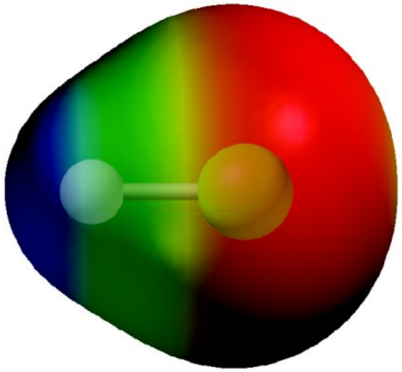
Chapter 12

Intermolecular Forces and the Physical Properties of Liquids and Solids

12.1 Intermolecular Forces

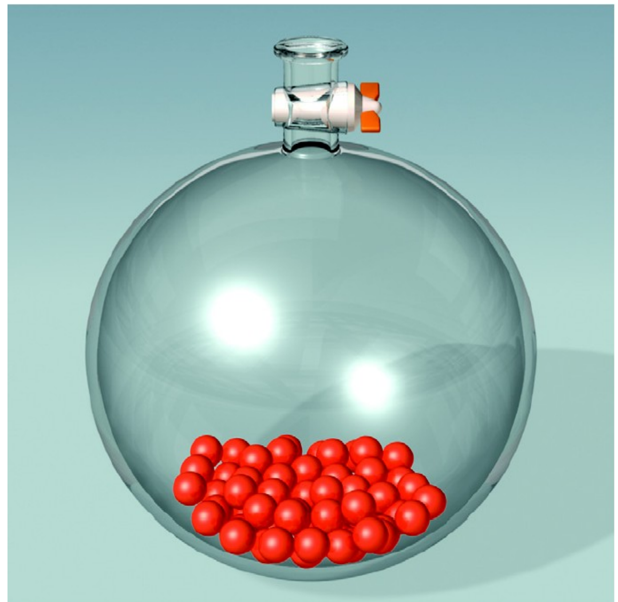
- ***Intermolecular forces*** are the attractive forces holding particles together in the ***condensed*** (liquid and solid) ***phases*** of matter
- Result from coulombic attractions
  - Dependent on the magnitude of the charge
  - Dependent on distance between charges
- Weaker than forces of ionic bonding
- Involve partial charges



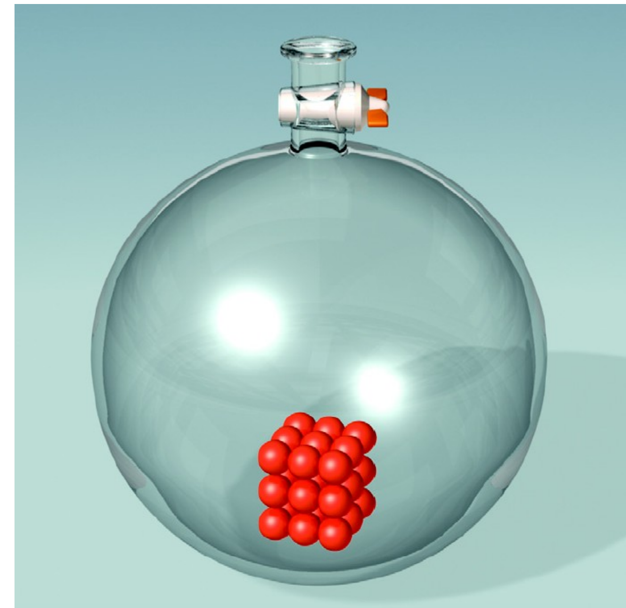
HCl

The Three Phases of Matter

Gas



Liquid



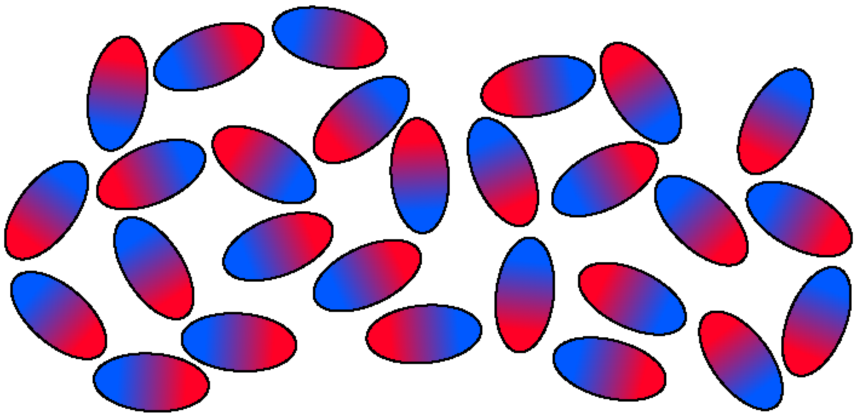
Solid

condensed phases

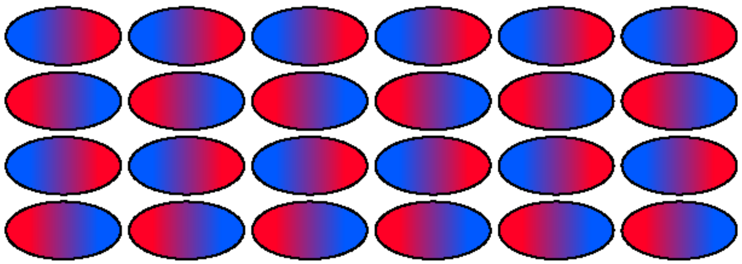
Types of Intermolecular Forces

- ***van der Waals forces*** –between atoms and molecules of pure substances
  - ***Dipole-dipole interactions*** – attractive forces between polar molecules
  - ***Hydrogen bonding*** – attractive force in polar molecules containing a H atom bonded to a small, highly electronegative element (N, O and F)
  - **(*London*) Dispersion forces** – attractive forces arising from instantaneous dipoles and induced dipoles

Arrangement of Polar Molecules in a Liquid and a Solid.



Liquid

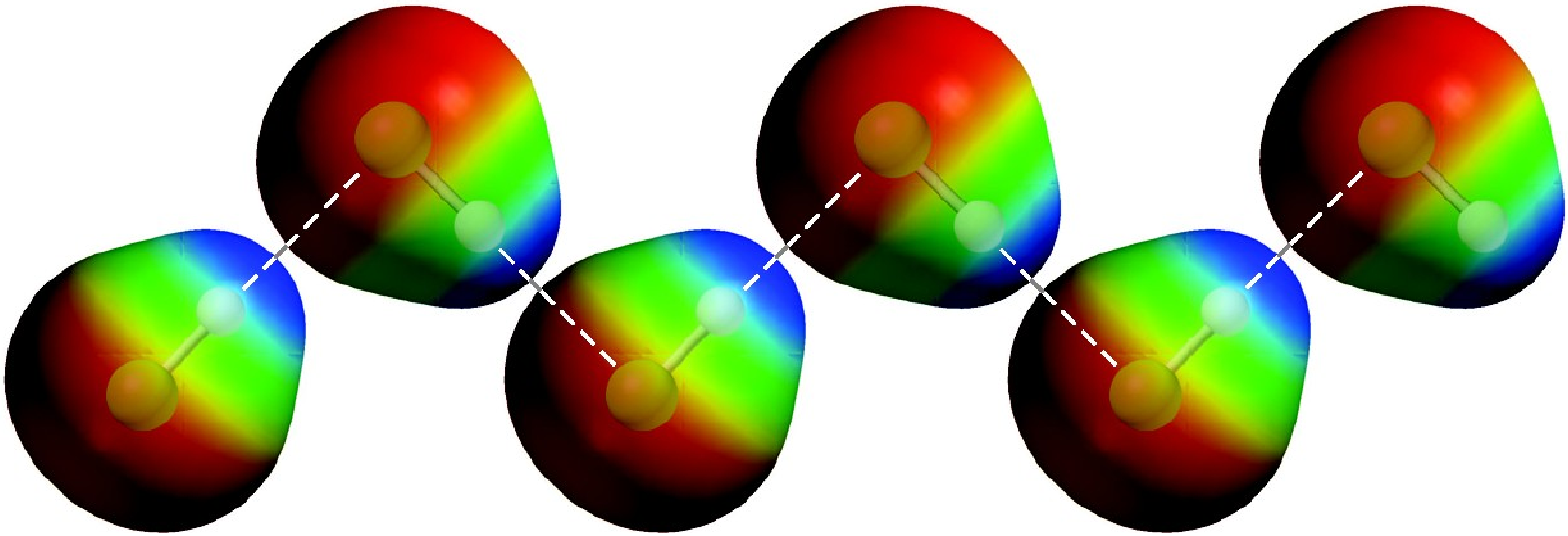


Solid

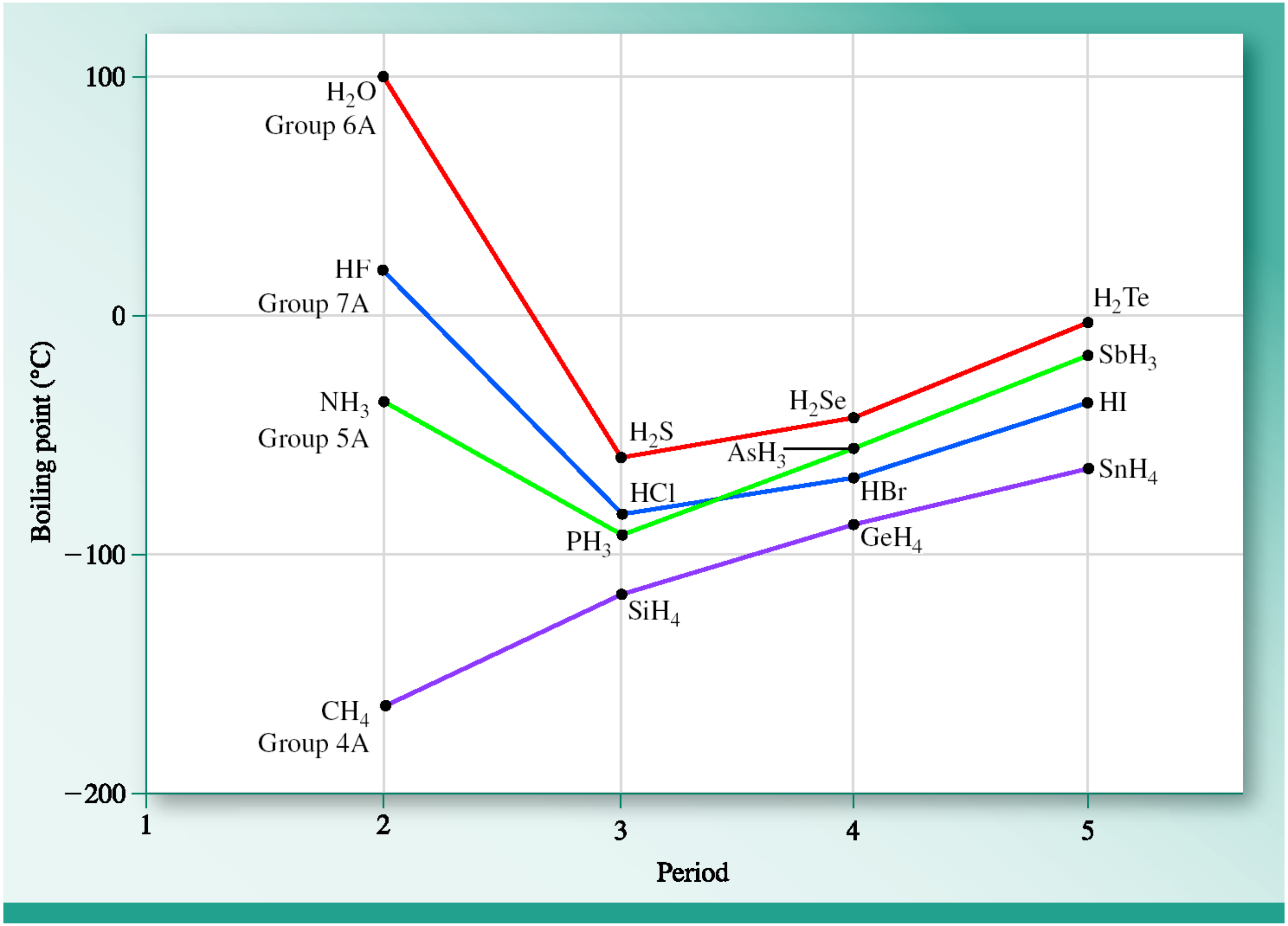
- Intermolecular forces determine certain physical properties.

TABLE 12.1	Dipole Moments and Boiling Points of Compounds with Similar Molecular Masses		
Compound	**Structural Formula**	**Dipole Moment (D)**	**Boiling Point (°C)**
Propane	$CH_3CH_2CH_3$	0.1	−42
Dimethyl ether	CH_3OCH_3	1.3	−25
Methyl chloride	CH_3Cl	1.9	−24
Acetaldehyde	CH_3CHO	2.7	21
Acetonitrile	CH_3CN	2.9	82

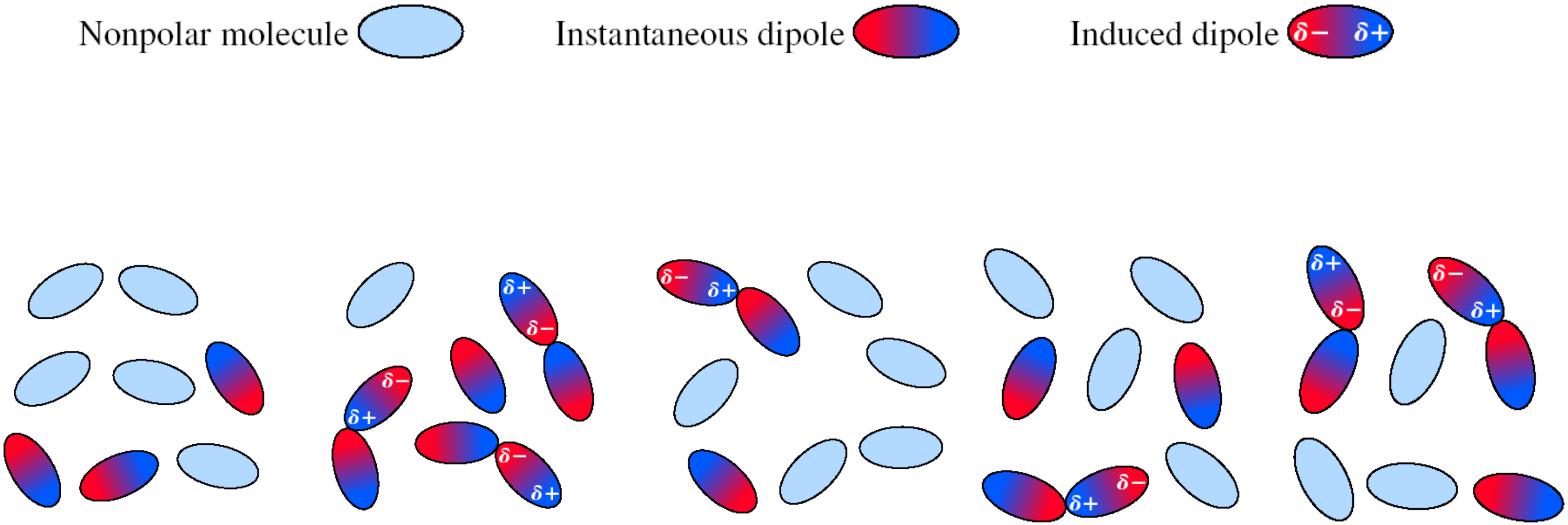
Hydrogen Bonds Between HF Molecules



Effect of Molar Mass and Hydrogen Bonding on Boiling Points



Instantaneous and Induced Dipoles



Magnitude depends on the ability to be ***polarized*** which is greater for larger molecules.

