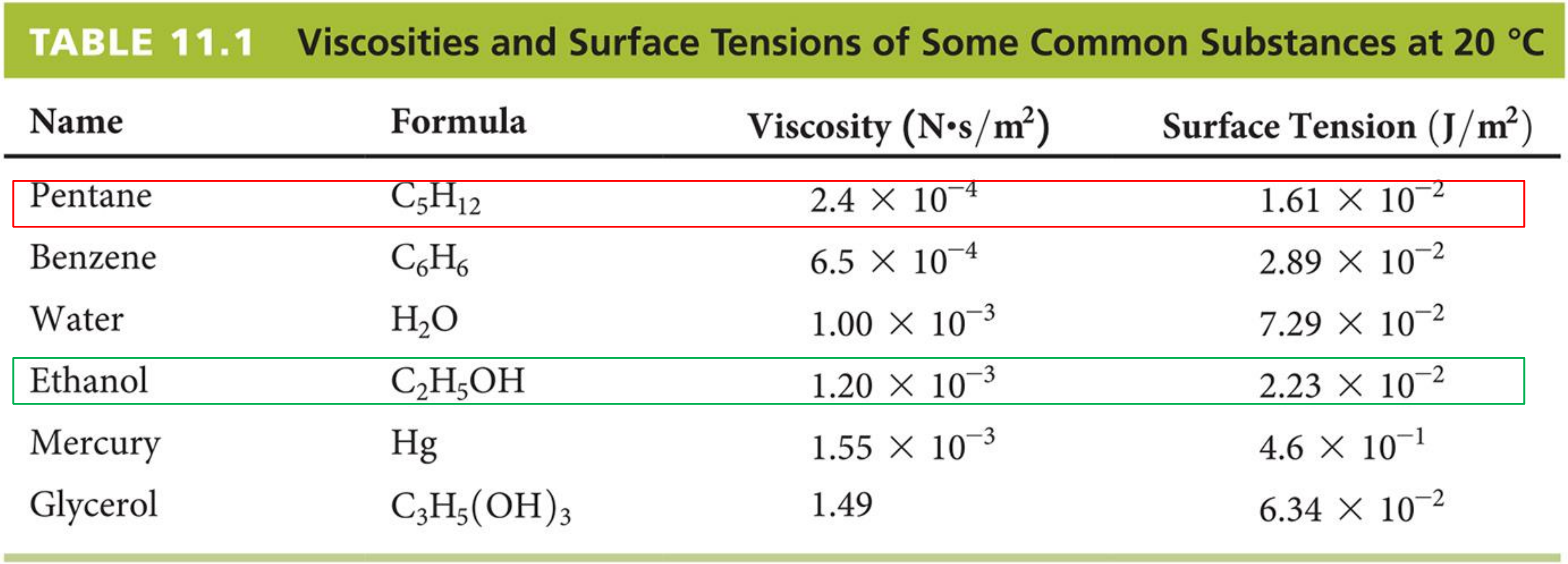


TABLE 11.1 Viscosities and Surface Tensions of Some Common Substances at 20 °C

Name	Formula	Viscosity (N•s/m^2)	Surface Tension (J/m^2)
Pentane	C_5H_{12}	2.4×10^{-4}	1.61×10^{-2}
Benzene	C_6H_6	6.5×10^{-4}	2.89×10^{-2}
Water	H_2O	1.00×10^{-3}	7.29×10^{-2}
Ethanol	C_2H_5OH	1.20×10^{-3}	2.23×10^{-2}
Mercury	Hg	1.55×10^{-3}	4.6×10^{-1}
Glycerol	$C_3H_5(OH)_3$	1.49	6.34×10^{-2}

high intermolecular force –
high viscosity, high surface tension

HW 11.1 Properties of Liquids

high intermolecular force –
high viscosity, high surface tension

For the following molecules which has the higher intermolecular force, viscosity and surface tension ? (LD structure, VSEPRT, dipole of molecule) (if the molecules are in the liquid state)

a. $CHCl_3$ vs CH_4

b. H_2O vs H_2

c. NCl_3 (changed from handout) vs $NHCl_2$

Phase Changes between Solids, Liquids, and Gases

Phase Change (State Change): A change in the physical state but not the chemical identity of a substance

Fusion (melting): solid to liquid

Freezing: liquid to solid

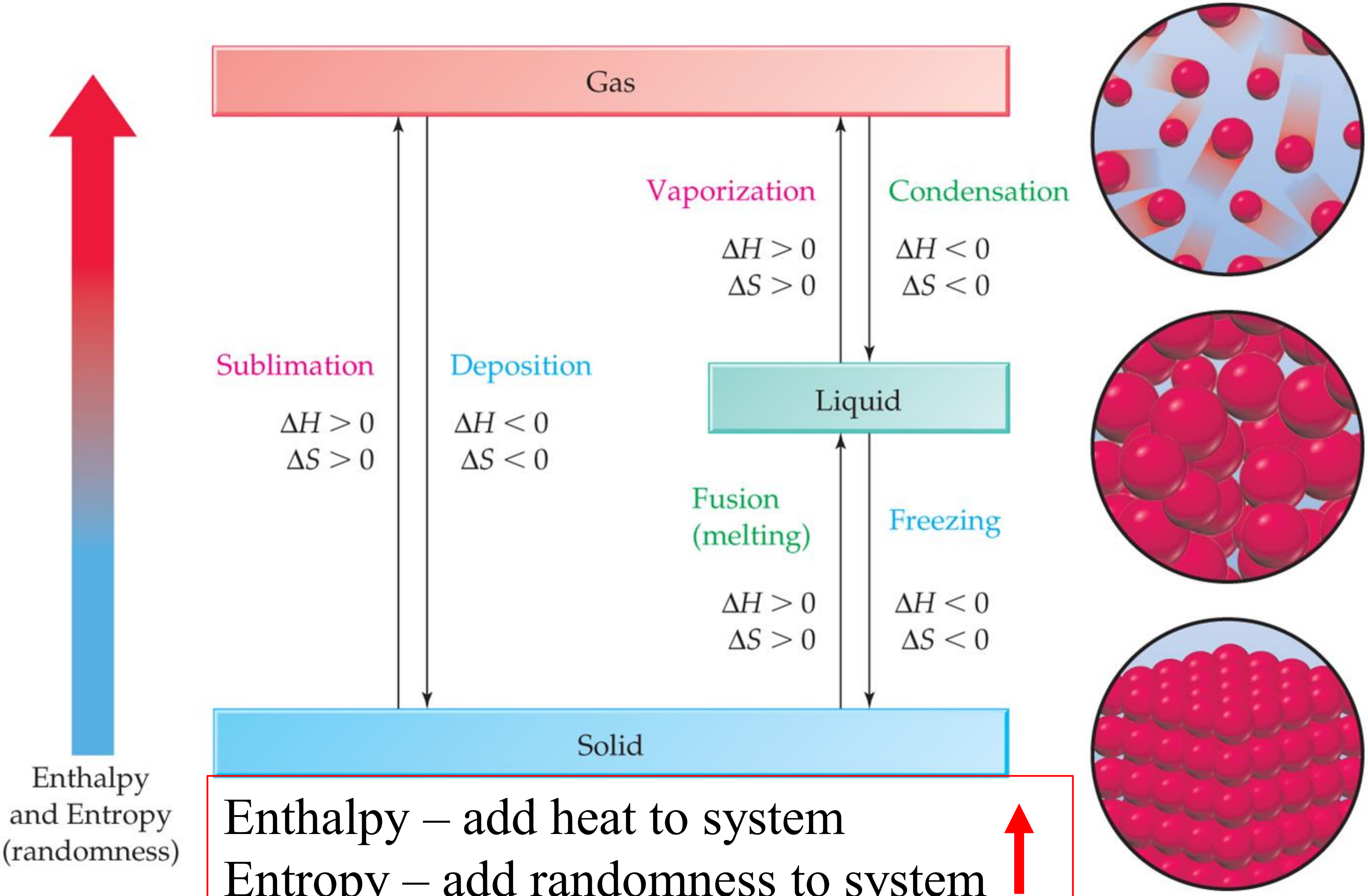
Vaporization: liquid to gas

Condensation: gas to liquid

Sublimation: solid to gas

Deposition: gas to solid

Phase Changes between Solids, Liquids, and Gases



Gas

Liquid

Solid

Sublimation

$\Delta H > 0$
$\Delta S > 0$

Deposition

$\Delta H < 0$
$\Delta S < 0$

Vaporization

$\Delta H > 0$
$\Delta S > 0$

Condensation

$\Delta H < 0$
$\Delta S < 0$

Fusion (melting)

$\Delta H > 0$
$\Delta S > 0$

Freezing

$\Delta H < 0$
$\Delta S < 0$

Enthalpy and Entropy (randomness)

Enthalpy – add heat to system ↑
Entropy – add randomness to system

Phase Changes between Solids, Liquids, and Gases

Heat (Enthalpy) of Fusion (ΔH_{fusion}**)**: The amount of energy required to overcome enough intermolecular forces to convert a solid to a liquid

Heat (Enthalpy) of Vaporization (ΔH_{vap}**)**: The amount of energy required to overcome enough intermolecular forces to convert a liquid to a gas

HW 11.2: Phase Changes between Solids, Liquids, & Gases

ΔH_{fusion} solid to a liquid ΔH_{vap} liquid to a gas

At phase change (melting, boiling, etc) :
$\Delta G = \Delta H - T\Delta S$ & ΔG = zero (bc 2 phases in equilibrium)
$\Delta H = T\Delta S$

a. BP of ethanol is 78.4°C $\Delta H_{\text{vap}} = 38.56$ kJ/mol. What is the entropy change for the vaporization (ΔS_{vap} in J/(Kmol) ?

$\Delta S = \Delta H/T = 38.56$ kJ/mol / (78.4°C + 273.15) K =
$\Delta S = 38.56$ kJ/351.55 (mol K) = 0.10969 kJ/(mol K) = 110 J/(mol K)

b. $CHCl_3$ has $\Delta H_{\text{vap}} = 29.2$ kJ/mol and $\Delta S_{\text{vap}} = 87.5$ J/(K mol). What is the BP of the $CHCl_3$ in Kelvin ?