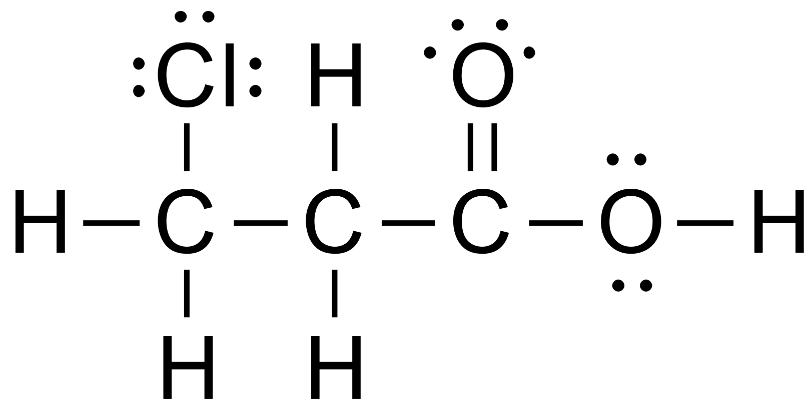
Polarization and Molar Mass

TABLE 12.2 Molar Masses, Boiling Points, and States of the Halogens at Room Temperature

Molecule	Molar Mass (g/mol)	Boiling Point (°C)	State (Room Temp.)
F_2	38.0	−188	Gas
Cl_2	70.9	−34	Gas
Br_2	159.8	59	Liquid
I_2	253.8	184	Solid

What kind(s) of intermolecular forces exist in

$CH_2ClCH_2COOH(l)$



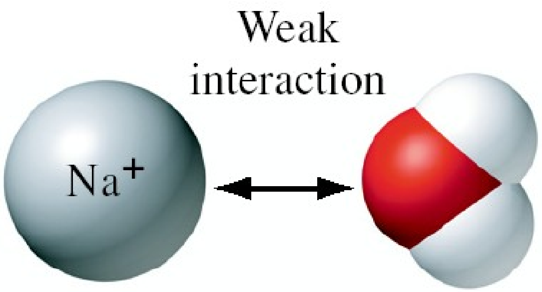
dispersion forces

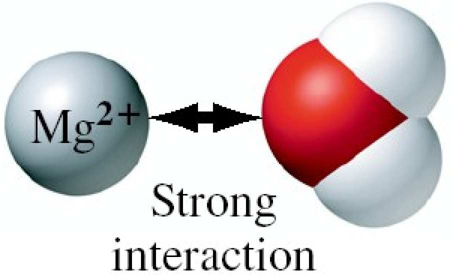
dipole-dipole interactions

hydrogen bonding

•*Ion-dipole Interactions*

- Occur in mixtures of ionic and polar species
- Coulombic attraction between ions and polar molecules
- Dependent upon
  - Size and charge of ion
  - Dipole moment of the molecule
  - Size of the molecule
- Can also be repulsive



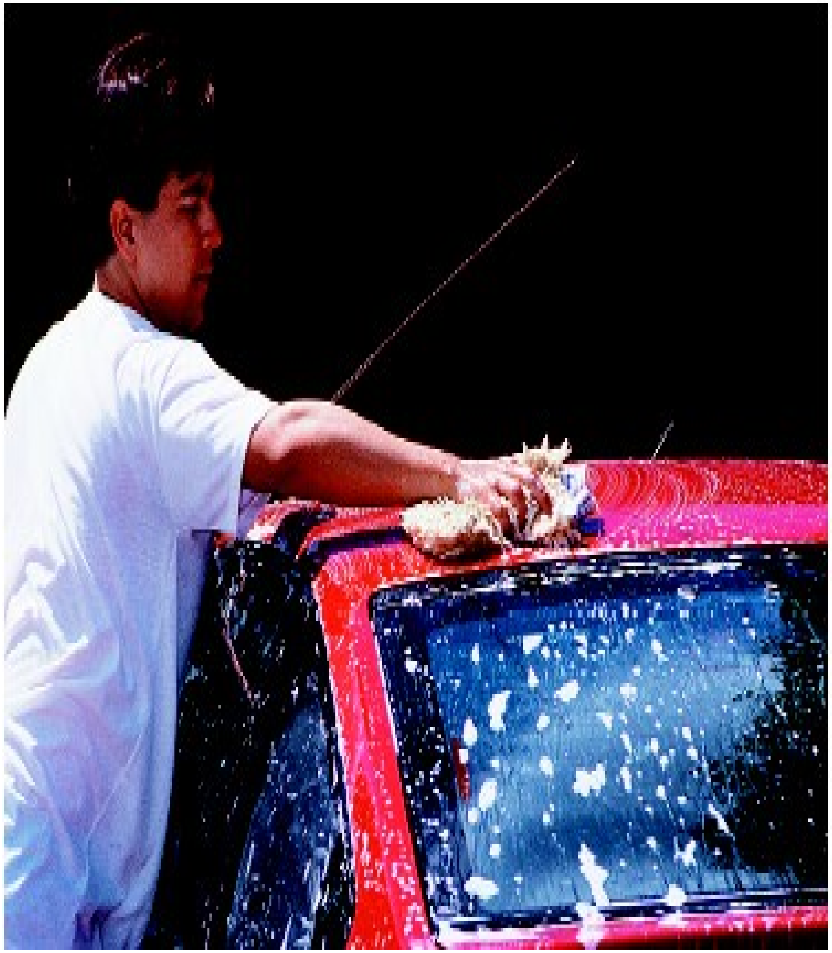


12.2 Properties of Liquids

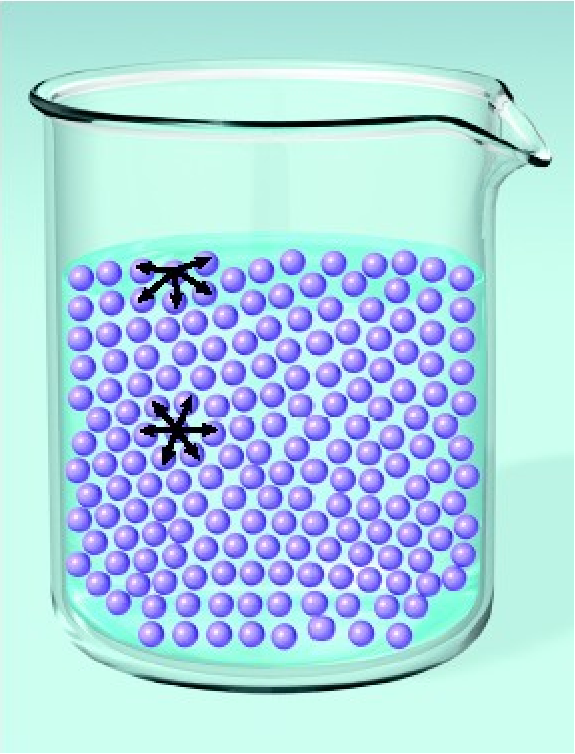
- ***Surface Tension*** – a quantitative measure of the elastic force at the surface of a liquid

- Manifestations
  - Formation of a *mensicus*
  - ***Capillary action*** which results from a combination of
    - ***Cohesion*** (attractions between like molecules, cohesive forces)
    - ***Adhesion*** (attractions between unlike molecules, adhesive forces)

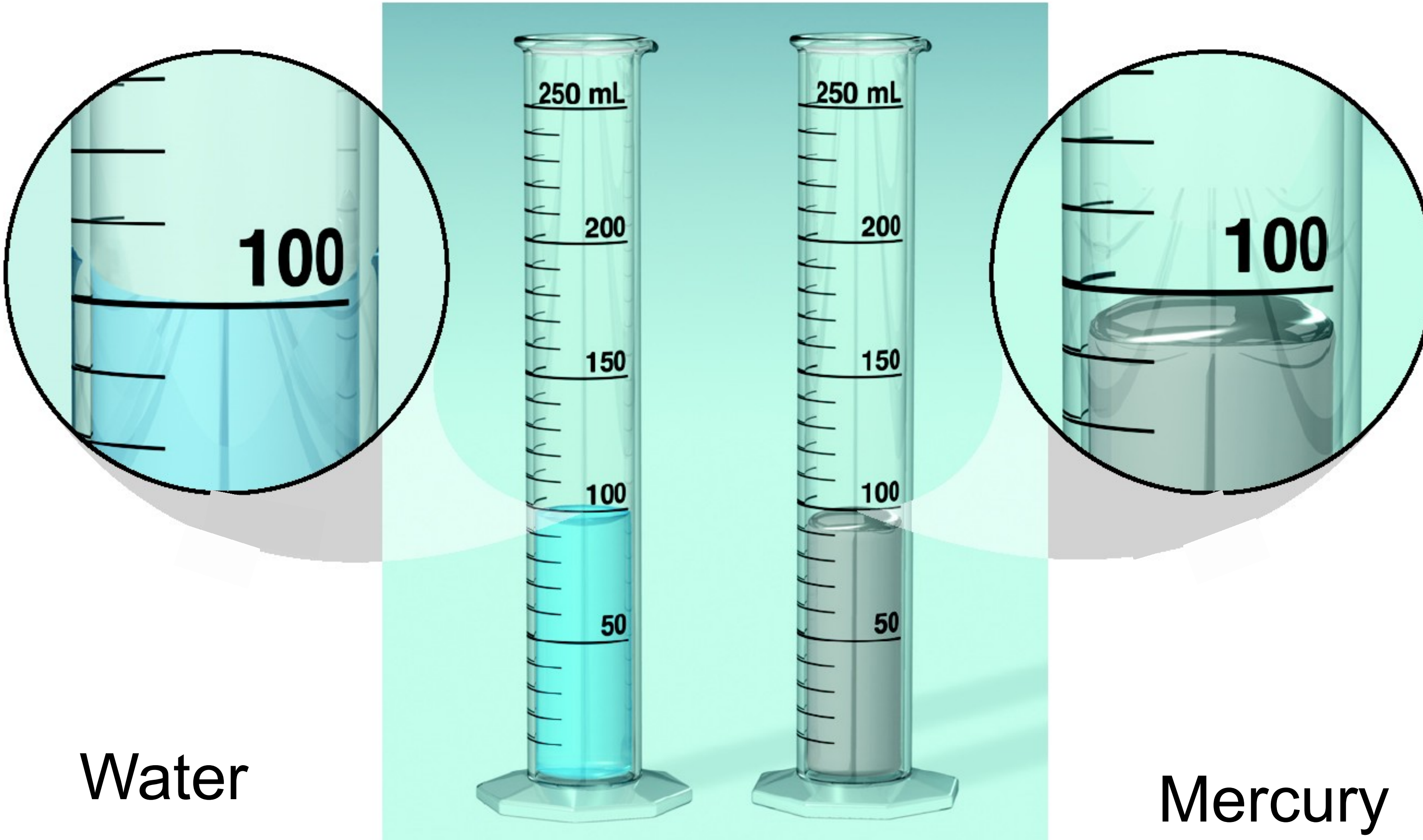
Effect of Surface Tension



Intermolecular Forces: Surface versus Interior of a Liquid



Cohesion and Adhesion



Water

Mercury

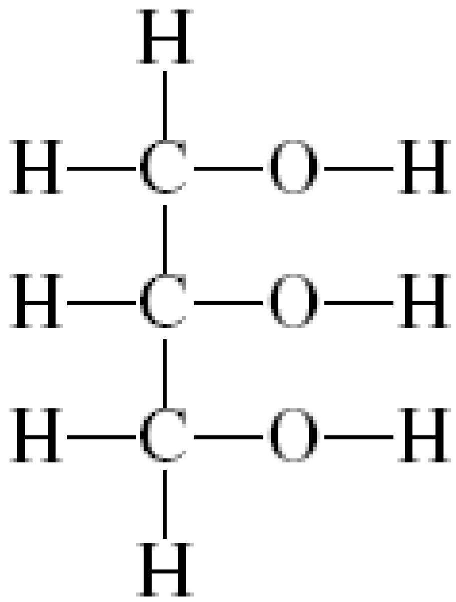
Adhesion > Cohesion

Cohesion > Adhesion

- ***Viscosity*** – a measure of a fluid's resistance to flow
  - Units: N·s/m^2
  - The higher the viscosity the greater the resistance to flow
  - Varies inversely with temperature
  - Stronger intermolecular forces produce higher viscosities

TABLE 12.3 Viscosities of Some Familiar Liquids at 20°C

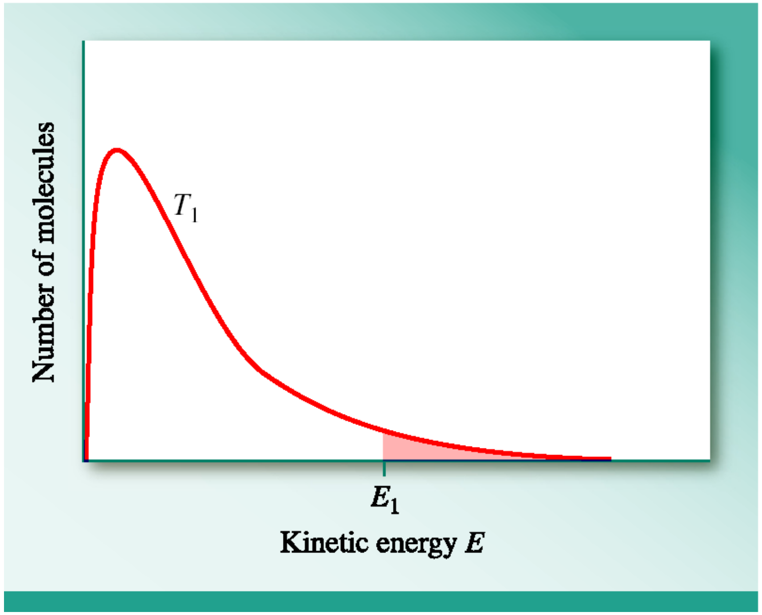
Liquid	Viscosity ($N \cdot s/m^2$)
Acetone (C_3H_6O)	3.16×10^{-4}
Water (H_2O)	1.01×10^{-3}
Ethanol (C_2H_5OH)	1.20×10^{-3}
Mercury (Hg)	1.55×10^{-3}
Blood	4×10^{-3}
Glycerol ($C_3H_8O_3$)	1.49

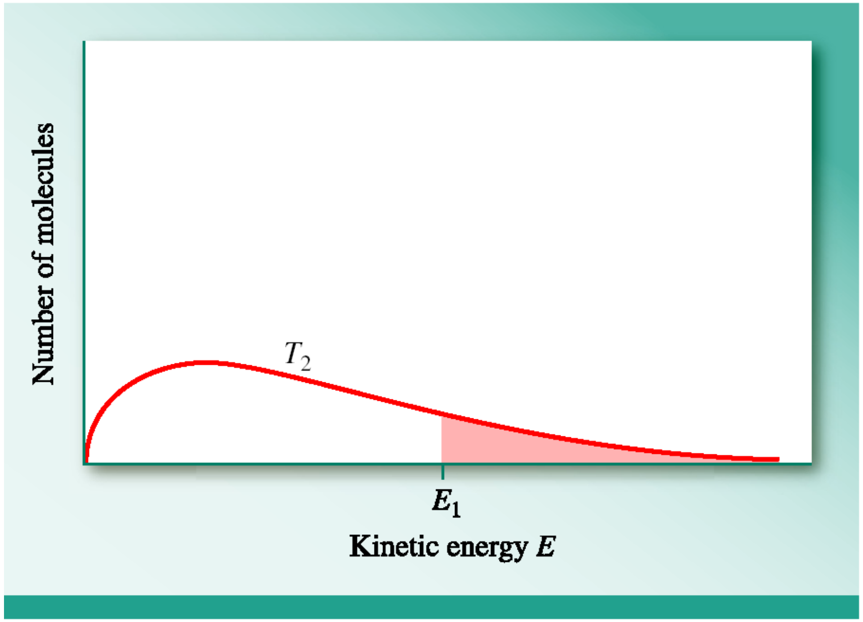


Glycerol – high viscocity due to

- Three hydrogen bonding sites
- Molecular shape

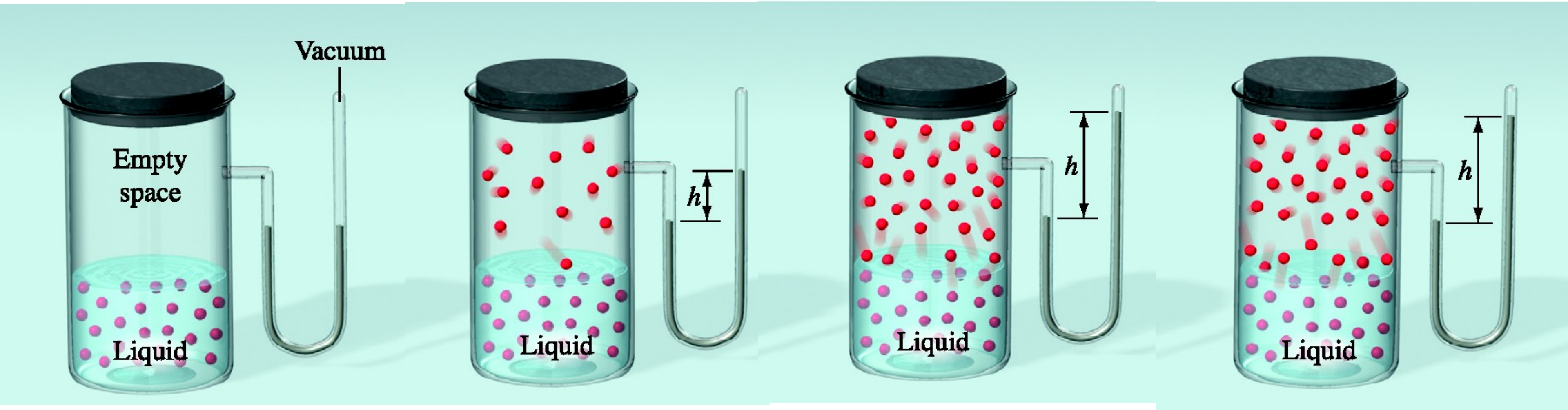
- ***Vapor Pressure*** of a Liquid
  – Depends on the magnitude of intermolecular forces
  – Temperature dependent





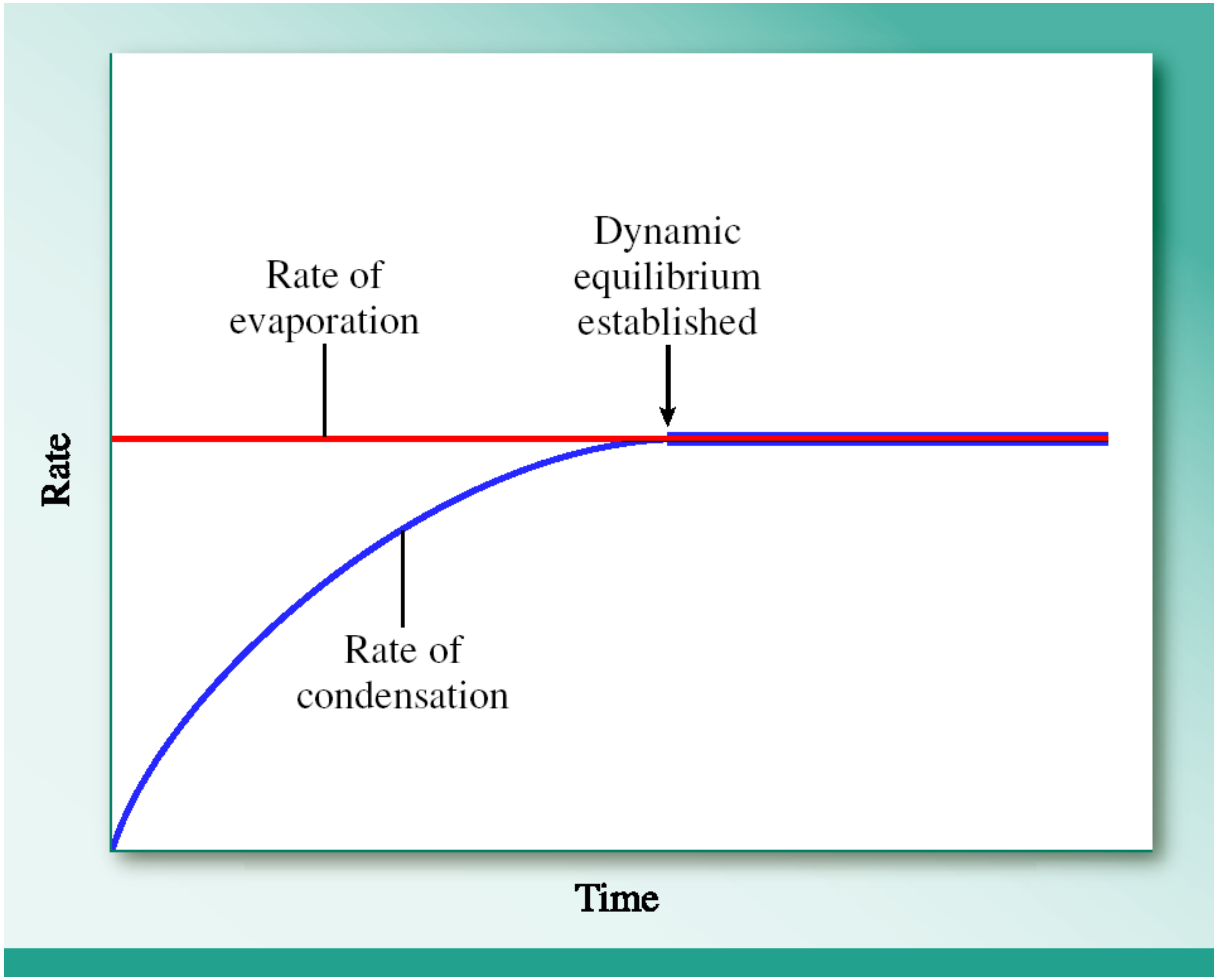
$T_1 < T_2$

- ***Equilibrium Vapor Pressure*** – a dynamic state

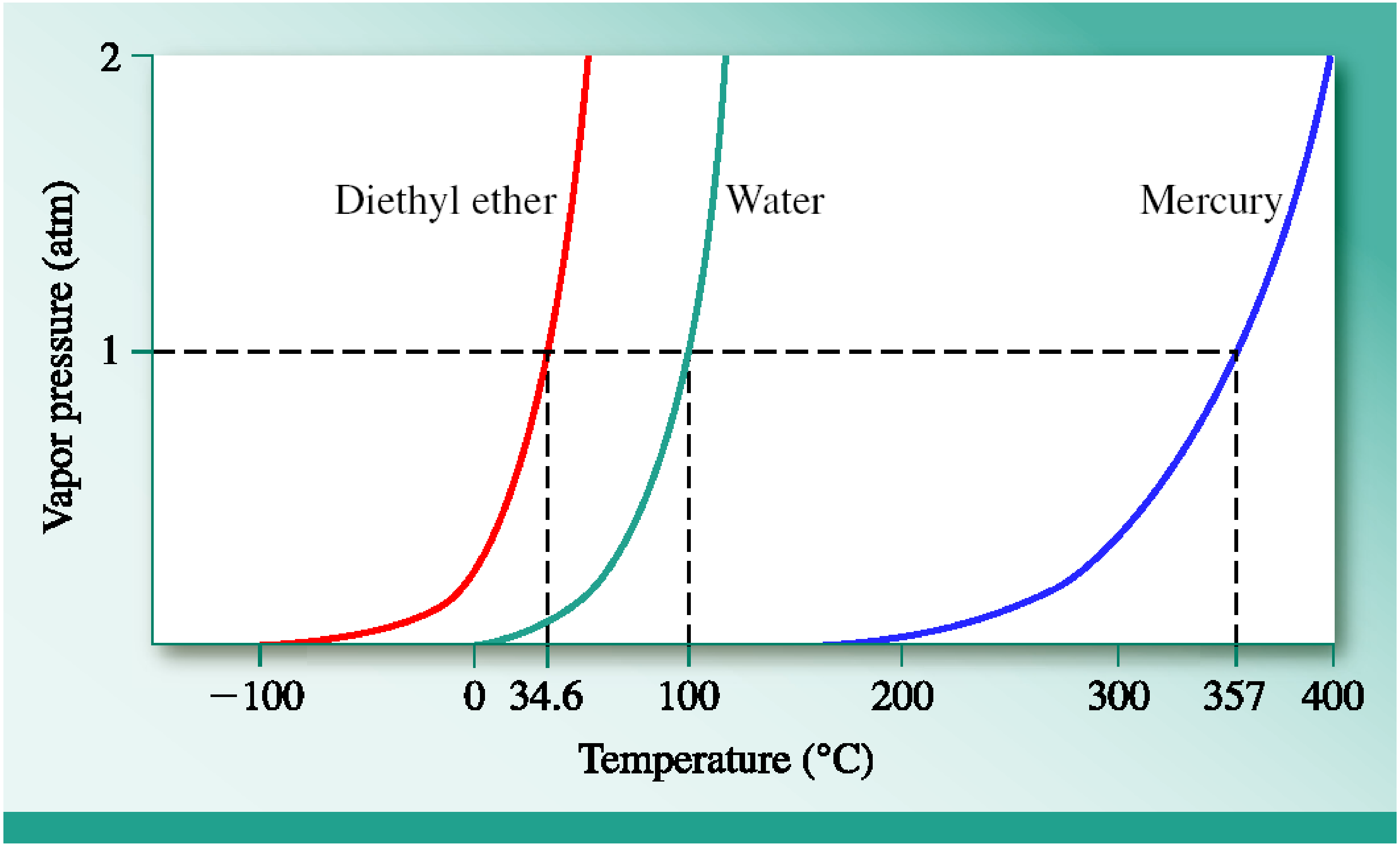


  - ***Evaporation*** (***vaporization***) – liquid molecules escape into the gas phase
  - ***Condensation*** – gas molecules return to the liquid phase

Comparison of Rates of Evaporation and Condensation at Constant Temperature



Effect of Temperature and Intermolecular Forces on Vapor Pressure



- ***Clausius-Clapeyron Equation*** – linear relation between temperature and vapor pressure

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

$$y \quad = \qquad mx \qquad + \ b$$

where R = 8.314 J/K · mol

– At two temperatures, T_1 and T_2:

$$\ln \frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

An unknown compound exhibits a vapor pressure of 255 mmHg at 25.5^{o}C and 434 mmHg at 48.8^{o}C. What is ΔH_{vap} of this substance?

$$T_1 = 25.5^o\text{C} + 273.15 = 298.65\text{ K}$$

$$T_2 = 48.8^o\text{C} + 273.15 = 321.95\text{ K}$$

$$\ln\frac{P_1}{P_2} = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{255\text{ mmHg}}{434\text{ mmHg}} = \frac{\Delta H_{vap}}{8.314\text{J/K}\cdot\text{mol}}\left(\frac{1}{321.95\text{ K}} - \frac{1}{298.65\text{ K}}\right)$$

$$-0.53178 = \frac{\Delta H_{vap}}{8.314\text{J/K}\cdot\text{mol}}\left(3.1061\text{x}10^{-3} - 3.3484\text{x}10^{-3}\right)$$

$$-0.53178 = \frac{\Delta H_{vap}}{8.314 \text{J/K} \cdot \text{mol}}\left(-2.423\text{x}10^{-4}\ \text{K}^{-1}\right)$$

$$\frac{(-0.53178)(8.314 \text{J/K} \cdot \text{mol})}{-2.423\text{x}10^{-4}\ \text{K}^{-1}} = \Delta H_{vap}$$

$$1.82 \text{ x } 10^{4} \text{ J/mol} = \Delta H_{\text{vap}}$$

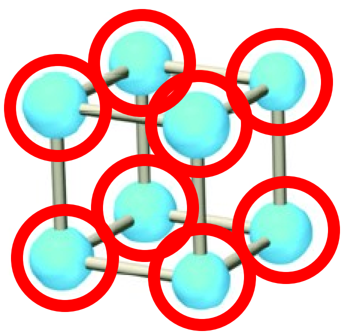
$$18.2 \text{ kJ/mol} = \Delta H_{\text{vap}}$$