End C sect 1/21 Tuesday

HW 11.2: Phase Changes between Solids, Liquids, & Gases

ΔH_{fusion} solid to a liquid ΔH_{vap} liquid to a gas

At phase change (melting, boiling, etc) :
$\Delta G = \Delta H - T\Delta S$ & **ΔG = zero** (bc 2 phases in equilibrium)
$\Delta H = T\Delta S$

a. BP of ethanol is $78.4^{o}C$ $\Delta H_{vap} = 38.56$ kJ/mol. What is the entropy change for the vaporization (ΔS_{vap} in J/(Kmol) ?

$\Delta S = \Delta H/T = 38.56$ kJ/mol / $(78.4^{o}C + 273.15)$ K =
$\Delta S = 38.56$ kJ/351.55 (mol K) = 0.10969 kJ/(mol K) = 110 J/(mol K)

b. $CHCl_3$ has $\Delta H_{vap} = 29.2$ kJ/mol and $\Delta S_{vap} = 87.5$ J/(K mol). What is the BP of the $CHCl_3$ in Kelvin ?

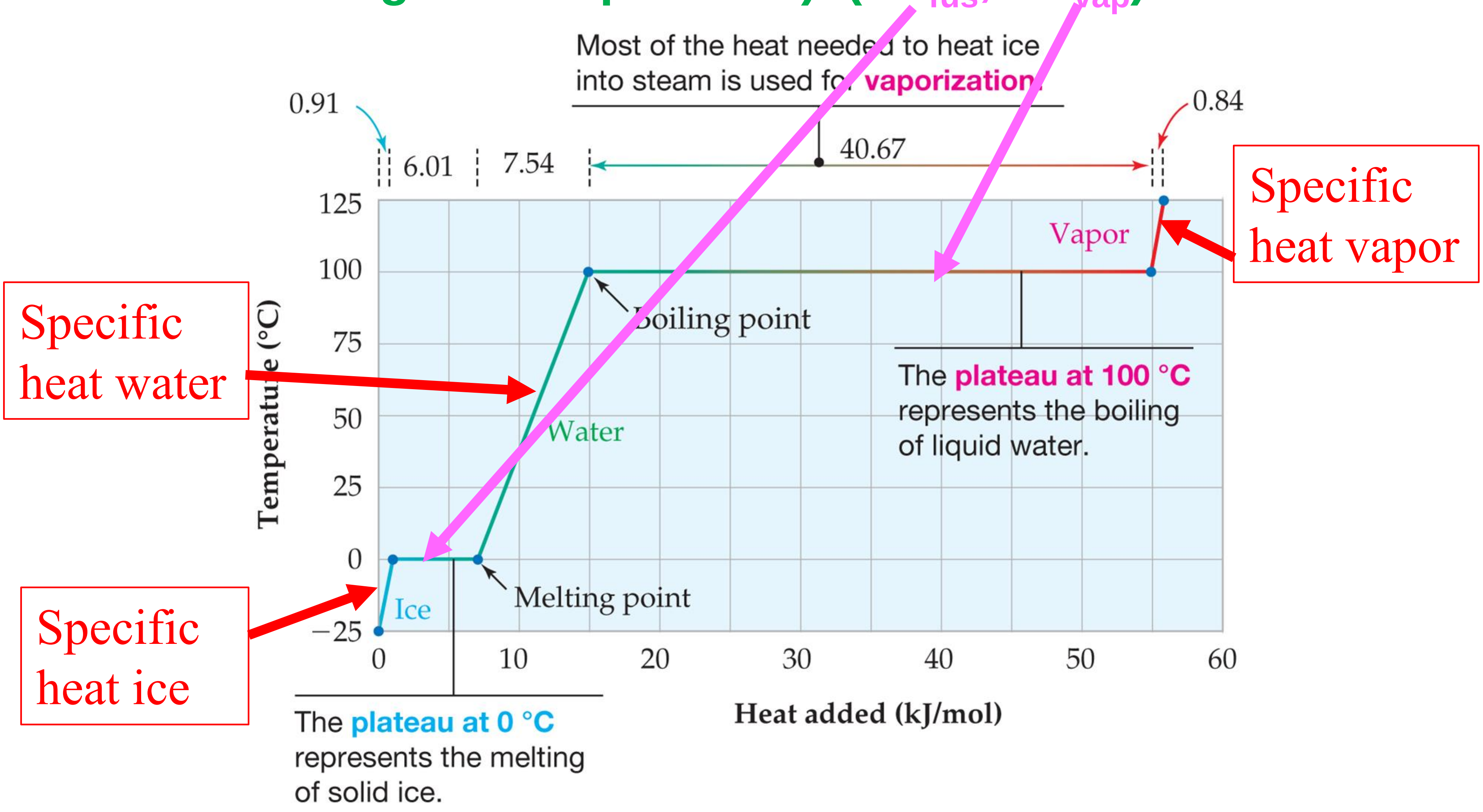
$T = = \Delta H_{vap} / \Delta S_{vap}$ = (29.2 kJ*1000 J/kJ) /mol / {87.5 J/ (K mol)}
T = 334 K

Quiz 2 ends here

End 1/22 A section

BP = T when vapor pressure of liquid equals atmospheric pressure

Phase Changes between Solids, Liquids, and Gases for water (physical state conversions – occurs with no change in temperature) (ΔH_{fus}, ΔH_{vap})


Most of the heat needed to heat ice into steam is used for **vaporization**.

The **plateau at 100 °C** represents the boiling of liquid water.

The **plateau at 0 °C** represents the melting of solid ice.

Specific heat water

Specific heat ice

Specific heat vapor

Heating Curve for Water

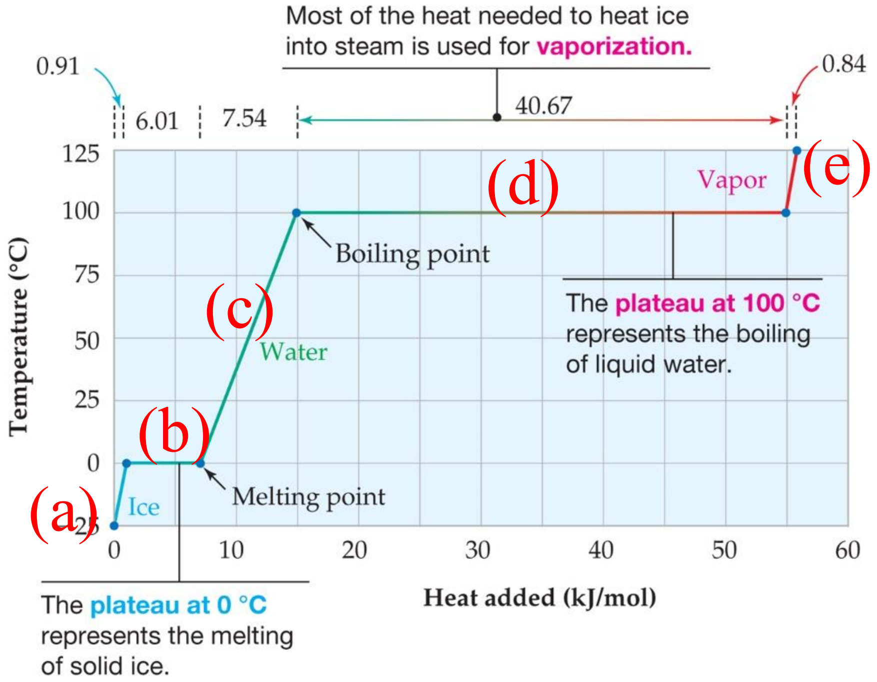
Phase Changes between Solids, Liquids, and Gases for water (physical state conversions – occurs with no change in temperature) (ΔH_{fus}, ΔH_{vap})

usually $\Delta H_{vap} \;>\; \Delta H_{fus}$

because for vaporization, you need to break ALL intermolecular force bonds between molecules

Phase Changes between Solids, Liquids, and Gases

Heating Curve for Water



Most of the heat needed to heat ice into steam is used for **vaporization.**

The **plateau at 100 °C** represents the boiling of liquid water.

The **plateau at 0 °C** represents the melting of solid ice.

(a) Heat ice from -25 to 0°C: molar heat capacity ice = 36.57 J/(mol °C)

(36.57 J/mol °C)($T_f – T_i$) = 0.914 kJ/mol

(b) *Melting ice: Δ H_{fusion} = +6.01 kJ / mol

(c) Heating liquid water from 0°C to 100 °C : molar heat capacity water = 75.4 J/(mol °C) (75.4 J/mol oC)* (100°C) = 7.54 x 10^3 J/mol = 7.54 kJ /mol

(d) *Vaporizing liquid water: Δ H_{vap} = +40.67 kJ/mol largest energy for process

(e) Heating water vapor from 100°C to 125°C:
Molar heat capacity of water vapor = 33.6 J/mol °C
33.6 J/mol °C * 25°C = 0.840 kJ/mol

$$q = n * C_m * \Delta T$$
$$q = n \Delta H_{fus}$$
$$q = n \Delta H_{vap}$$

HW 11.3: Phase Changes between Solids, Liquids, and Gases

Heating Curve for Water

$q = n * C_m * \Delta T$
$q = n \Delta H_{fus}$
$q = n \Delta H_{vap}$

$C_{m\ [H2O\ (l)]}$ =75.4 J/mol oC
$C_{m\ [H2O\ (s)]}$ = 36.57J/mol oC
$C_{m\ [H2O\ (g)]}$ = 33.6 J/mol oC
ΔH_{fus} =6.01 kJ/mol
ΔH_{vap} =40.67 kJ/mol

If you have 0.351 moles of liquid water, what would be the heat needed to vaporize that water ?

If you have 1.2 moles of ice, what is the heat needed to raise the temperature of the ice from -17.5 ^{o}C to – 0.4 ^{o}C ?