12.3 Crystal Structure

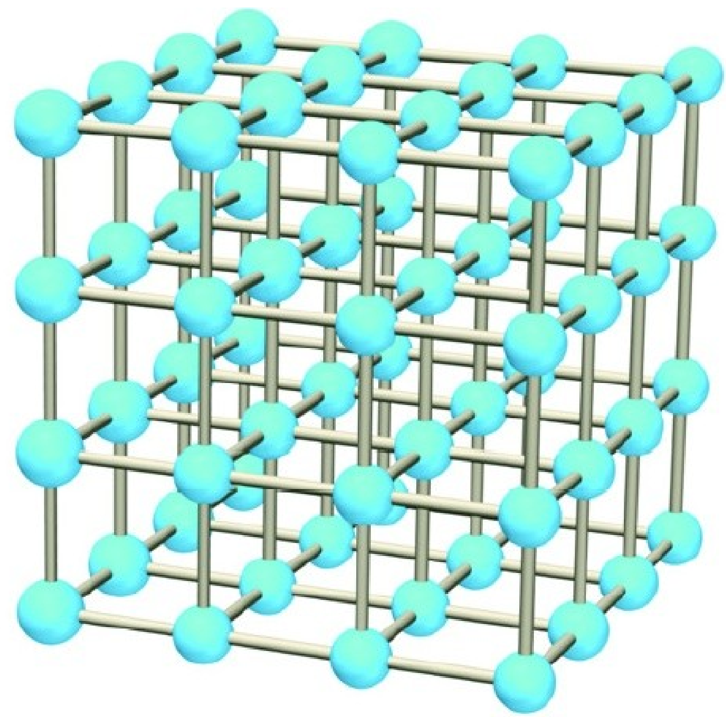
- ***Crystalline solid*** – possesses rigid and long-range order
- ***Lattice structure*** – arrangement of particles in a crystalline solid
  - Depends on nature of particles
  - Depends on size of particles
- Stability depends on type of force between particles (ionic or covalent bonds and/or intermolecular forces)

unit cell – basic repeating structural unit of a crystalline solid

lattice point – each atom ion or molecule in a unit cell

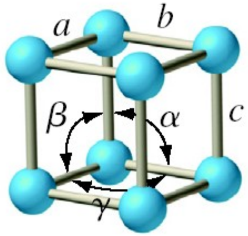


single unit cell

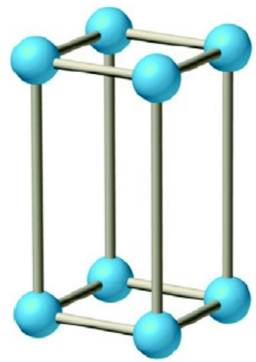


3-D array of unit cells

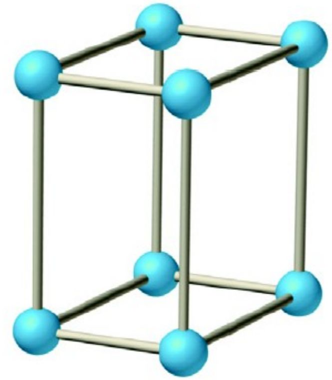
Seven Types of Unit Cells



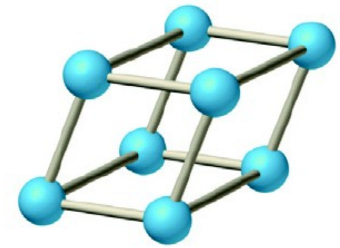
Simple cubic
$a = b = c$
$\alpha = \beta = \gamma = 90^\circ$



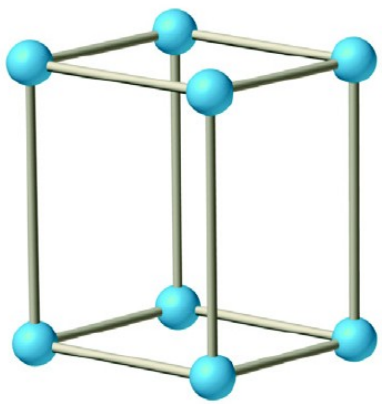
Tetragonal
$a = b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



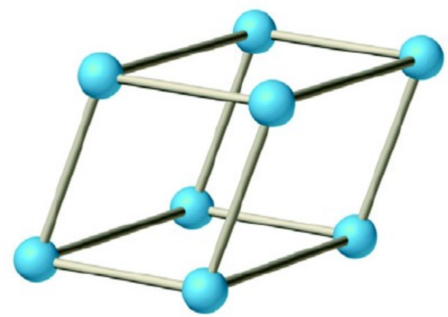
Orthorhombic
$a \neq b \neq c$
$\alpha = \beta = \gamma = 90^\circ$



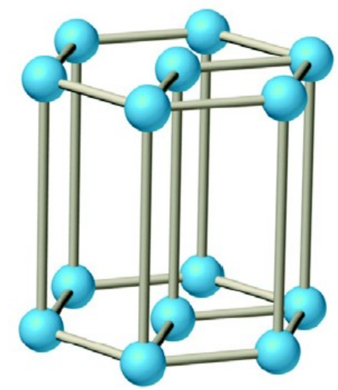
Rhombohedral
$a = b = c$
$\alpha = \beta = \gamma \neq 90^\circ$



Monoclinic
$a \neq b \neq c$
$\gamma \neq \alpha = \beta = 90^\circ$



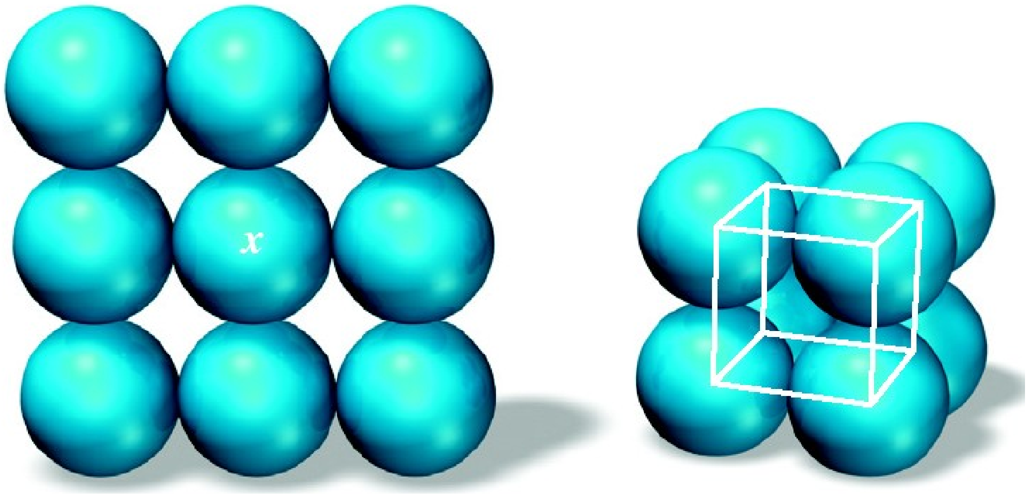
Triclinic
$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90^\circ$



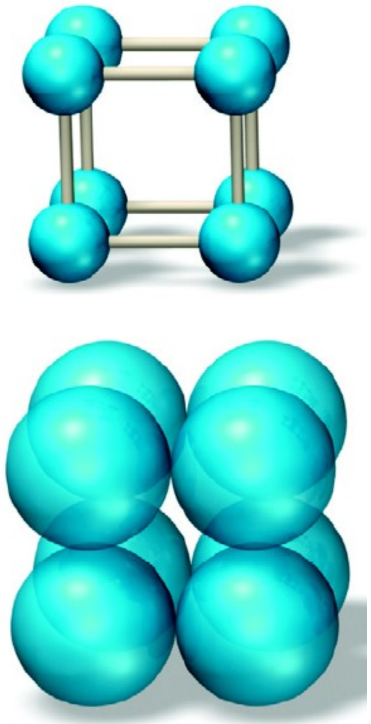
Hexagonal
$a = b \neq c$
$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

Coordination number – number of atoms (particles) surrounding an atom in a crystal lattice

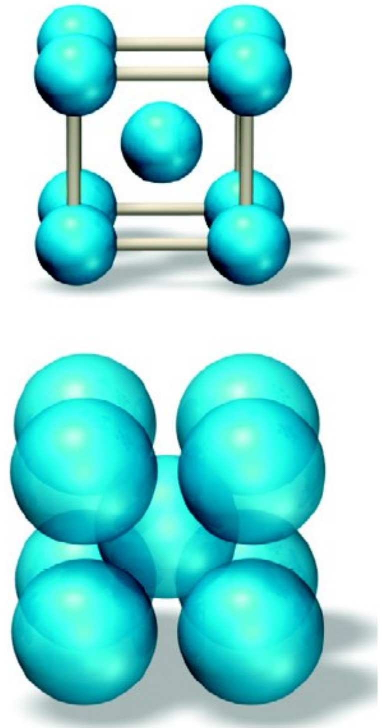
- Indicates how tightly atoms pack
- Larger coordination numbers indicate tighter packing



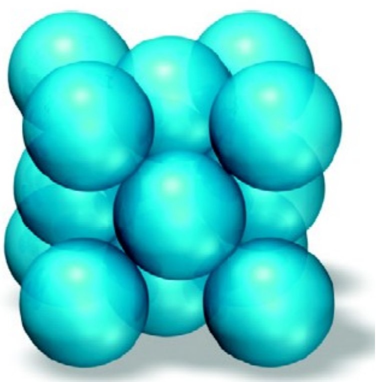
- Types of cubic unit cells
  - simple or primitive (scc)
  - body-centered (bcc)
  - face-centered (fcc)



Primitive cubic

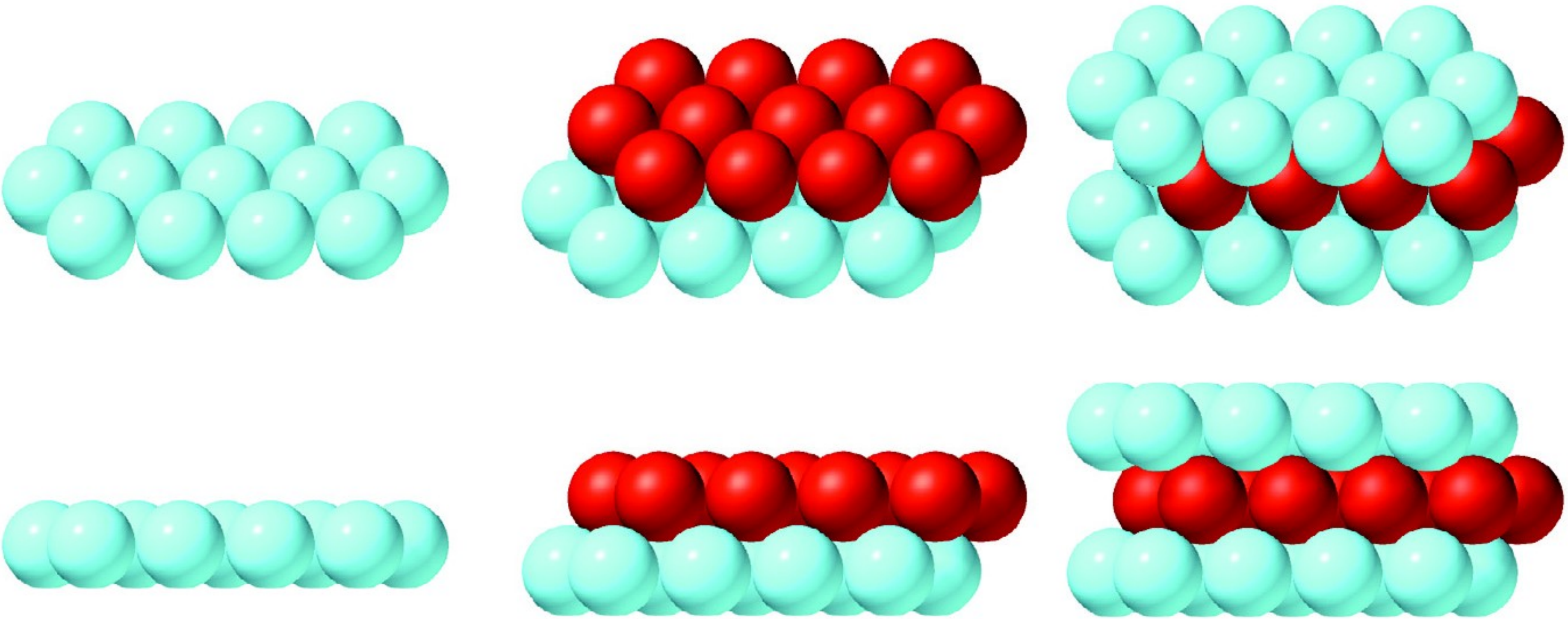


Body-centered cubic

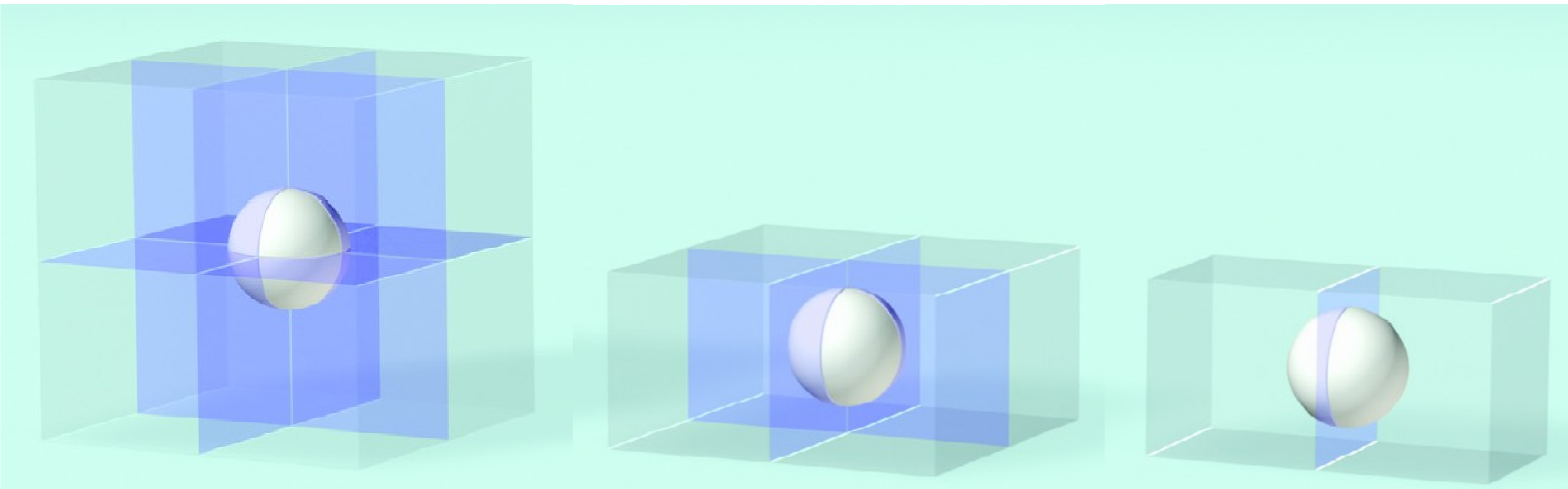


Face-centered cubic

Alternate Perspective of bcc Arrangement

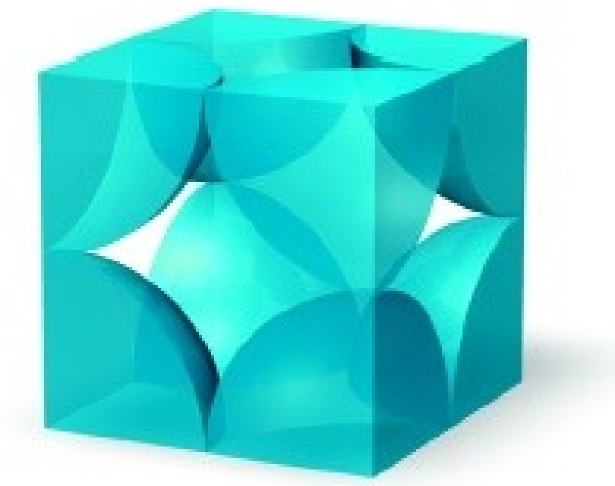


Sharing of Atoms by Adjacent Unit Cells



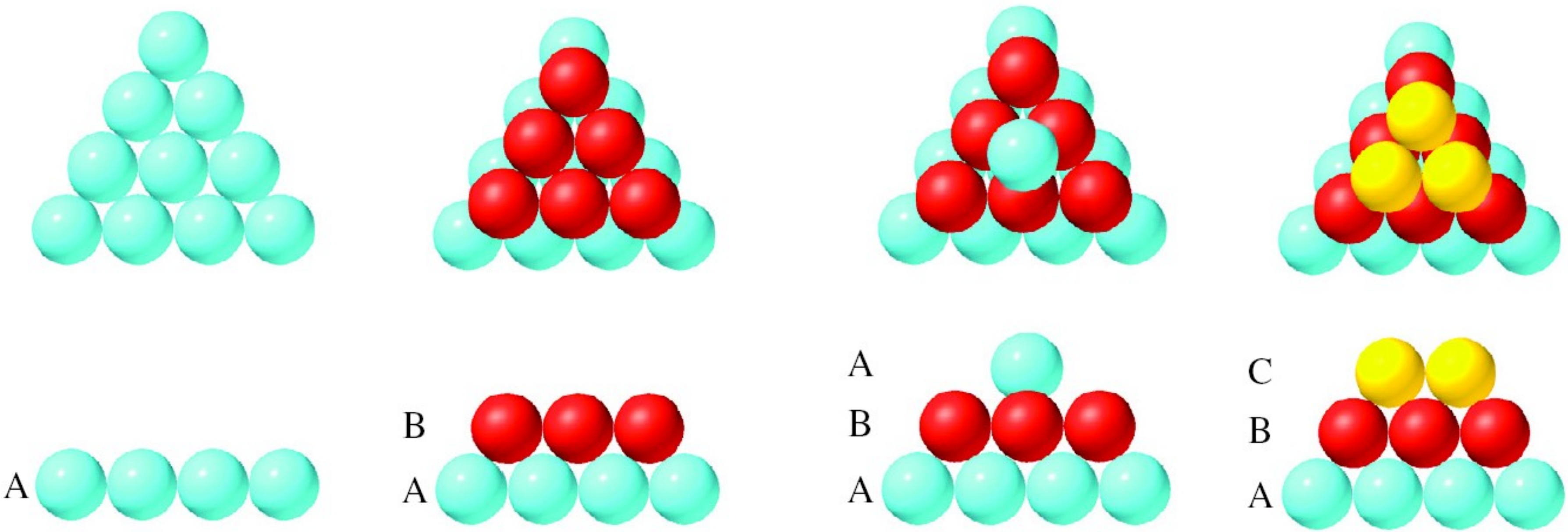
corner atom   edge atom   face atom

- Allocation of atoms among unit cells
  - corner atoms – $^1/_8$ atom within unit cell
  - face atoms – $^1/_2$ atom within unit cell
  - body atoms – 1 atom within unit cell



- Number of atoms per unit cel
  - scc: 1 atom
  - bcc: 2 atoms
  - fcc: 4 atoms

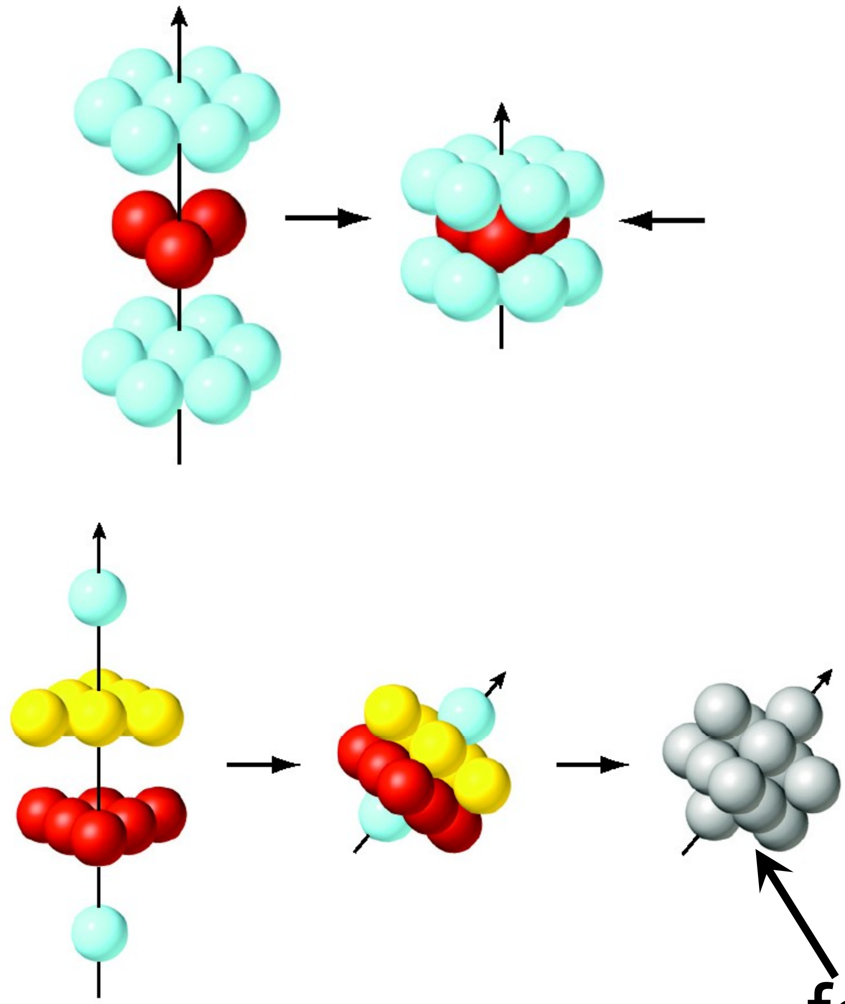
- ***Closest Packing*** – most efficient way to arrange atoms in a crystal
  - hexagonal closest packed (ABA)
  - cubic closest packed (ABC)



Closest Packing and Cubic Unit Cells

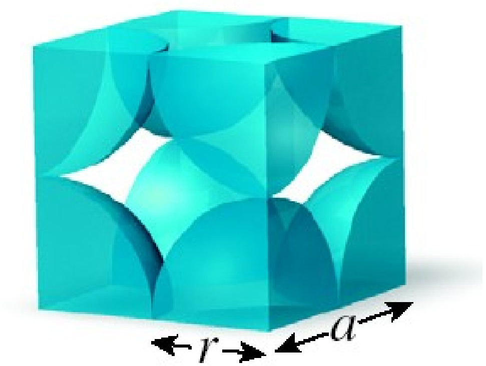
hexagonal

cubic



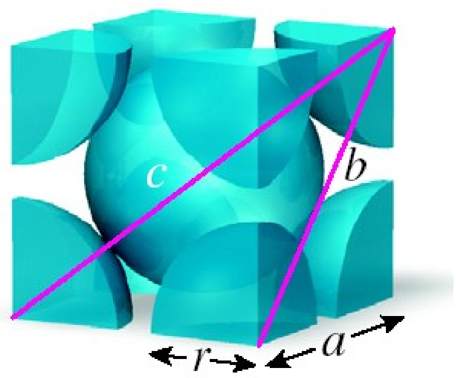
fcc

Geometric Relationships



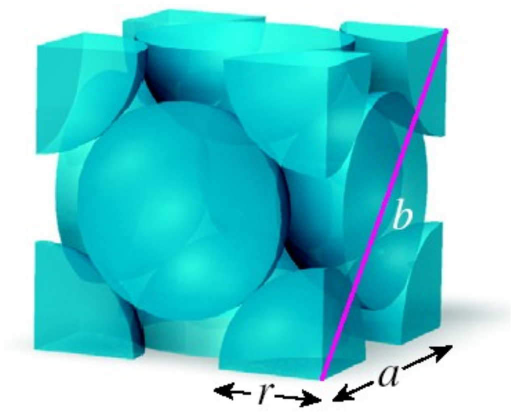
scc

$$a = 2r$$



bcc

$$\begin{aligned} b^2 &= a^2 + a^2 \\ c^2 &= a^2 + b^2 \\ &= 3a^2 \\ c &= \sqrt{3}a = 4r \\ a &= \frac{4r}{\sqrt{3}} \end{aligned}$$



fcc

$$\begin{aligned} b &= 4r \\ b^2 &= a^2 + a^2 \\ 16r^2 &= 2a^2 \\ a &= \sqrt{8}r \end{aligned}$$

When silver crystallizes, it forms face-centered cubic cells. The unit cell edge length is 4.087Å . Calculate the density of silver.

Mass of unit cell

$$m = \frac{4 \text{ atoms}}{\text{unit cell}} \times \frac{107.9 \text{ amu}}{\text{atom}} \times \frac{1 \text{ g}}{6.022 \times 10^{23} \text{ amu}} = 7.167 \times 10^{-22} \text{ g}$$

Volume of unit cell

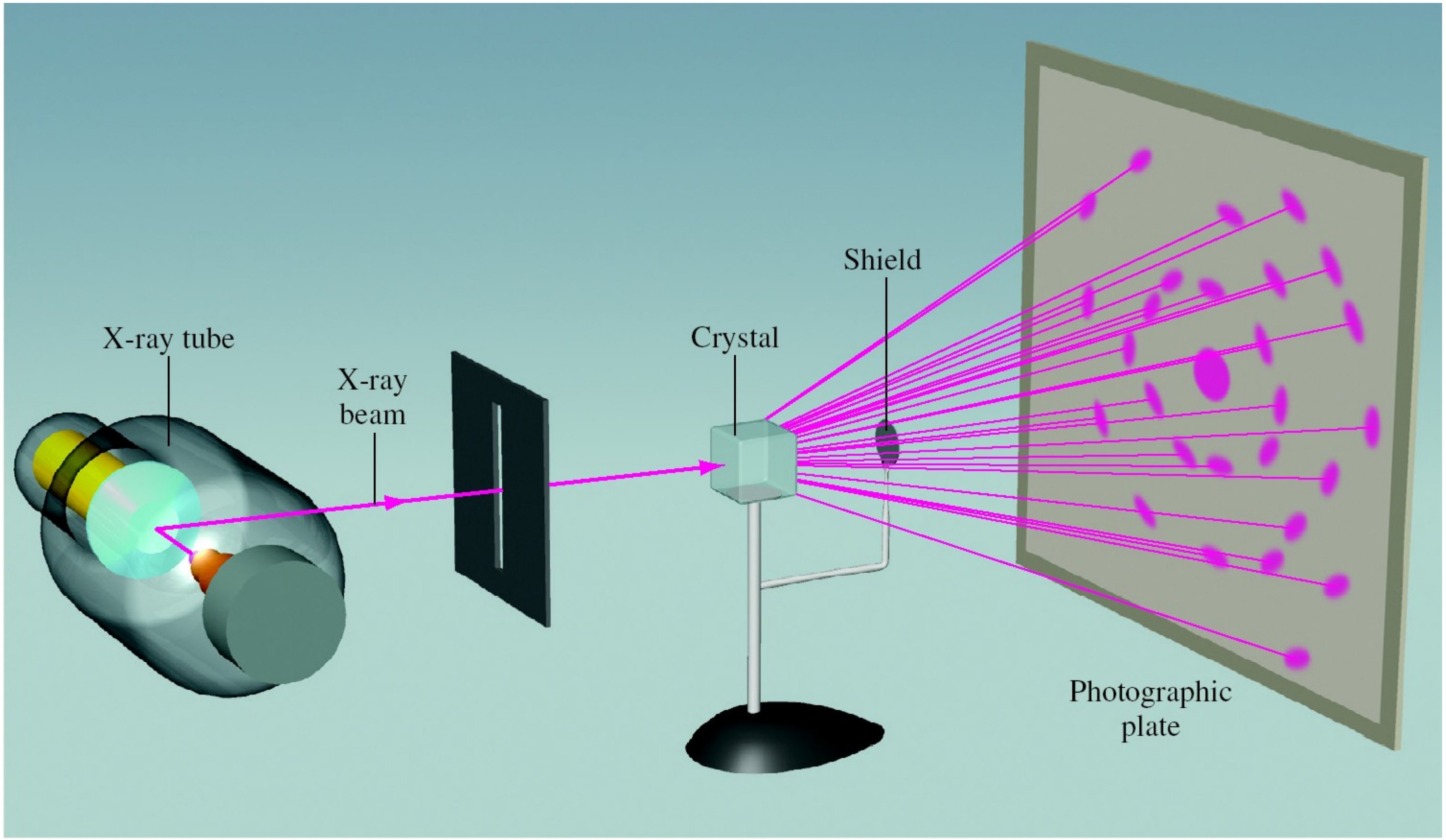
$$a = 4.087 \text{ Å} \times \frac{1 \text{ m}}{1 \times 10^{10} \text{ Å}} \times \frac{100 \text{ cm}}{1 \text{ m}} = 4.087 \times 10^{-8} \text{ cm}$$