HW 11.3: Phase Changes between Solids, Liquids, and Gases

Heating Curve for Water

$q = n * C_m * \Delta T$

$q = n\,\Delta H_{fus}$

$q = n\,\Delta H_{vap}$

$C_{m\,[H2O\,(l)]} = 75.4$ J/mol °C

$C_{m\,[H2O\,(s)]} = 36.57$ J/mol °C

$C_{m\,[H2O\,(g)]} = 33.6$ J/mol °C

$\Delta H_{fus} = 6.01$ kJ/mol

$\Delta H_{vap} = 40.67$ kJ/mol

If you have 0.351 moles of liquid water, what would the heat needed to vaporize that water ?

$q = (0.351\text{ mol}) * 40.67\text{ kJ/mol} = 14.3\text{ kJ}$

End 1/22 Wed C section,
end 1/24 Friday A section

If you have 1.2 moles of ice, what is the heat needed to raise the temperature of the ice from -17.5 °C to – 0.4 °C ?

$q = (1.2\text{ moles ice})\,(36.57\text{ J/mol °C})\,(-0.4\text{ °C} + 17.5\text{°C}) = 750\text{ J}$

Phase Changes between Solids, Liquids, and Gases

TABLE 11.2 Heats of Fusion and Heats of Vaporization for Some Common Compounds

Name	Formula mass	Formula	ΔH_{fusion} (kJ/mol)	ΔH_{vap} (kJ/mol)
Ammonia	17	NH_3	5.66	23.33
Benzene	78	C_6H_6	9.87	30.72
Ethanol	46	C_2H_5OH	4.93	38.56
Helium	2	He	0.02	0.08
Mercury	200	Hg	2.30	59.11
Water	18	H_2O	6.01	40.67

(a) in general: $\Delta H_{vap} > \Delta H_{fusion}$

(b) ΔH_{vap} = negative $\Delta H_{condensation}$ ΔH_{fusion} = negative $\Delta H_{freezing}$

(c) 1 Hydrogen bond vs. 2 Hydrogen bonds

(d) London dispersion forces - sometimes larger effect than H bond (largest Formula Mass, greatest enthalpy of fusion & vaporization)

For the same molecule:

Largest ΔS for gaseous form of compound
Medium ΔS for liquid form of compound
Smallest ΔS for solid form of compound

For a Reaction:

Largest ΔS for the side of the reaction with larger number of gaseous molecules.

ex: $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (g)$

$$\Delta S_{\text{reactant}} > \Delta S_{\text{product}}$$

End Test 1

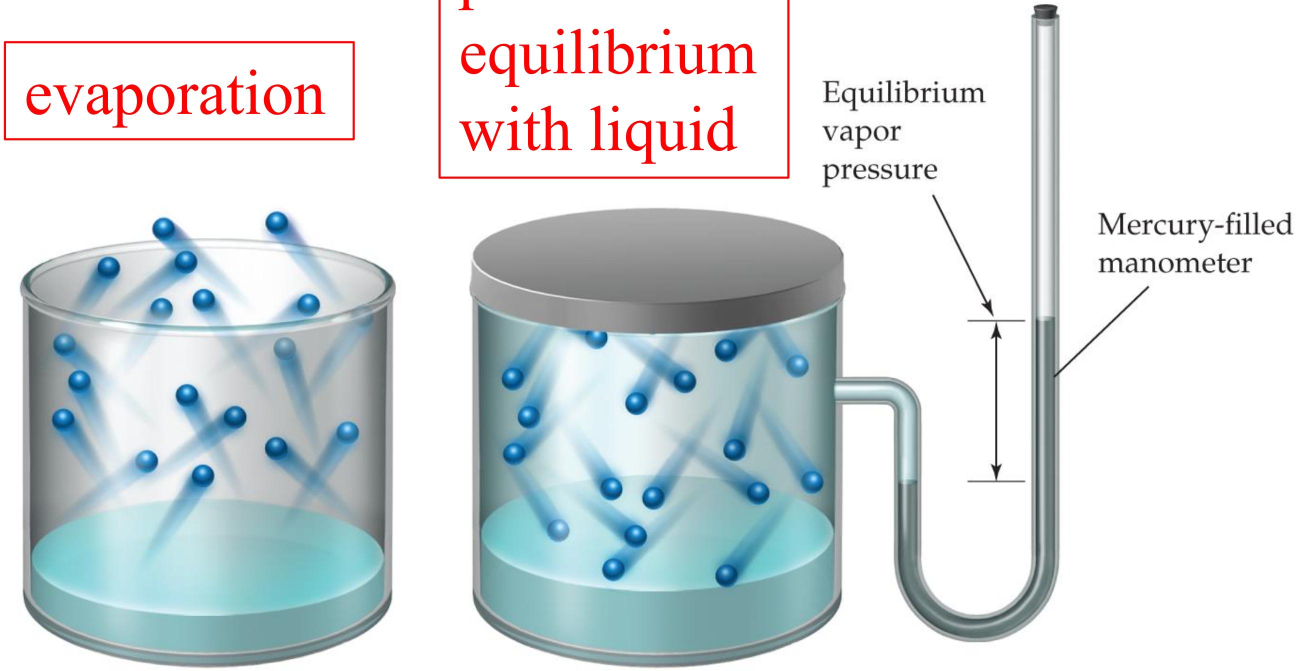
Start Test 2,
Quiz 3

Evaporation, Vapor Pressure, and Boiling Point

Vapor Pressure: The partial pressure of a gas in equilibrium with a liquid at a constant temperature

evaporation

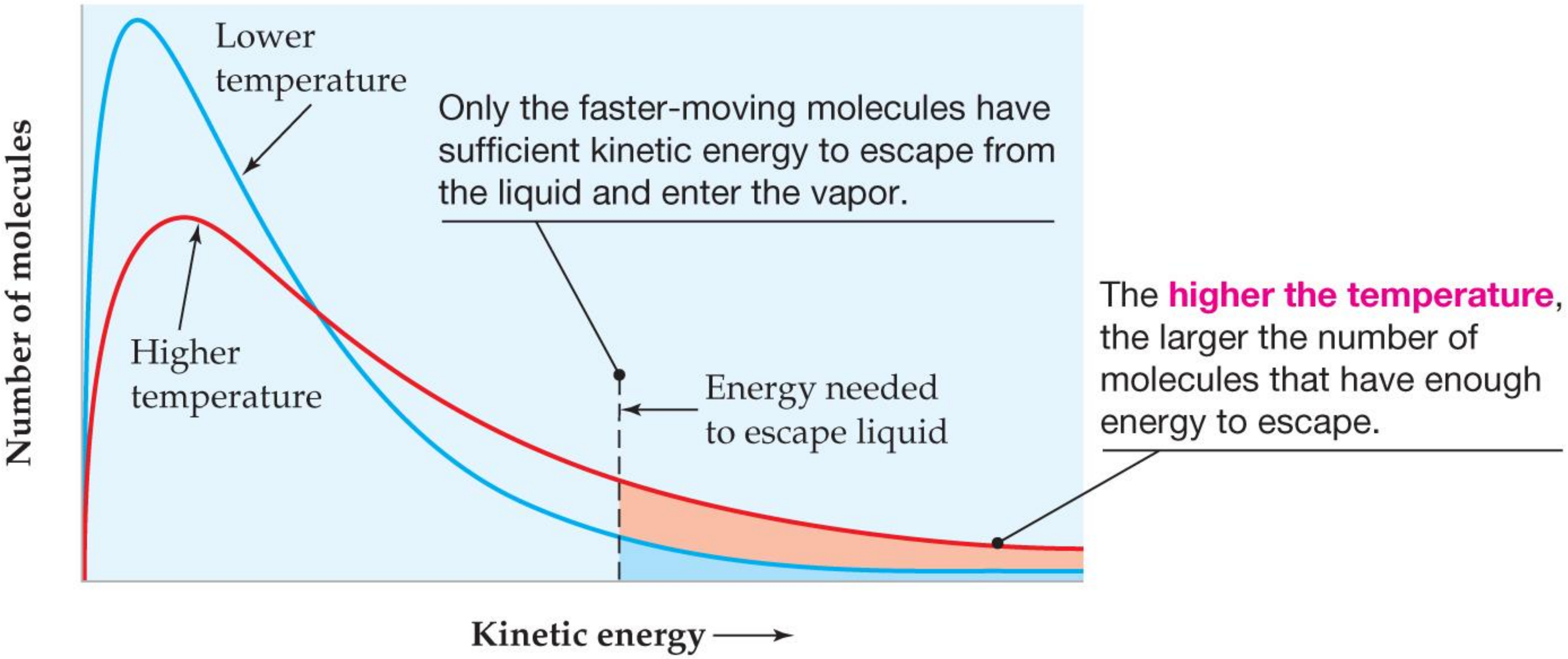
Vapor pressure in equilibrium with liquid



A liquid sitting for a length of time in an open container evaporates, but …

… a liquid sitting in a closed container causes a rise in pressure.

Evaporation, Vapor Pressure, and Boiling Point



Only the faster-moving molecules have sufficient kinetic energy to escape from the liquid and enter the vapor.

The **higher the temperature**, the larger the number of molecules that have enough energy to escape.

Evaporation, Vapor Pressure, and Boiling Point

Clausius–Clapeyron Equation

$$\ln P_{\text{vap}} = \left(-\frac{\Delta H_{\text{vap}}}{R} \right) \frac{1}{T} + C$$

$$y \quad = \quad m \quad x + b$$

Omit this equation –
Omission from
Departmental Syllabus

End C section: Friday 1/24/20

Kinds of Solids

Amorphous Solids: Particles are randomly arranged and have no ordered long-range structure.
examples: rubber, window glass, plastic, butter

Crystalline Solids: Particles have an ordered arrangement extending over a long range.

- ionic solids (ex: NaCl, BaF_2)
- molecular (covalent molecule) solids (ex: $C_{12}H_{26}$, I_2, naphthalene, sucrose)
- covalent network solids (ex: carbon, silicon dioxide)
- metallic solids (ex: metallic Fe, metallic Na, metallic Pt, etc)

End 1/27 Monday A section

Kinds of Solids

crystalline

(a) A crystalline solid, such as this amethyst, has flat faces and distinct angles. These regular macroscopic features reflect a similarly ordered arrangement of particles at the atomic level.

amorphous

(b) An amorphous solid like rubber has a disordered arrangement of its constituent particles.