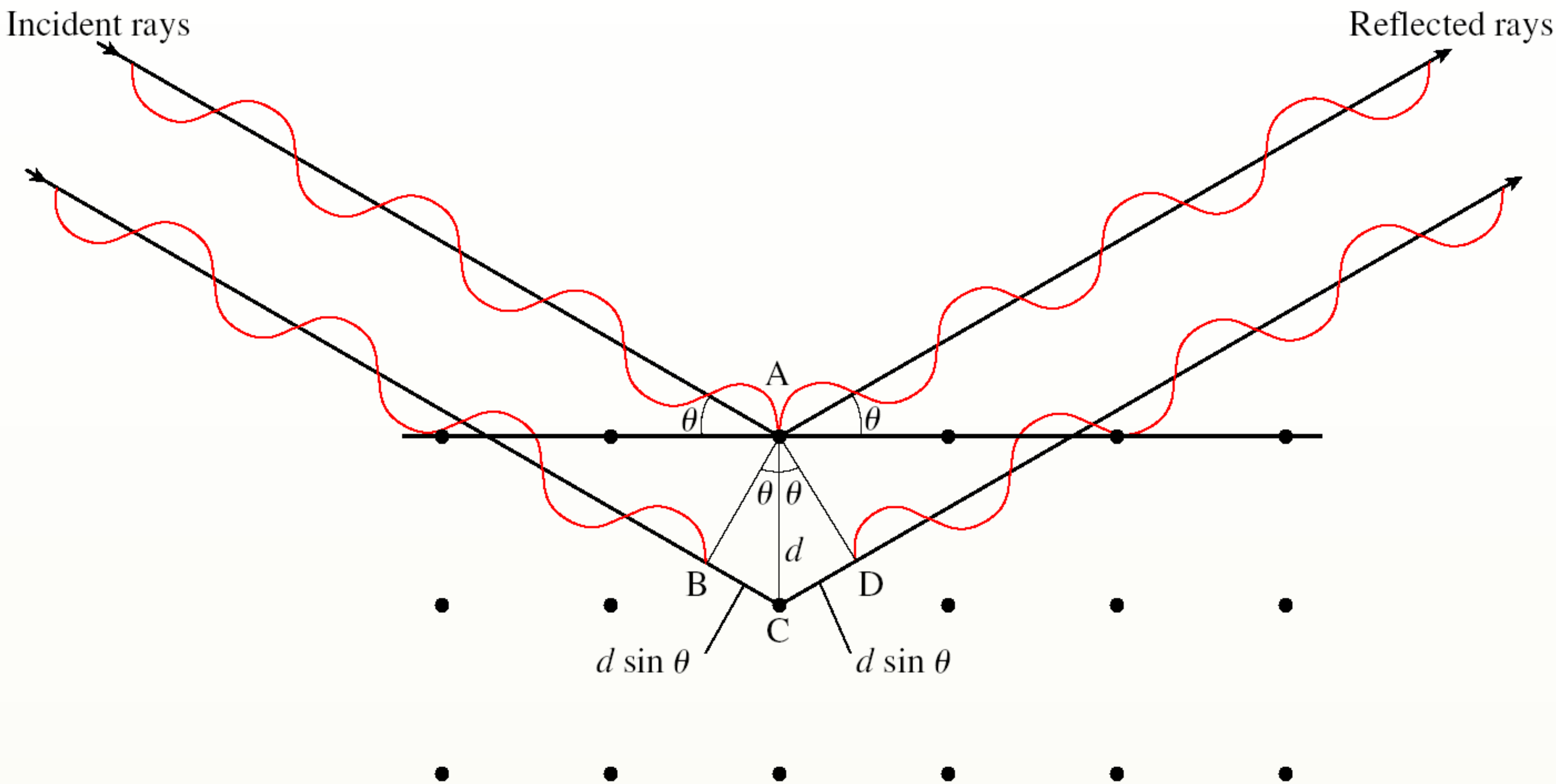
$$V = a^3 = \left(4.087 \times 10^{-8} \text{ cm}\right)^3 = 6.827 \times 10^{-23} \text{ cm}^3$$

Density of unit cell

$$d = \frac{m}{V} = \frac{7.167 \times 10^{-22} \text{ g/unit cell}}{6.827 \times 10^{-23} \text{ cm}^3\text{/unit cell}} = 10.5 \text{ g/cm}^3$$

- ***X-ray diffraction*** utilizes the scattering of X-rays and the resulting scattering patterns to deduce arrangement of particles





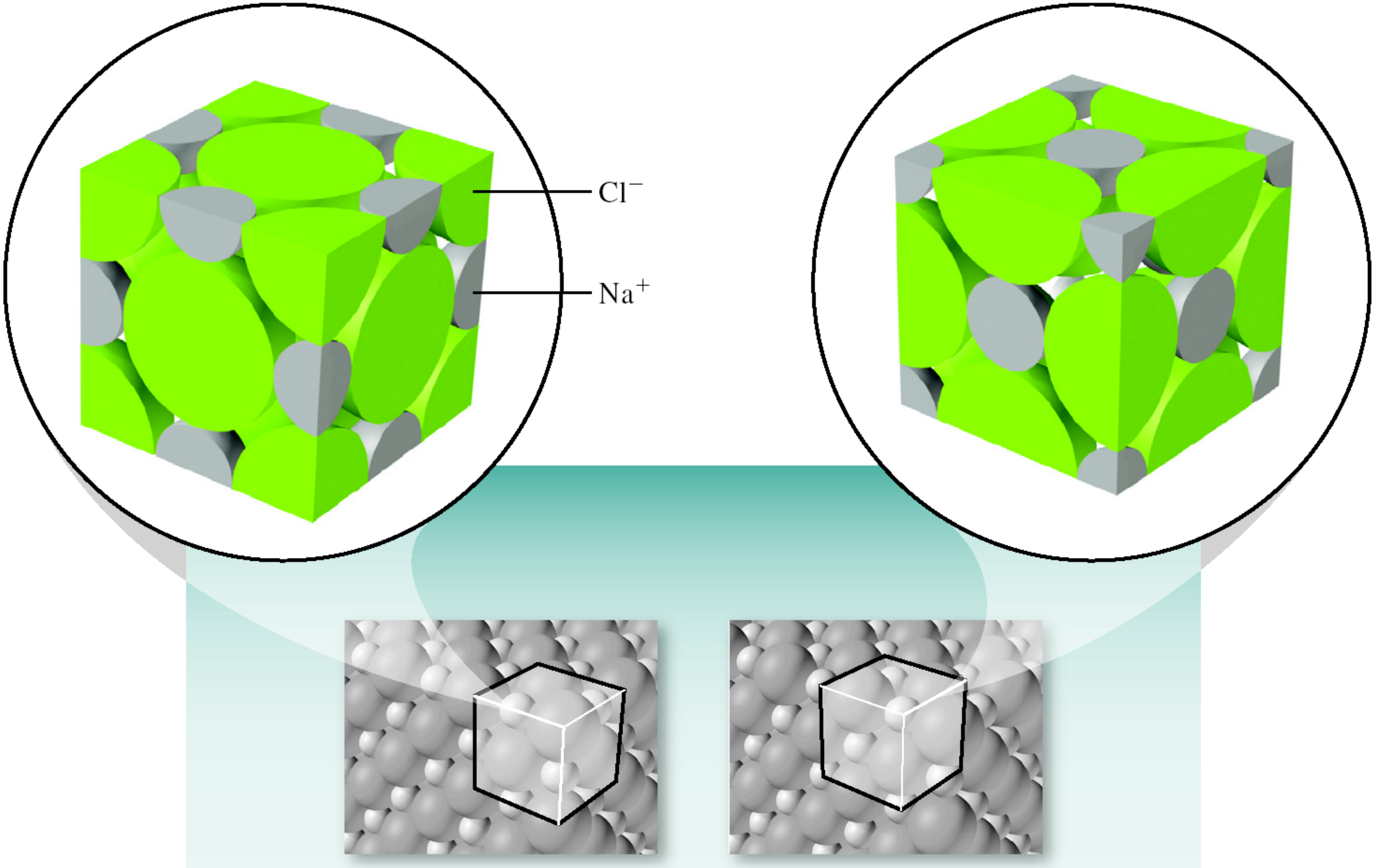
– ***Bragg equation***

$$BC + CD = 2d \sin \theta = n\lambda \qquad n = 1, 2, 3, \ldots$$

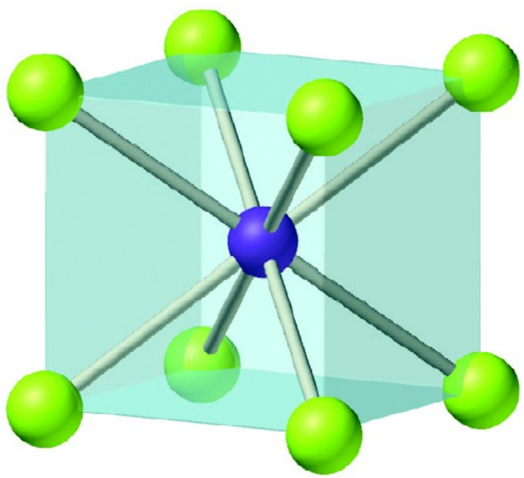
12.4 Types of Crystals

- Ionic Crystals
  - Composed of anions and cations
  - Held together by coulombic forces
  - Anions generally are bigger than cations
  - Size and relative number of each ion determines the crystal structure

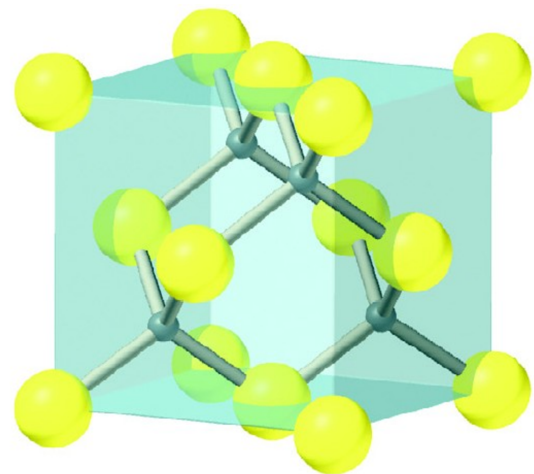
Unit cell of NaCl as Defined by Cl^- or Na^+



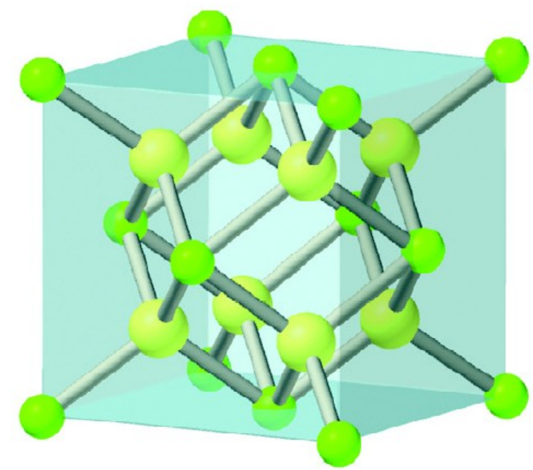
Examples of Ionic Crystal Lattices



$CsCl$

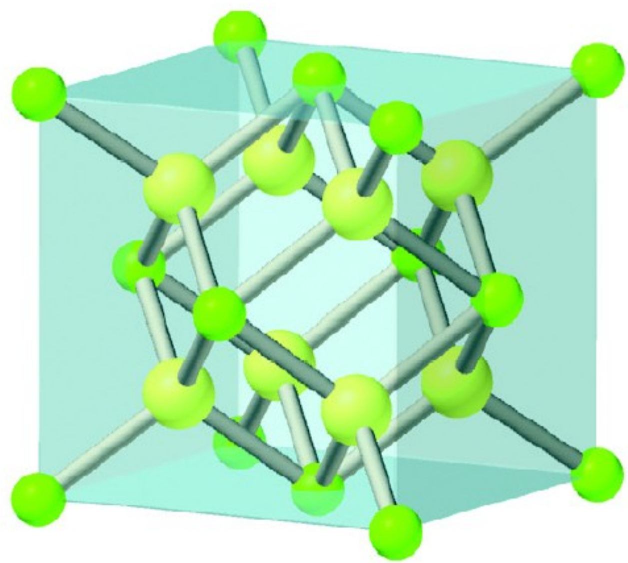


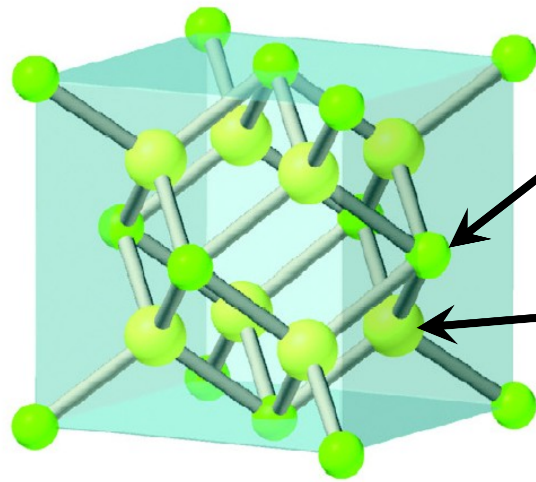
ZnS



CaF_2

How many of each ion are contained within a unit cell of CaF_2?