Kinds of Solids

types of crystalline solids

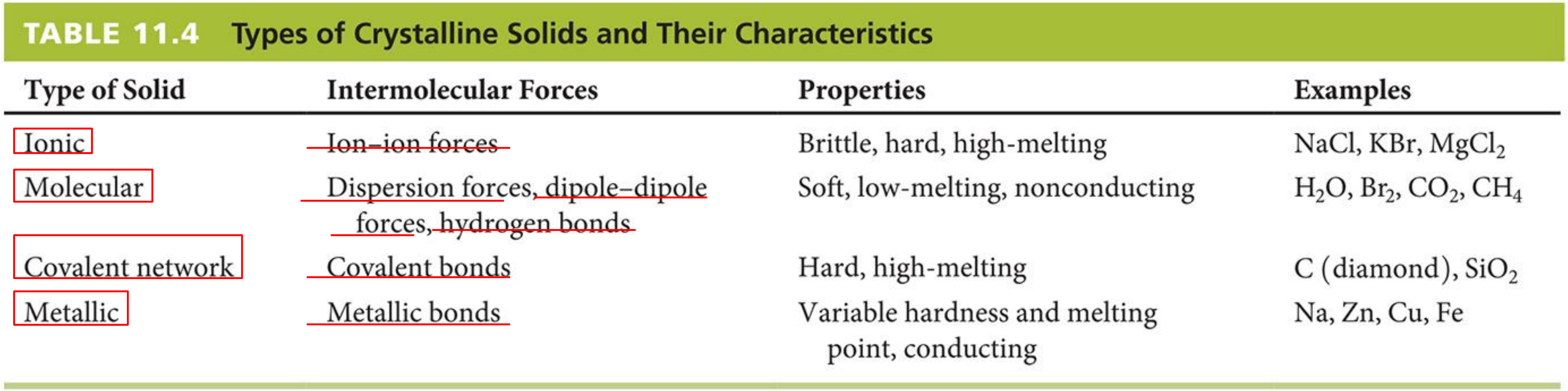
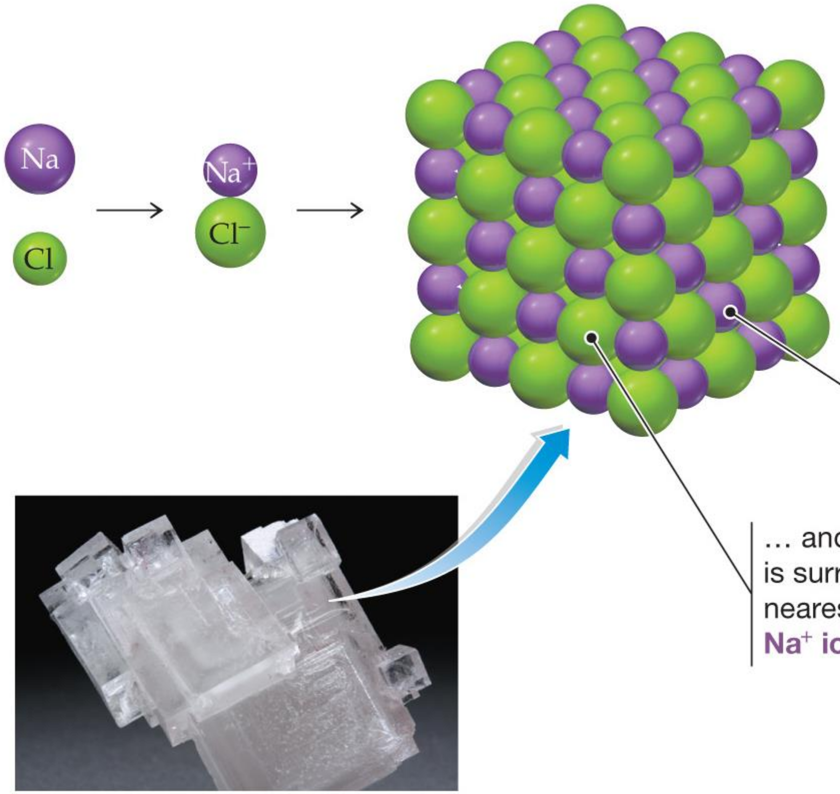


TABLE 11.4 Types of Crystalline Solids and Their Characteristics

Type of Solid	Intermolecular Forces	Properties	Examples
Ionic	Ion–ion forces	Brittle, hard, high-melting	NaCl, KBr, $MgCl_2$
Molecular	Dispersion forces, dipole–dipole forces, hydrogen bonds	Soft, low-melting, nonconducting	H_2O, Br_2, CO_2, CH_4
Covalent network	Covalent bonds	Hard, high-melting	C (diamond), SiO_2
Metallic	Metallic bonds	Variable hardness and melting point, conducting	Na, Zn, Cu, Fe

Kinds of Solids

Ionic Solids: Particles are ions ordered in a regular, three-dimensional arrangement and held together by ionic bonds. An example is sodium chloride.



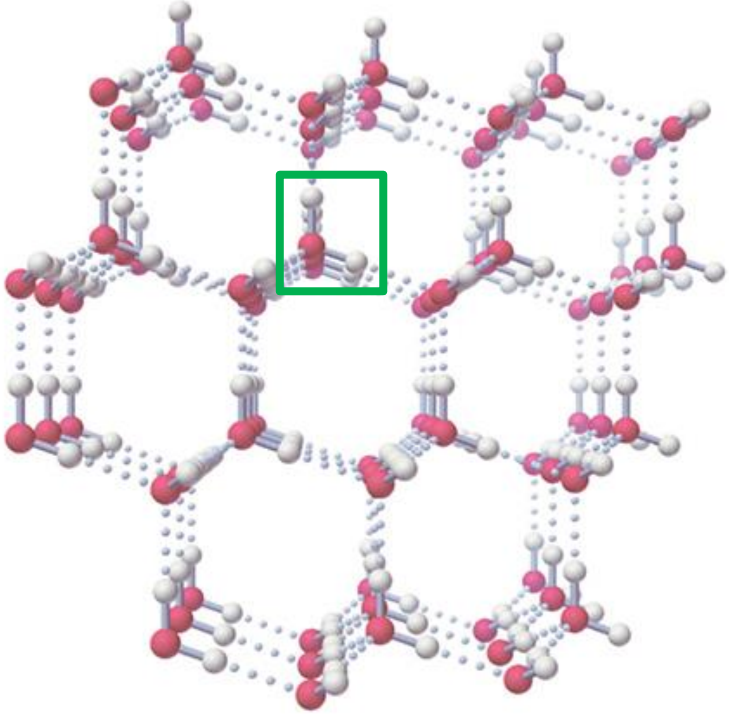
In the sodium chloride crystal, each **Na^+ ion** is surrounded by six nearest-neighbor **Cl^- ions** …

… and each **Cl^- ion** is surrounded by six nearest-neighbor **Na^+ ions**.

Kinds of Solids

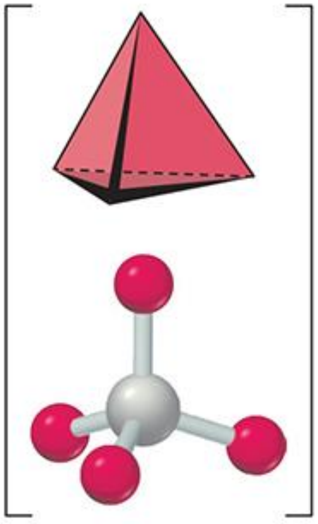
Molecular Solids: Particles are covalent molecules held together by intermolecular forces. example: H_2O (solid) ice – held together by H bond

(a) Ice consists of individual H_2O molecules held together in a regular manner by hydrogen bonds.

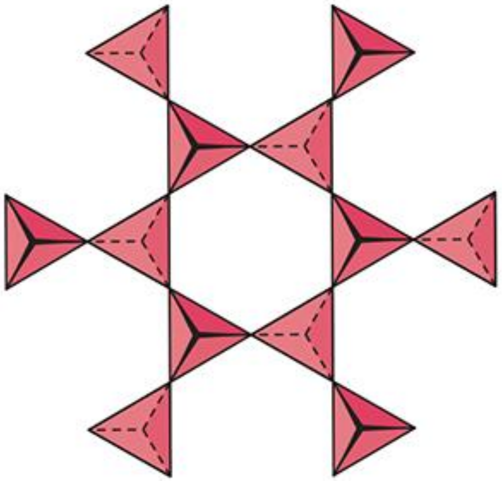


Kinds of Solids

Covalent Network Solids: Particles are atoms linked together by covalent bonds into a giant, three-dimensional array. example quartz (SiO_2), diamond (C), graphite (C) – held together by covalent bond



(b) Quartz (SiO_2) is essentially one very large molecule with Si–O covalent bonds. Each silicon atom has tetrahedral geometry and is bonded to four oxygens; each oxygen has approximately linear geometry and is bonded to two silicons.



(c) This shorthand representation shows how SiO_4 tetrahedra join at their corners to share oxygen atoms.

Kinds of Solids

Metallic Solids: Particles are metal atoms whose crystals have metallic properties such as electrical conductivity.
example: Fe (metallic elemental iron), Na (metallic elemental sodium), etc.