Ca^{2+}

8 corner ions x $^{1}/_{8}$ = 1 ion

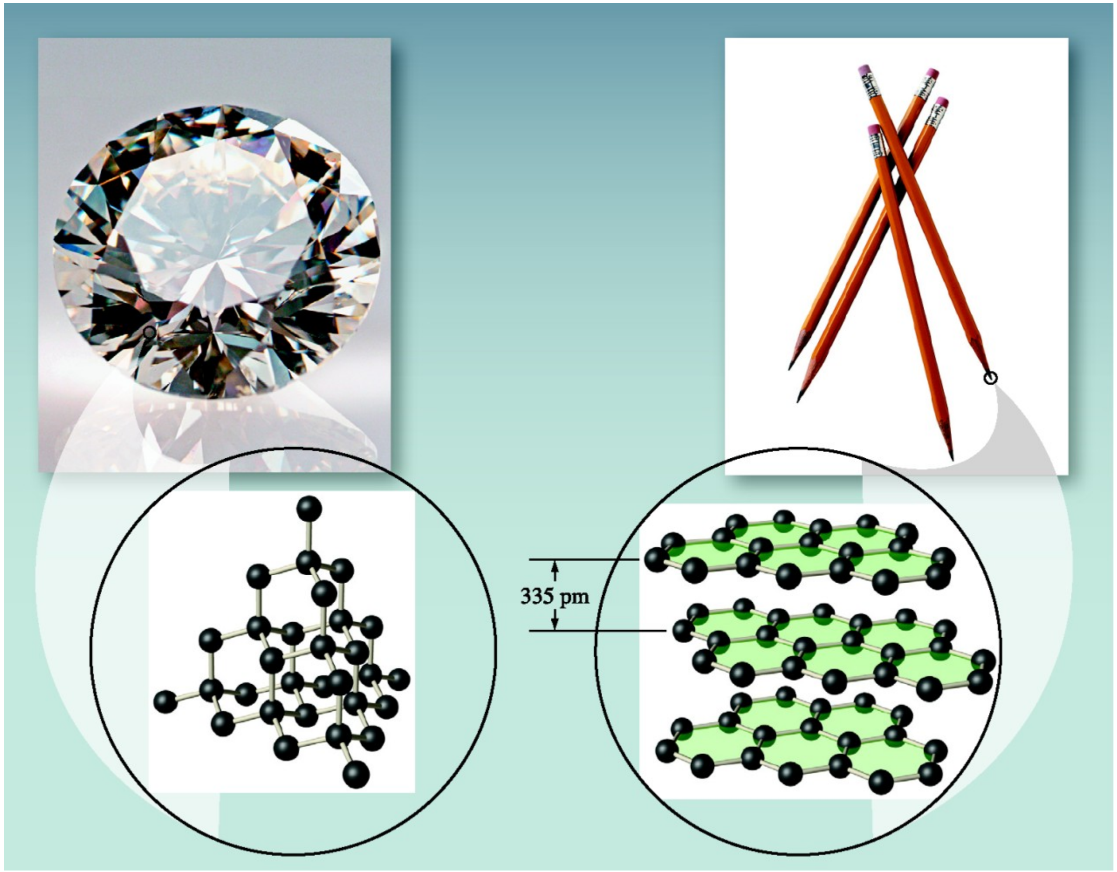
6 face ions x ½ = $\underline{\text{ 3 ions}}$

4 ions of Ca^{2+}

F^{-}

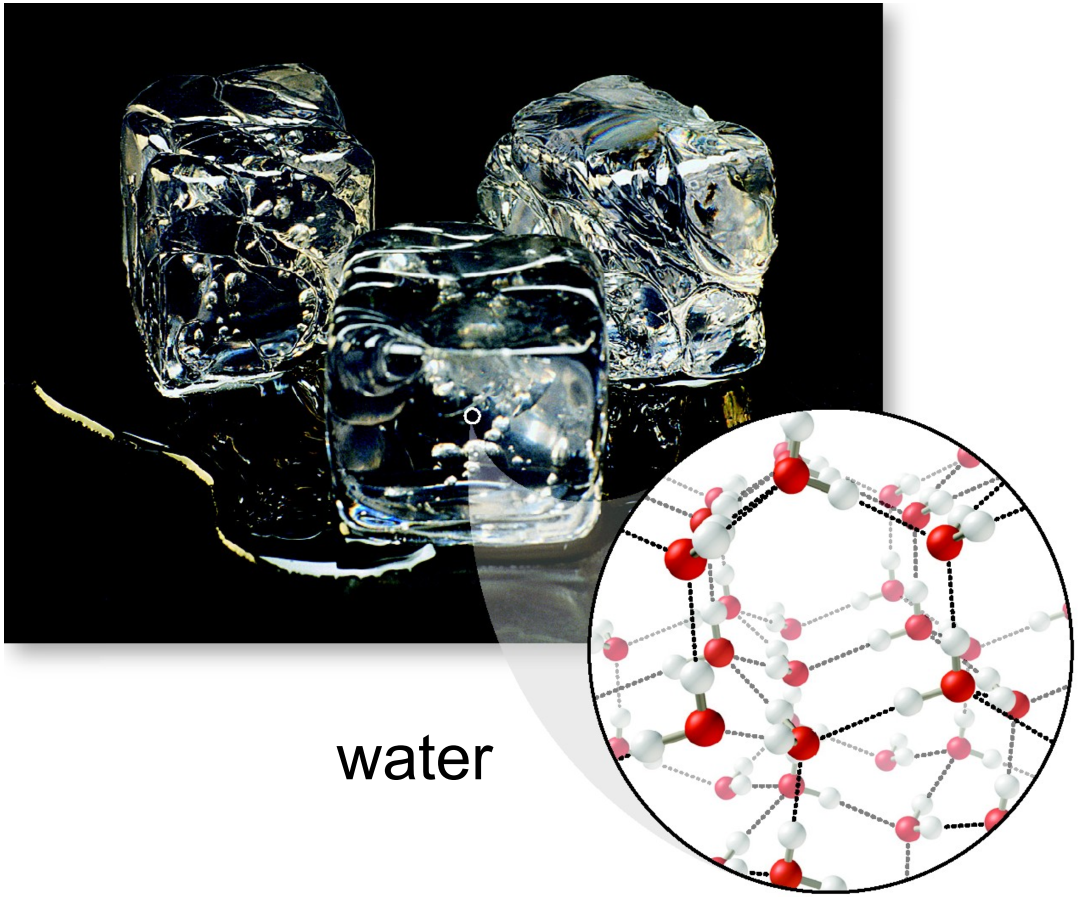
8 body ions x 1 = 8 ions of F^{-}

- Covalent crystals
  - Held together by covalent bonds



diamond graphite

- Molecular crystals
  - Lattice points occupied by molecules
  - Held together by intermolecular forces



water

- Metallic crystals
  - Lattice points occupied by atoms
  - Generally bcc, fcc, hexagonal closest packed
  - Very dense
  - Bonding arises from delocalized electrons

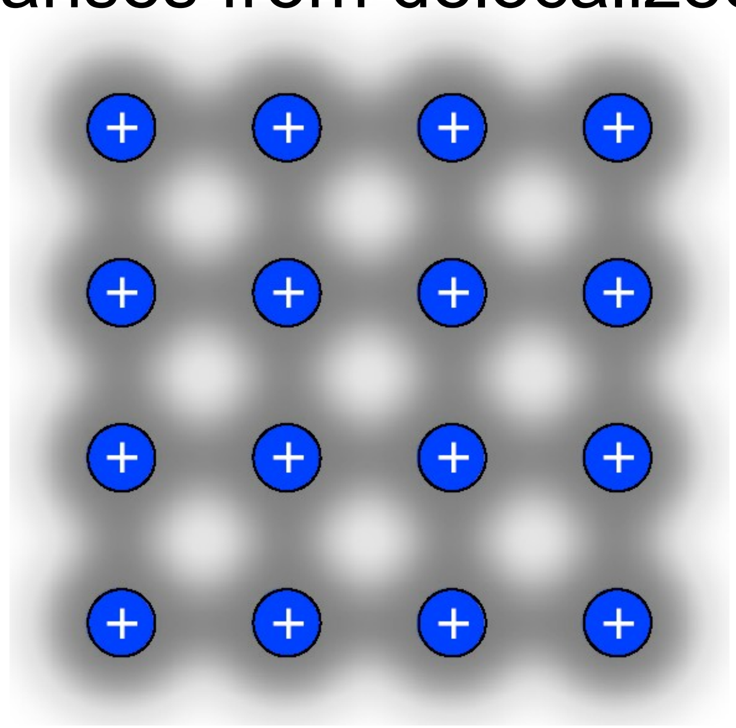


TABLE 12.4 Types of Crystals and Their General Properties

Type of Crystal	Cohesive Forces	General Properties	Examples
Ionic	Coulombic attraction and dispersion forces	Hard, brittle, high melting point, poor conductor of heat and electricity	$NaCl$, LiF, MgO, $CaCO_3$
Covalent	Covalent bonds	Hard, brittle, high melting point, poor conductor of heat and electricity	C (diamond),* SiO_2 (quartz)
Molecular†	Dispersion and dipole-dipole forces, hydrogen bonds	Soft, low melting point, poor conductor of heat and electricity	Ar, CO_2, I_2, H_2O, $C_{12}H_{22}O_{11}$
Metallic	Metallic bonds	Variable hardness and melting point, good conductor of heat and electricity	All metallic elements, such as Na, Mg, Fe, Cu

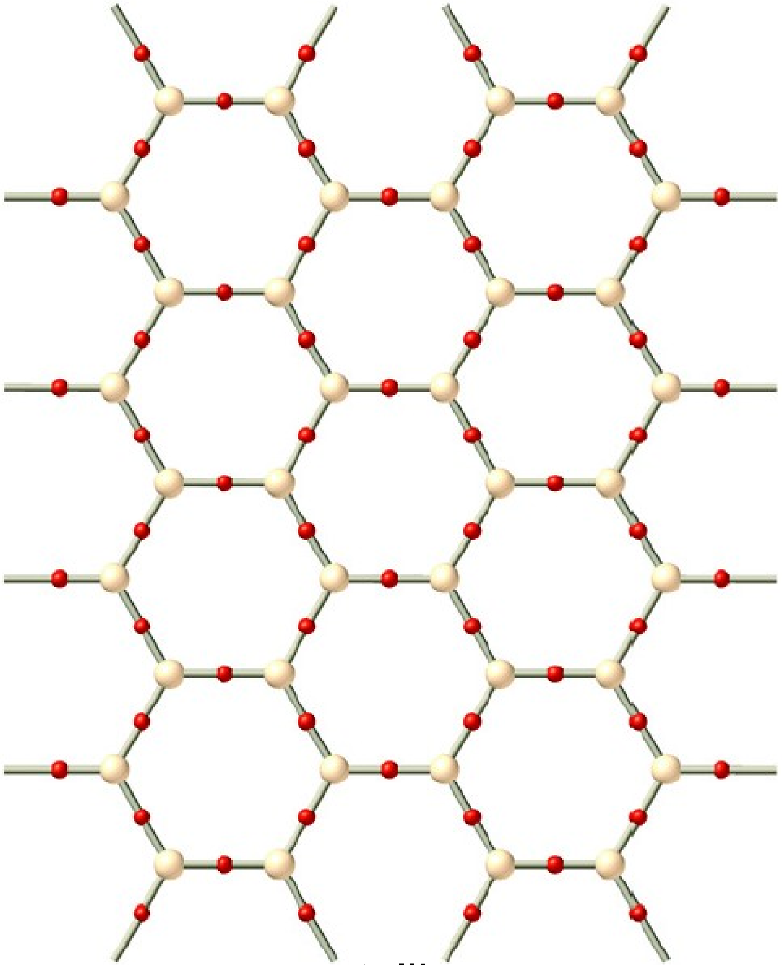
*Diamond is a good conductor of heat.

†Included in this category are crystals made up of individual atoms.

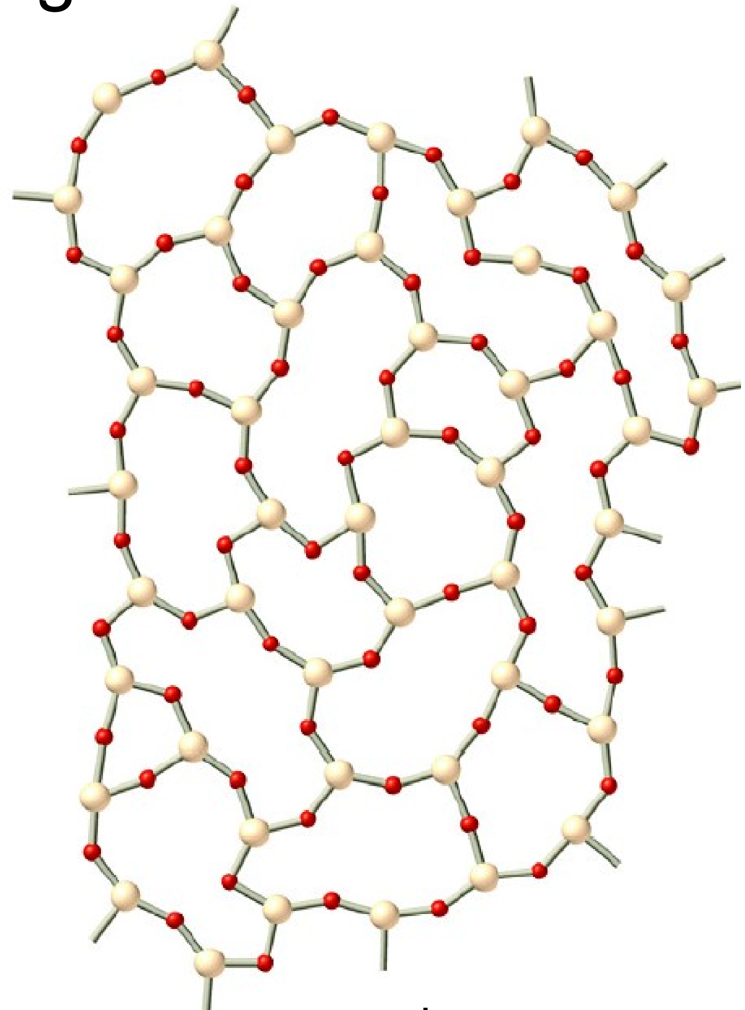
12.5 Amorphous Solids

- Lack regular arrangement of atoms
- Glass is a familiar and important amorphous solid
  - Transparent fusion of inorganic materials
  - Chief component SiO_2
  - Behaves more as a liquid than a solid

Comparison of crystalline quartz and amorphous quartz glass



crystalline



amorphous

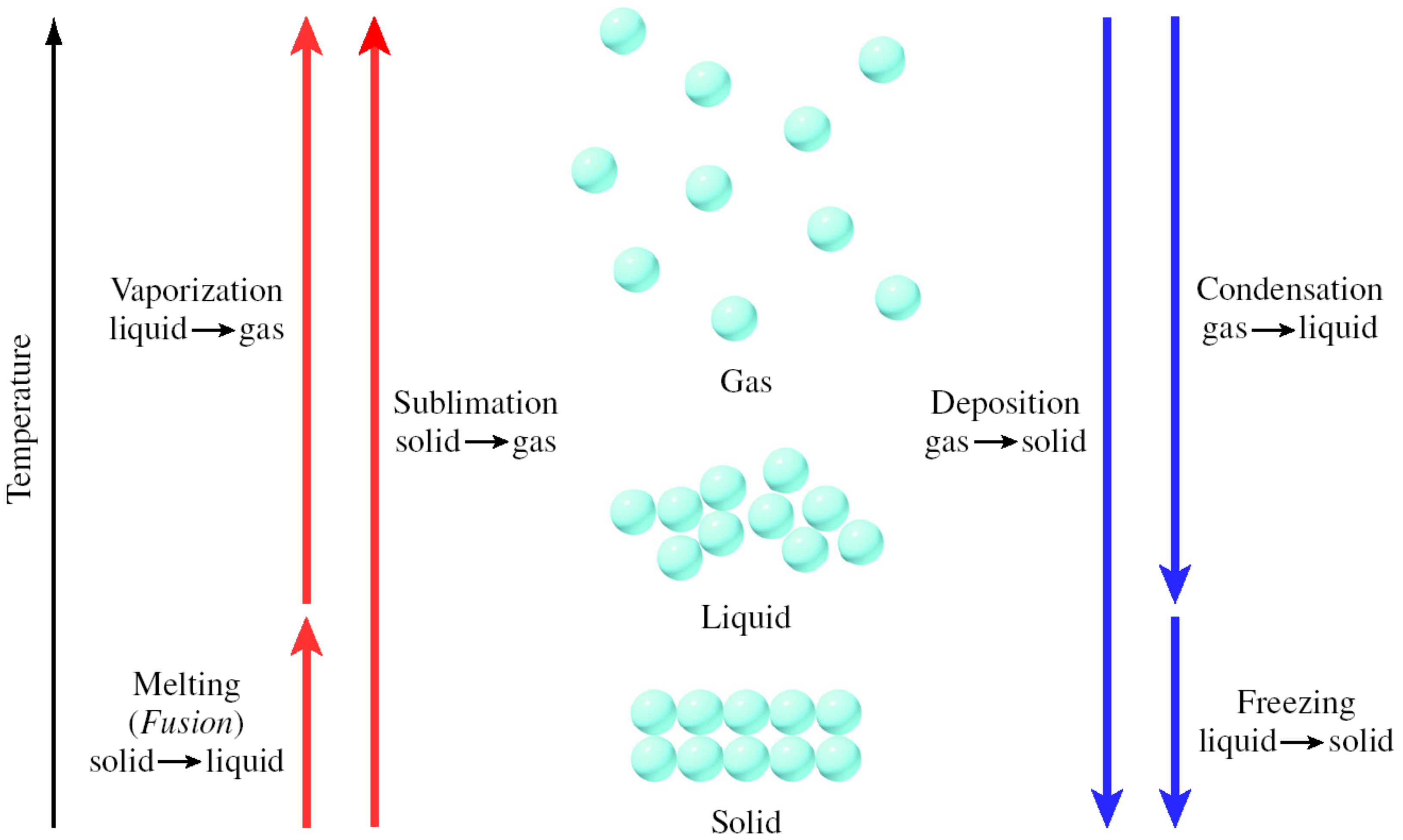
TABLE 12.5 Composition and Properties of Three Types of Glass