Structures of Some Covalent Network Solids – large network held together by covalent bonding

Carbon Allotropes

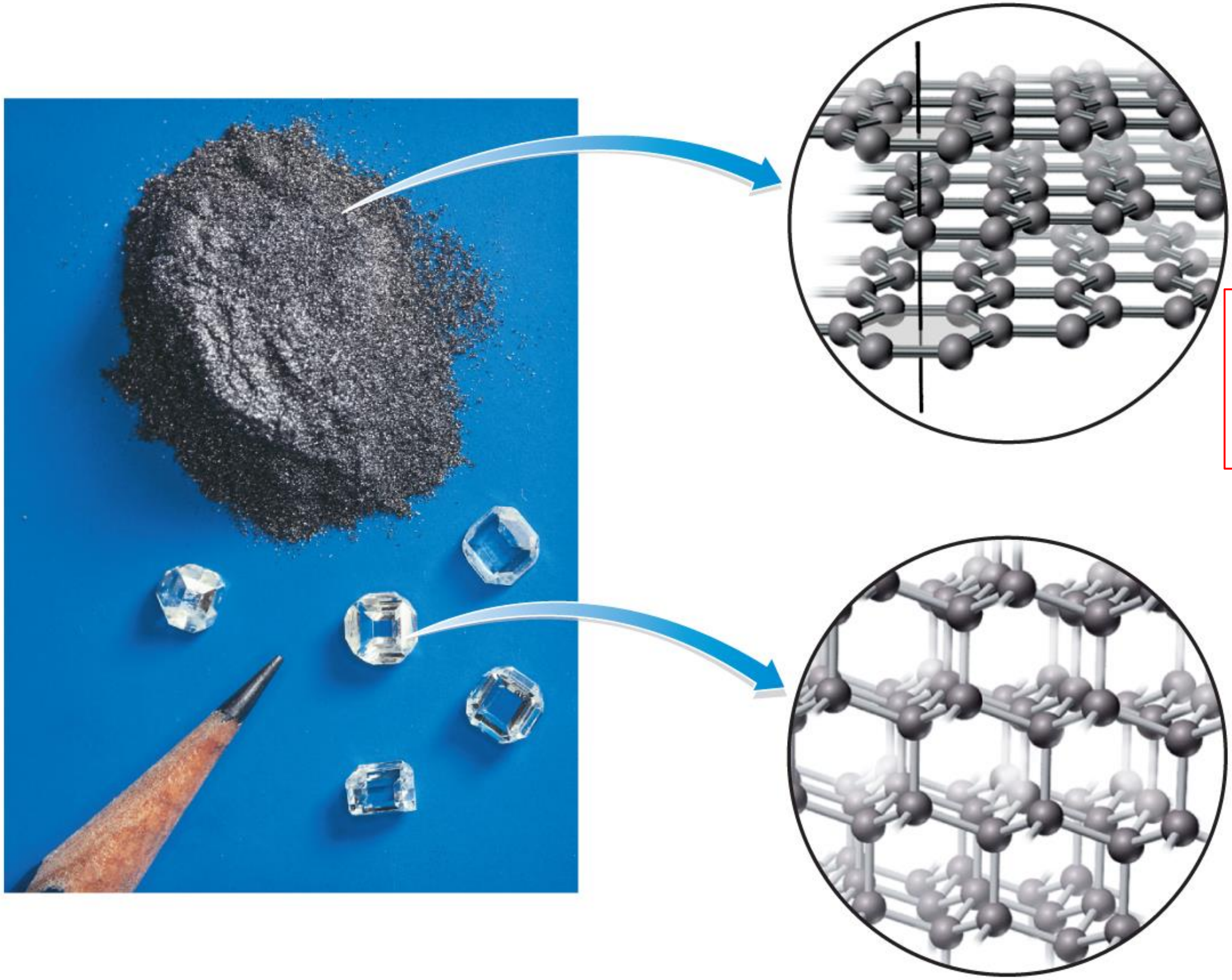
Allotropes: Different structural forms of an element

Carbon Allotropes

- Graphite
- Diamond
- Fullerene
- Nanotubes

Structures of some Covalent Network Solids Carbon Allotropes

(a) Graphite is a covalent network solid consisting of two-dimensional sheets of *sp*^{2}-hybridized carbon atoms organized into six-membered rings.



The atoms in each sheet are offset slightly from the atoms in neighboring sheets.

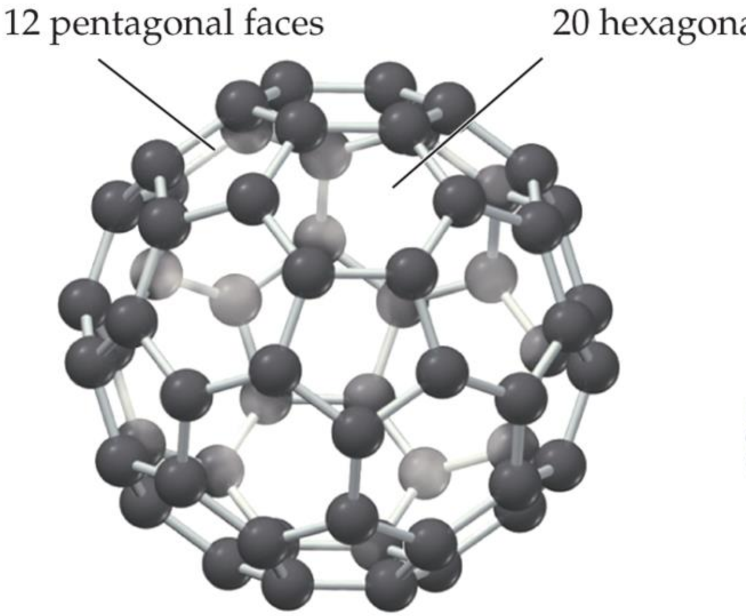
Sheets held together by dispersion forces

(b) Diamond is a vast, three-dimensional array of *sp*^{3}-hybridized carbon atoms, each of which is bonded with tetrahedral geometry to four other carbons.

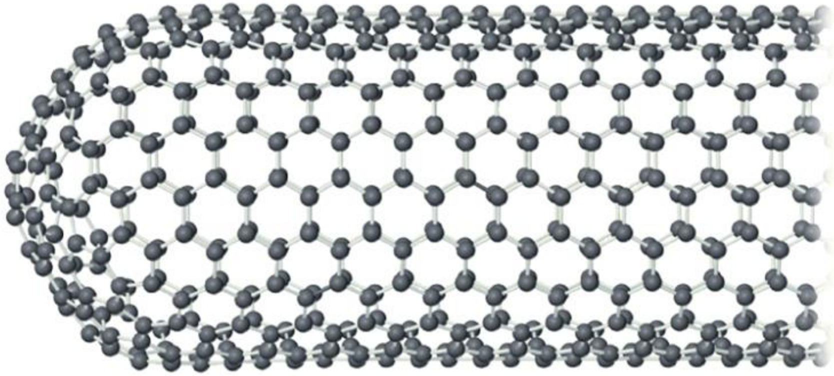
held together by covalent bonds

Structures of Some Covalent Network Solids

Carbon Allotropes



(a) Fullerene is a molecular solid whose molecules have the shape of a soccer ball. The ball has 12 pentagonal and 20 hexagonal faces, and each carbon atom is *sp*^{2}-hybridized.



(b) Carbon nanotubes consist of sheets of graphite rolled into tubes of 2–30 nm diameter.

Structures of Some Covalent Network Solids

Silica (SiO_2)

- Quartz
- Sand

window glass, quartz glass

SiO_2 melted and then solidified into an amorphous form

HW 11.4: Kinds of Solids

Amorphous Solids:

Crystalline Solids: ionic solids, molecular solids, covalent network solids, metallic solids

Classify each as one of the above types of solid.
(example: amorphous, or crystalline-metallic, etc)
(accidentally left off the * on HW)

$CaCl_2$
diamond (C)
Li F
Zinc (Zn)
window glass
SiO_2 (quartz crystal)
$C_{10}H_8$ (naphthalene)*
H_2O (solid)*

HW 11.4: Kinds of Solids

Amorphous Solids:

Crystalline Solids: ionic solids, molecular solids, covalent network solids, metallic solids

Classify each as one of the above types of solid.
(example: amorphous, or crystalline-metallic, etc)
(accidentally left off the * on HW)

$CaCl_2$	crystalline, ionic
diamond (C)	crystalline, covalent network
Li F	crystalline, ionic
Zinc (Zn)	crystalline, metallic
window glass	amorphous
SiO_2 (quartz crystal)	crystalline, covalent network
$C_{10}H_8$ (naphthalene)*	crystalline, molecular solid
H_2O (solid)*	crystalline, molecular solid

HW 11.4: Kinds of Solids

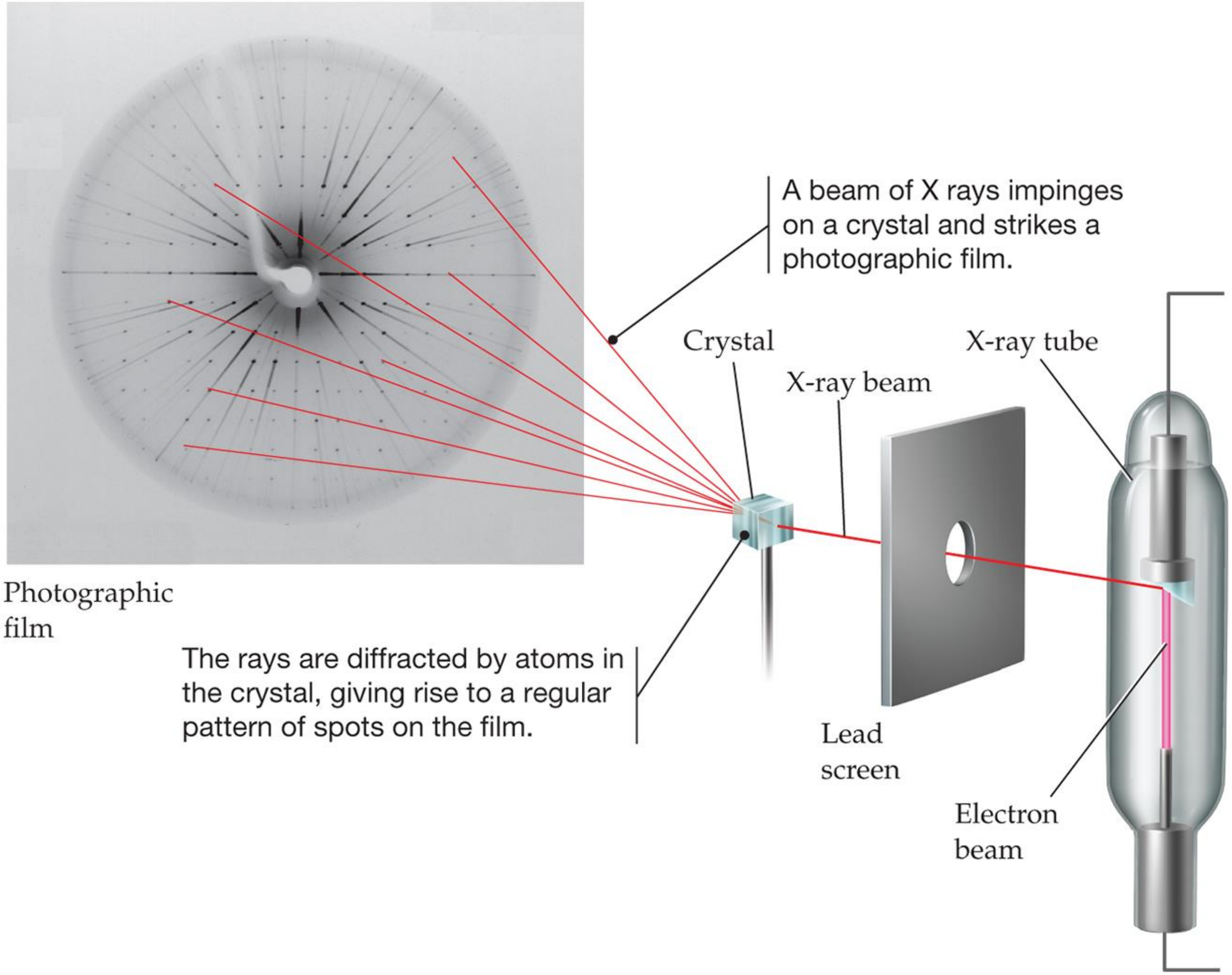
Amorphous Solids:

Crystalline Solids: ionic solids, molecular solids, covalent network solids, metallic solids

Classify each as one of the above types of solid.
(example: amorphous, or crystalline-metallic, etc)

$CaCl_2$	crystalline, ionic
diamond (C)	crystalline, covalent network
Li F	crystalline, ionic
Zinc (Zn)	crystalline, metallic
window glass	amorphous
SiO_2 (quartz crystal)	crystalline, covalent network

Probing the Structure of Solids: X-Ray Crystallography – spectroscopic method to view crystal structure (using X-ray electromagnetic radiation & diffraction) (not responsible on test)

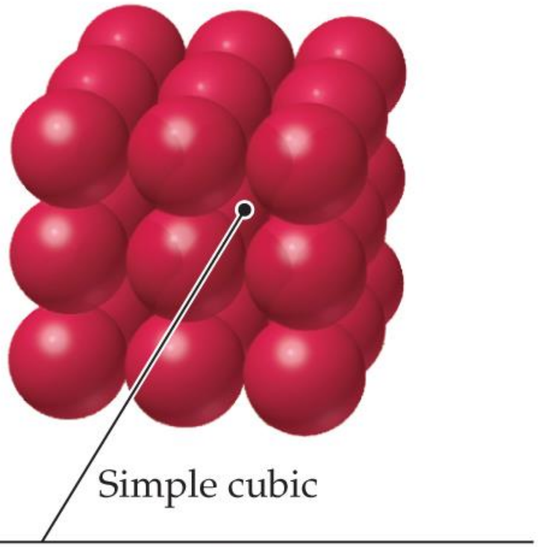


A beam of X rays impinges on a crystal and strikes a photographic film.

The rays are diffracted by atoms in the crystal, giving rise to a regular pattern of spots on the film.

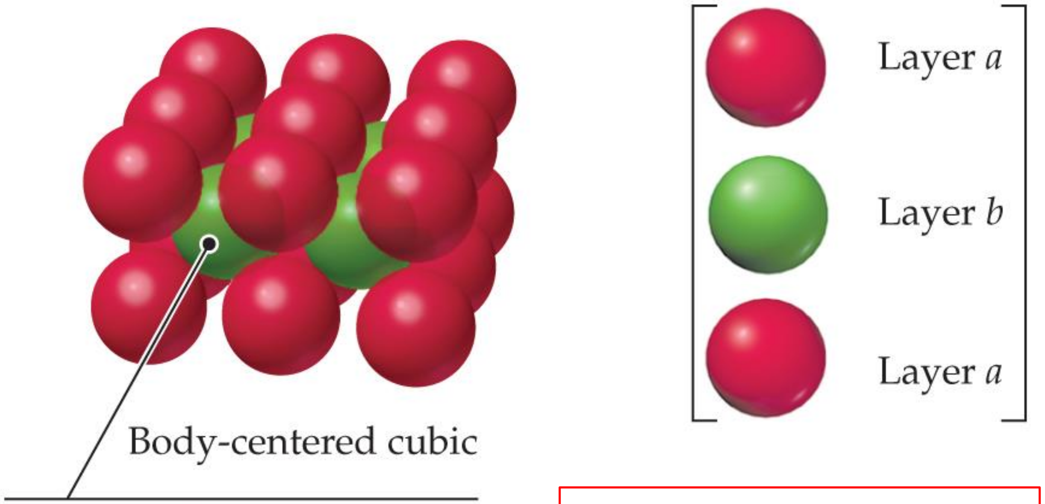
The Packing of Spheres in Crystalline Solids: Unit Cells (this slide crystalline metallic) (not on test)

(a) Simple Cubic Packing:
All layers are identical, and all atoms are lined up in stacks and rows.



Coordination Number 6:
Each sphere is touched by six neighbors, four in the same layer, one directly above, and one directly below.

(b) Body-Centered Cubic Packing:
The spheres in layer *a* are separated slightly and the spheres in layer *b* are offset so that they fit into the depressions between atoms in layer *a*. The third layer is a repeat of the first.



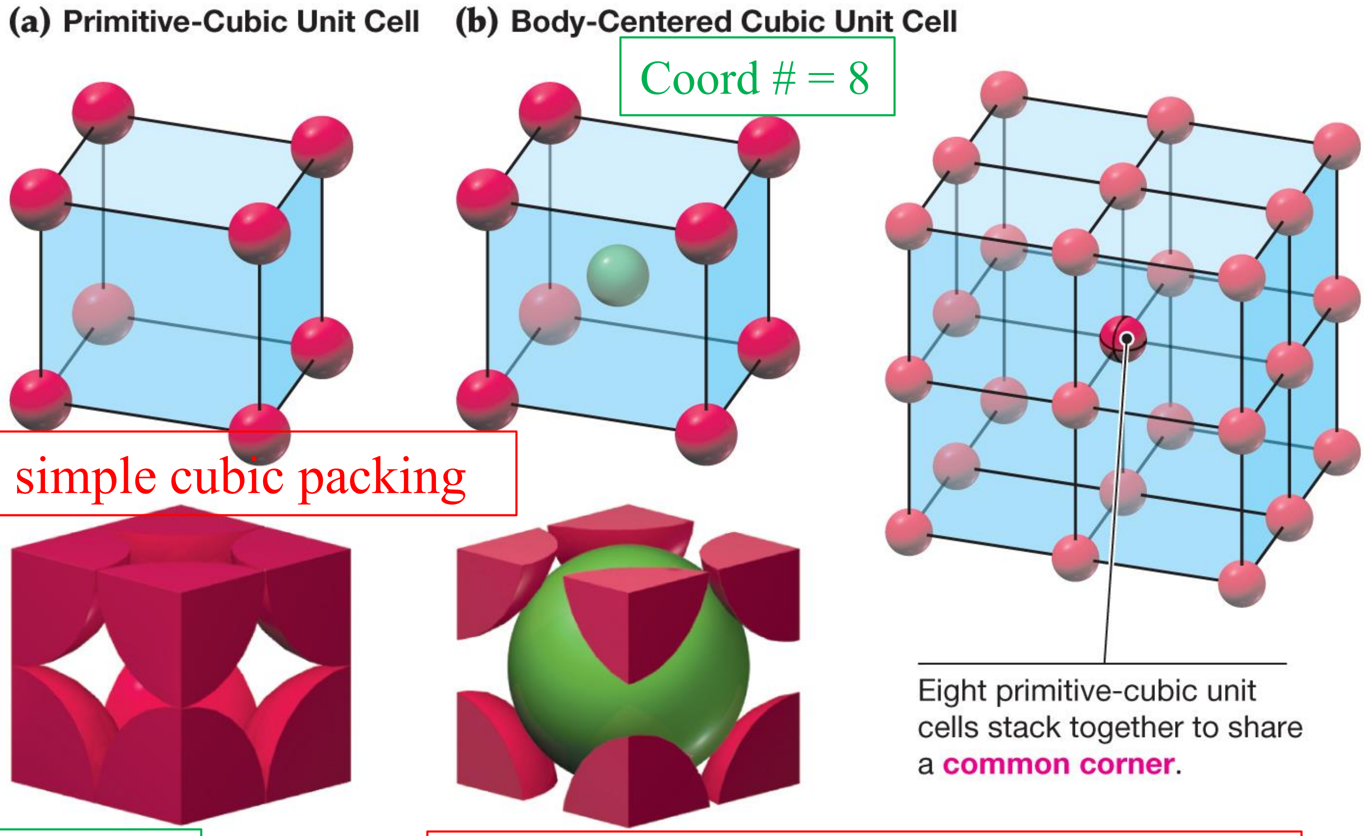
Coordination Number 8:
Each sphere is touched by eight neighbors, four in the layer below, and four in the layer above.

If with more space between them then get next slide.

The Packing of Spheres in Crystalline Solids: Unit Cells (not on test) (fig a and b for all other crystals except metals)

Unit Cell: A small, repeating unit that makes up a crystal

Primitive Cubic **Body-Centered Cubic**



(a) Primitive-Cubic Unit Cell

(b) Body-Centered Cubic Unit Cell

Eight primitive-cubic unit cells stack together to share a **common corner**.

Coord # = 8

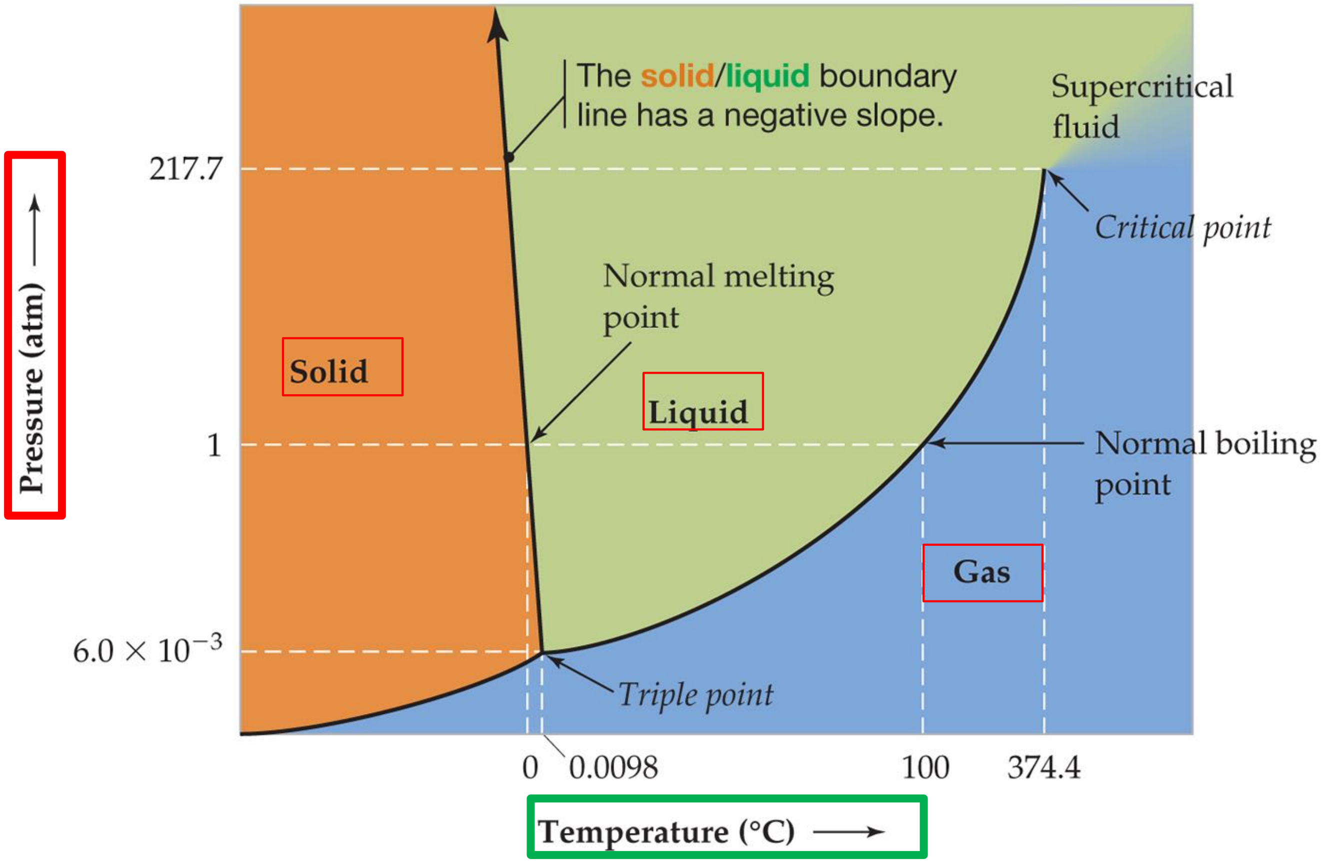
Same as simple cubic packing

Coord # = 6

Same as body centered cubic packing

Phase Diagrams

A plot of Pressure (y scale) and Temperature (x scale)



Increase T → solid melts to liquid to gas

Increase P ↑ gas becomes liquid or solid

Phase Diagrams

Normal Boiling Point: T (BP) at 1 atm of external pressure

Normal Melting Point: T (MP) at 1 atm of external pressure

Triple Point: equilibrium point with gas, liquid and solid

Phase Diagrams

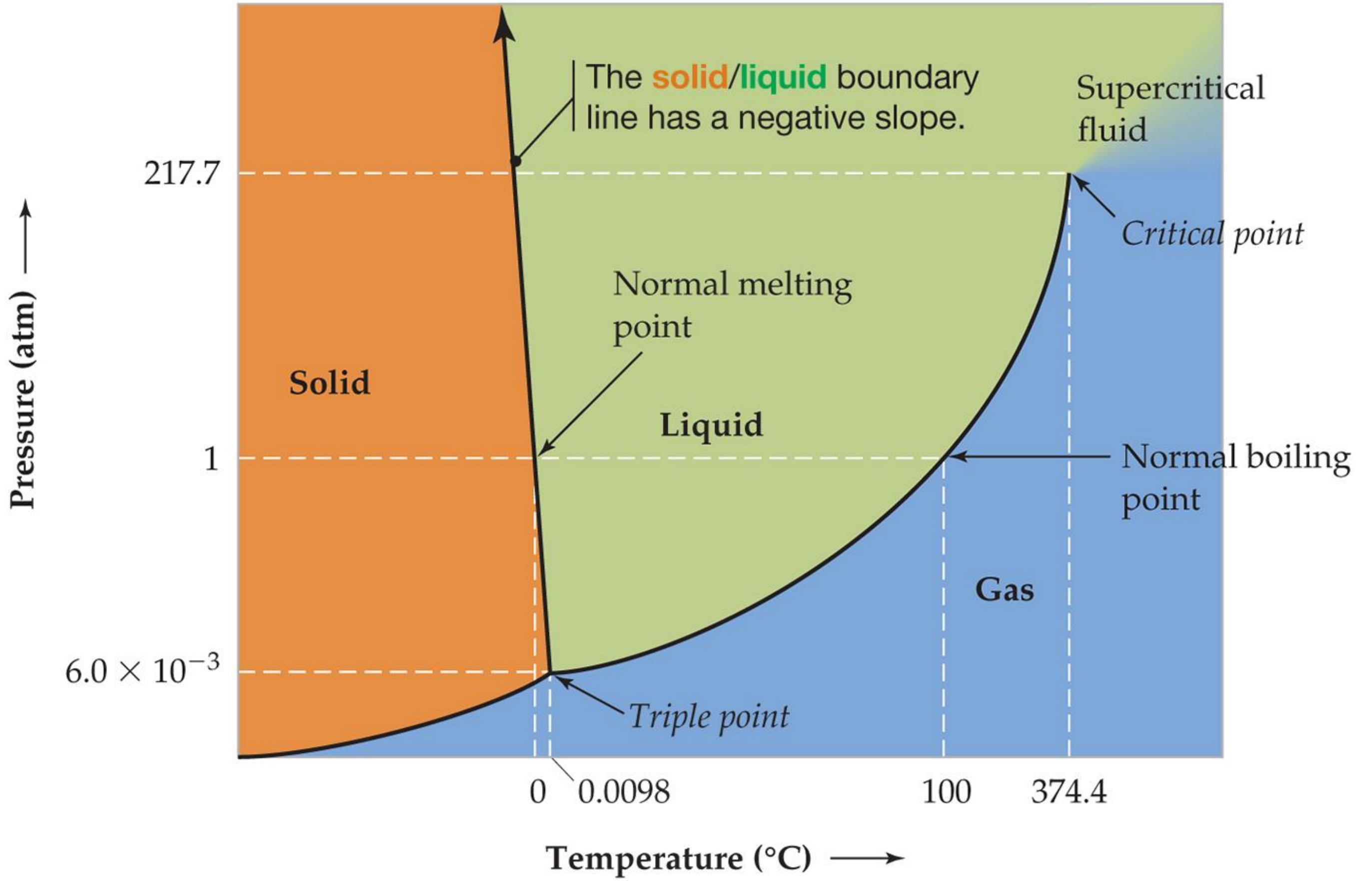
Critical Point: T & P beyond which gas can't be made liquid

- **Critical Temperature**: T beyond which a gas can't be made liquid regardless of P
- **Critical Pressure**: P beyond which a liquid can't be made gas regardless of T

Supercritical Fluid: A state of matter beyond the critical point that is neither liquid nor gas

Phase Diagrams Water

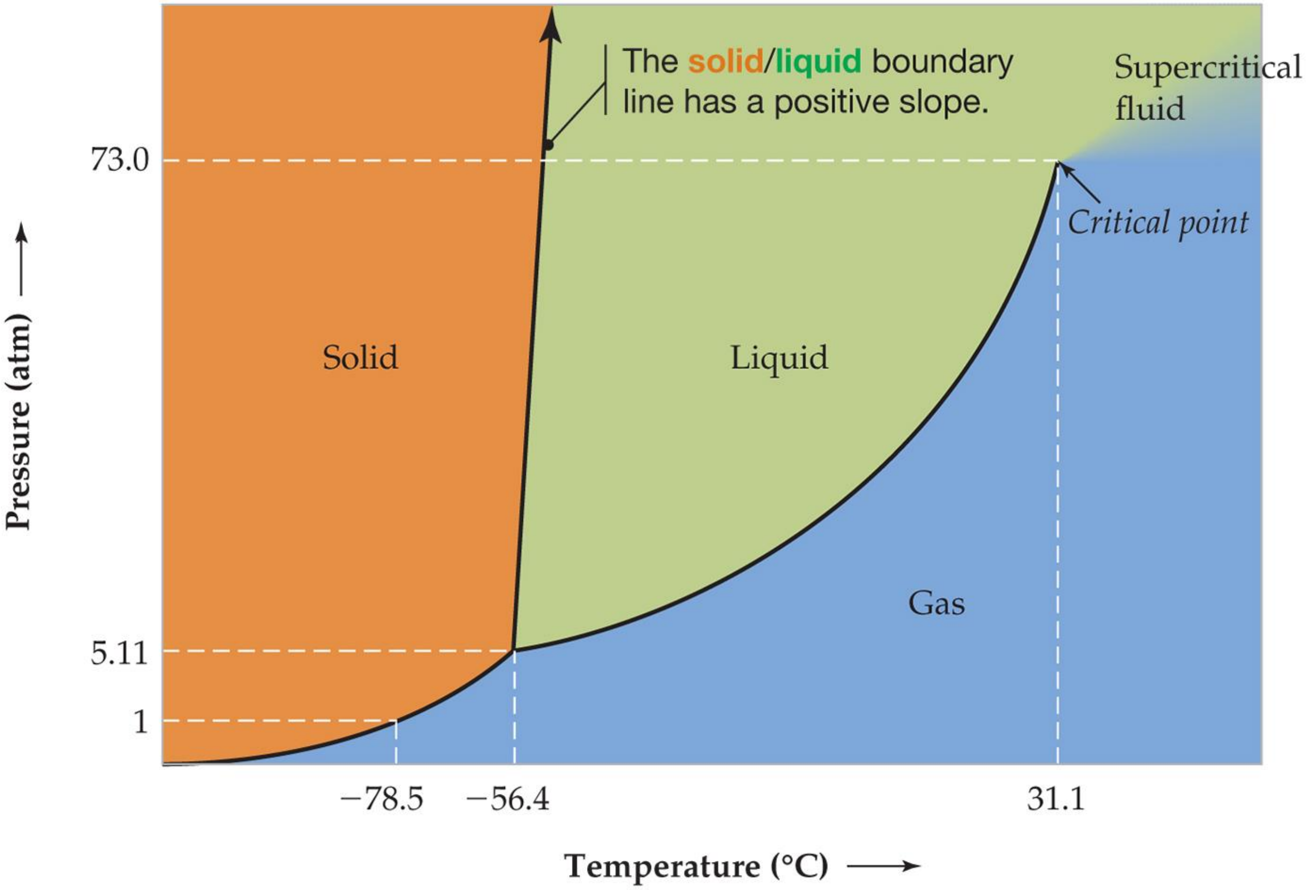
Normal Boiling Point: T (BP) at 1 atm of external pressure
Normal Melting Point: T (MP) at 1 atm of external pressure
Triple Point: equilibrium point with gas, liquid and solid



Critical Point: T & P beyond which gas can't be made liquid
Supercritical Fluid: A state of matter beyond the critical point that is neither liquid nor gas

Phase Diagrams Carbon Dioxide

Normal Boiling Point: T (BP) at 1 atm of external pressure
Normal Melting Point: T (MP) at 1 atm of external pressure
Triple Point: equilibrium point with gas, liquid and solid

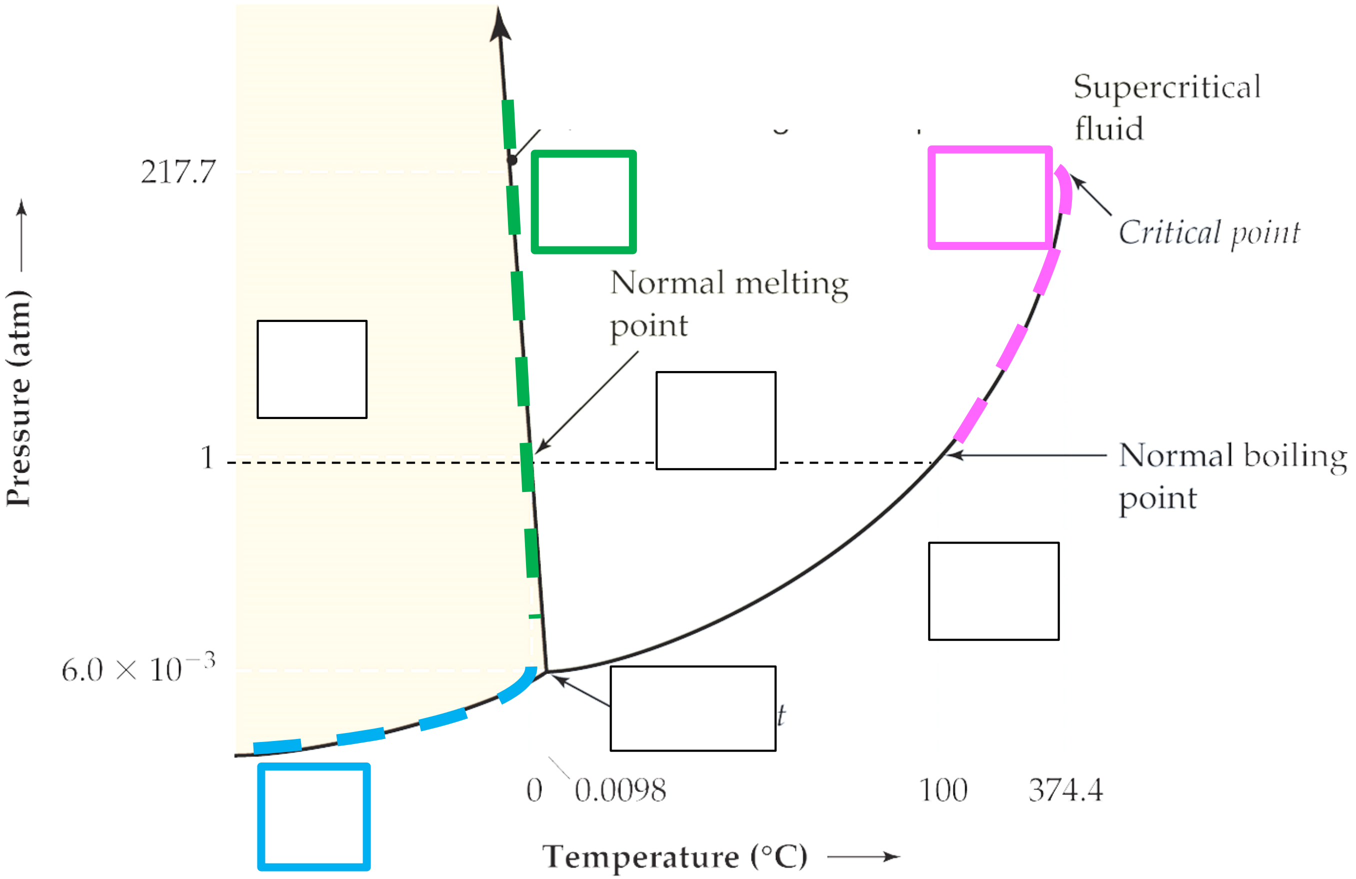


Critical Point: T & P beyond which gas can't be made liquid
Supercritical Fluid: A state of matter beyond the critical point that is neither liquid nor gas

HW 11.5: Phase Diagrams **Fill in the blank with a letter**

(a) Solid
(b) Liquid
(c) Gas
(d) line transition s → l
(e) line transition l → g
(f) line transition s → g
(g) Triple Point

Water



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HW 11.5: Phase Diagrams

Fill in the blank with a letter

(a) Solid
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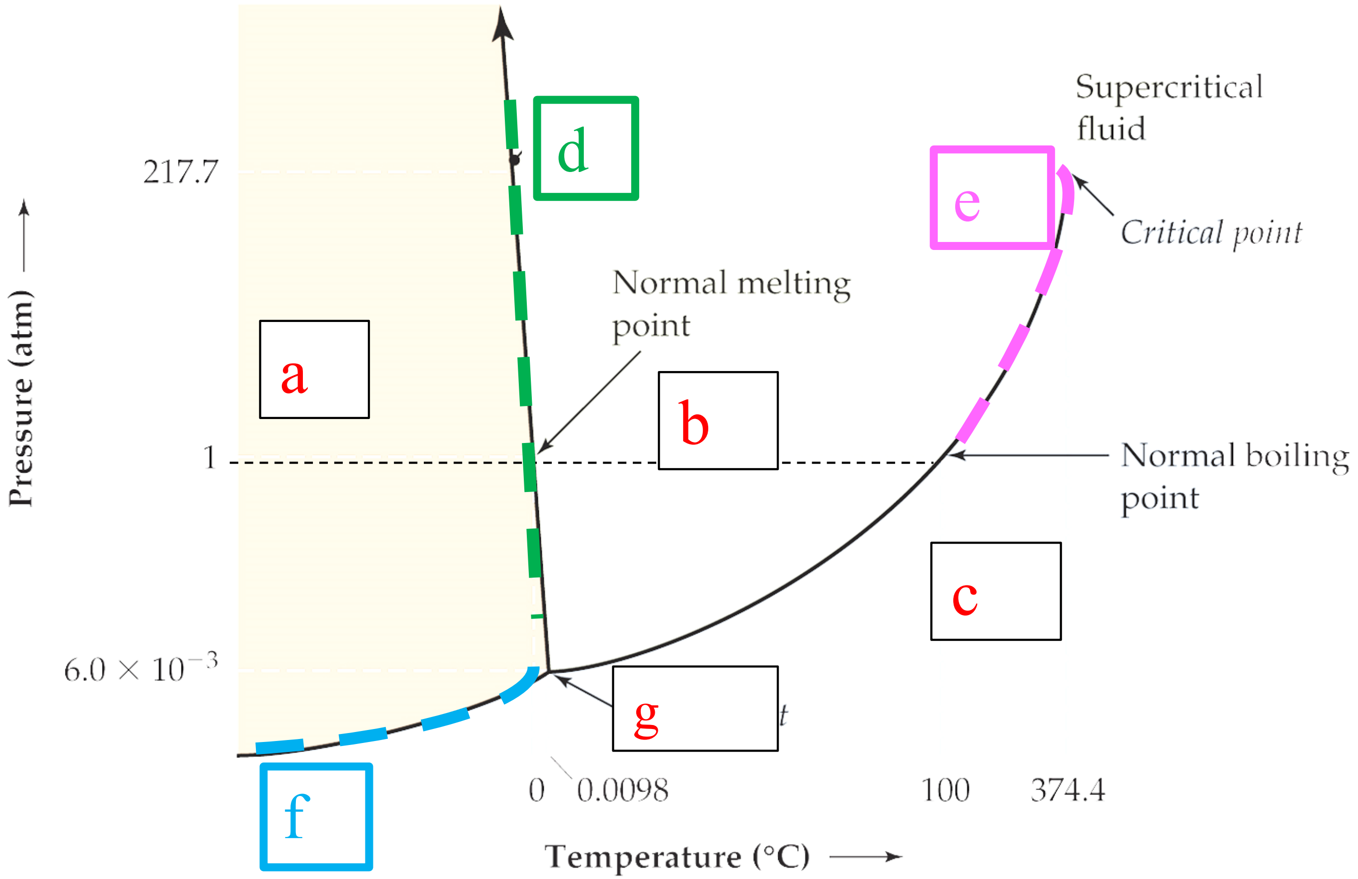
Water



Supercritical Fluid: A state of matter beyond the critical point that is neither liquid nor gas

Phase Diagrams

Water

Shows water at triple point equilibrium solid, liquid & gas

End 1/31 A,C section