Pure quartz glass	100% SiO_2	Low thermal expansion, transparent to a wide range of wavelengths. Used in optical research.
Pyrex glass	60%–80% SiO_2, 10%–25% B_2O_3, some Al_2O_3	Low thermal expansion; transparent to visible and infrared, but not to ultraviolet light. Used in cookware and laboratory glassware.
Soda-lime glass	75% SiO_2, 15% Na_2O, 10% CaO	Easily attacked by chemicals and sensitive to thermal shocks. Transmits visible light but absorbs ultraviolet light. Used in windows and bottles.

12.6 Phase Changes

- ***Phase*** – homogenous part of a system that is separated from the rest of the system by a well-defined boundary
- ***Phase change*** – transition from one phase to another
  - Caused by the removal or addition of energy
  - Energy involved is usually in the form of heat

The Six Possible Phase Changes



- Liquid-Vapor Phase Transition
  - ***Boiling point*** – the temperature at which the vapor pressure of liquid equals atmospheric pressure
  - ***Molar heat of vaporization*** (ΔH_{vap}) – the amount of heat required to vaporize one mole of a substance at its boiling point usually in kJ/mol
  - Dependent on the strength of intermolecular forces
  - ***Condensation*** – opposite of vaporization

TABLE 12.6 Molar Heats of Vaporization for Selected Liquids

Substance	Boiling Point (°C)	ΔH_{vap} (kJ/mol)
Argon (Ar)	−186	6.3
Benzene (C_6H_6)	80.1	31.0
Ethanol (C_2H_5OH)	78.3	39.3
Diethyl ether ($C_2H_5OC_2H_5$)	34.6	26.0
Mercury (Hg)	357	59.0
Methane (CH_4)	−164	9.2
Water (H_2O)	100	40.79

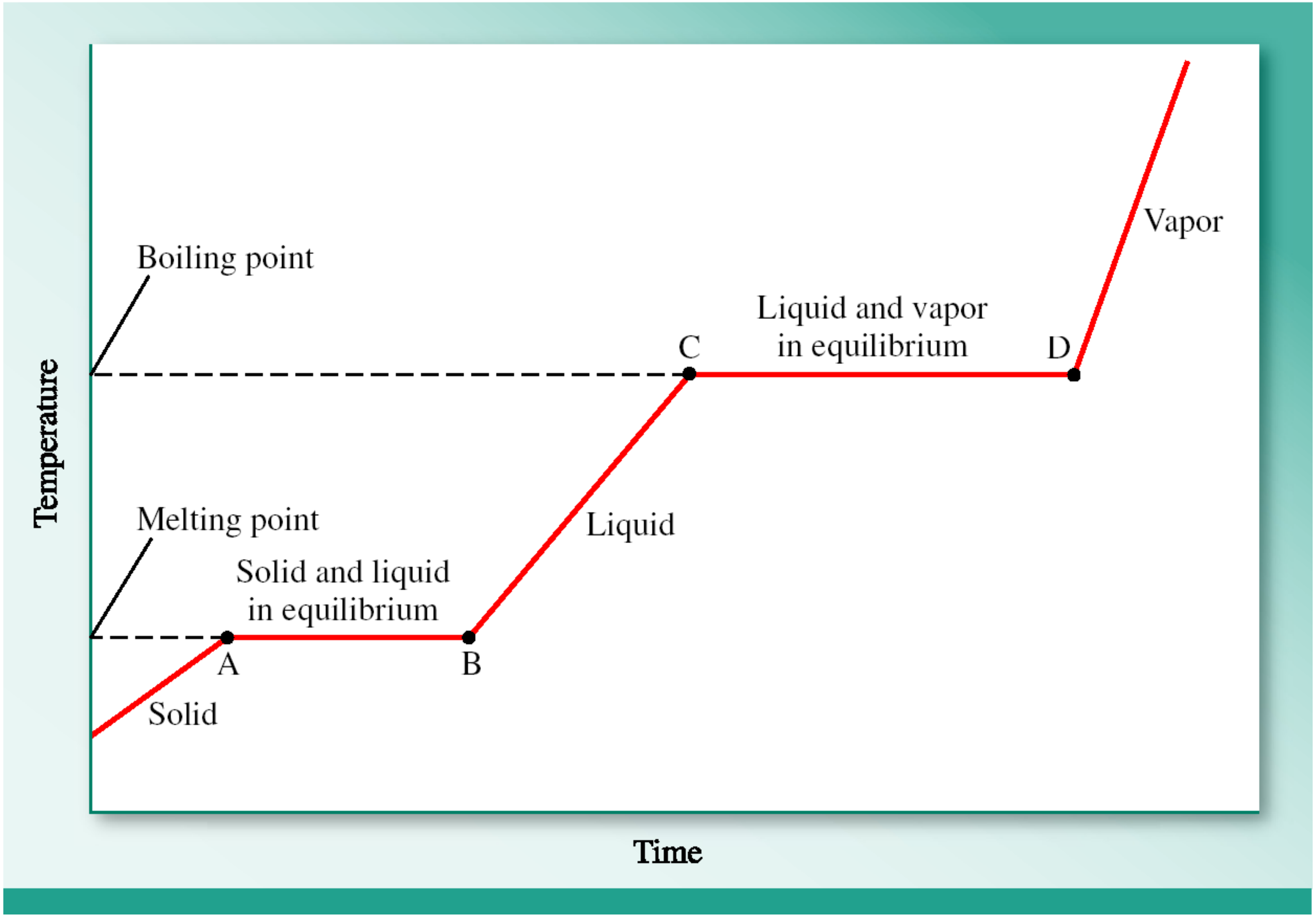
- ***Critical temperature*** (T_c) – the temperature above which a gas cannot be liquified by application of pressure
- ***Critical pressure*** (P_c) – the pressure that must be applied to liquefy a gas at T_c.
- ***Supercritical fluid*** – the fluid that exists above T_c and P_c.

TABLE 12.7 Critical Temperatures and Critical Pressures of Selected Substances

Substance	T_c (°C)	P_c (atm)
Ammonia (NH_3)	132.4	111.5
Argon (Ar)	−122.2	6.3
Benzene (C_6H_6)	288.9	47.9
Carbon dioxide (CO_2)	31.0	73.0
Ethanol (C_2H_5OH)	243	63.0
Diethyl ether ($C_2H_5OC_2H_5$)	192.6	35.6
Mercury (Hg)	1462	1036
Methane (CH_4)	−83.0	45.6
Molecular hydrogen (H_2)	−239.9	12.8
Molecular nitrogen (N_2)	−147.1	33.5
Molecular oxygen (O_2)	−118.8	49.7
Sulfur hexafluoride (SF_6)	45.5	37.6
Water (H_2O)	374.4	219.5

- Solid-Liquid Phase Transition
  - ***Freezing*** – transformation of liquid to solid
  - ***Melting*** (***fusion***) – opposite of freezing
  - ***Melting point*** of solid (or ***freezing point*** of liquid) – temperature at which the solid and liquid phases coexist in equilibrium
    - Dynamic equilibrium in which the forward and reverse processes are occurring at the same rate
  - ***Molar heat of fusion*** (ΔH_{fus}) – energy to melt one mole of a solid usually in kJ/mol

Typical Heating Curve

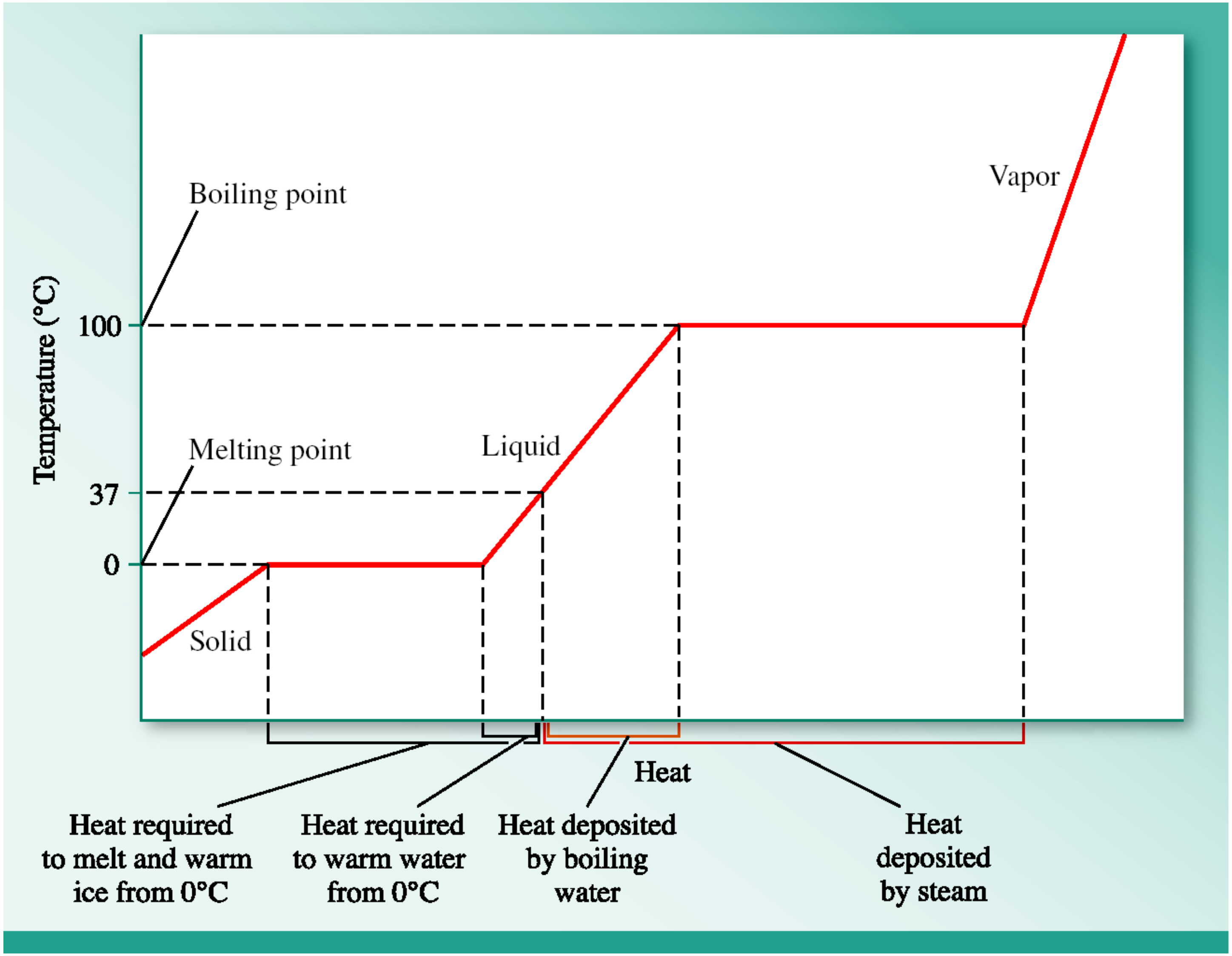


- Solid-Vapor Phase Transition
  - ***Sublimation*** – process by which molecules go directly from the solid phase to the vapor phase
  - ***Deposition*** – reverse of sublimation
  - ***Molar heat of sublimation*** (ΔH_{sub}) – energy required to sublime one mole of solid usually in kJ/mol

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

iodine

Heating Curve for Water



Calculate the amount of energy (in kJ) required to convert 125 g of ice at $-10.0^{o}C$ to liquid water at the normal boiling point. Assume that the specific heat of ice is $2.050\ J/g^{o}C$.

Energy to warm ice from –10^{o}C to 0^{o}C

$$\Delta T = 0.0^\circ\text{C} - (-10.0^\circ\text{C}) = 10.0^\circ\text{C}$$

$$q = ms\Delta T = 125 \text{ g} \times \frac{2.050 \text{ J}}{\text{g}\cdot{}^\circ\text{C}} \times 10.0^\circ\text{C} = 2.563\times 10^3\,\text{kJ}$$

$$2.563\times 10^3\,\text{J} \times \frac{\text{kJ}}{1\times 10^3\,\text{J}} = 2.563 \text{ kJ}$$

Energy to melt ice at 0^{o}C

$$125 \text{ g} \times \frac{\text{mol}}{18.02 \text{ g}} = 6.937 \text{ mol}$$

$$q = n\Delta H_{\text{vap}} = 6.937 \text{ mol} \times \frac{6.01\,\text{kJ}}{\text{mol}} = 4.169\times 10^1 \text{ kJ}$$

Energy to warm water from 0.0°C to 100.0°C

$$\Delta T = 100.0^{\circ}\text{C} - 0.0^{\circ}\text{C} = 100.0^{\circ}\text{C}$$

$$q = ms\Delta T = 125\ \text{g} \times \frac{4.184\ \text{J}}{\text{g}\cdot{}^{\circ}\text{C}} \times 100.0^{\circ}\text{C} = 5.230 \times 10^{4}\ \text{J}$$

$$5.230 \times 10^{4}\ \text{J} \times \frac{1\ \text{kJ}}{1 \times 10^{3}\ \text{J}} = 5.230 \times 10^{1}\ \text{kJ}$$

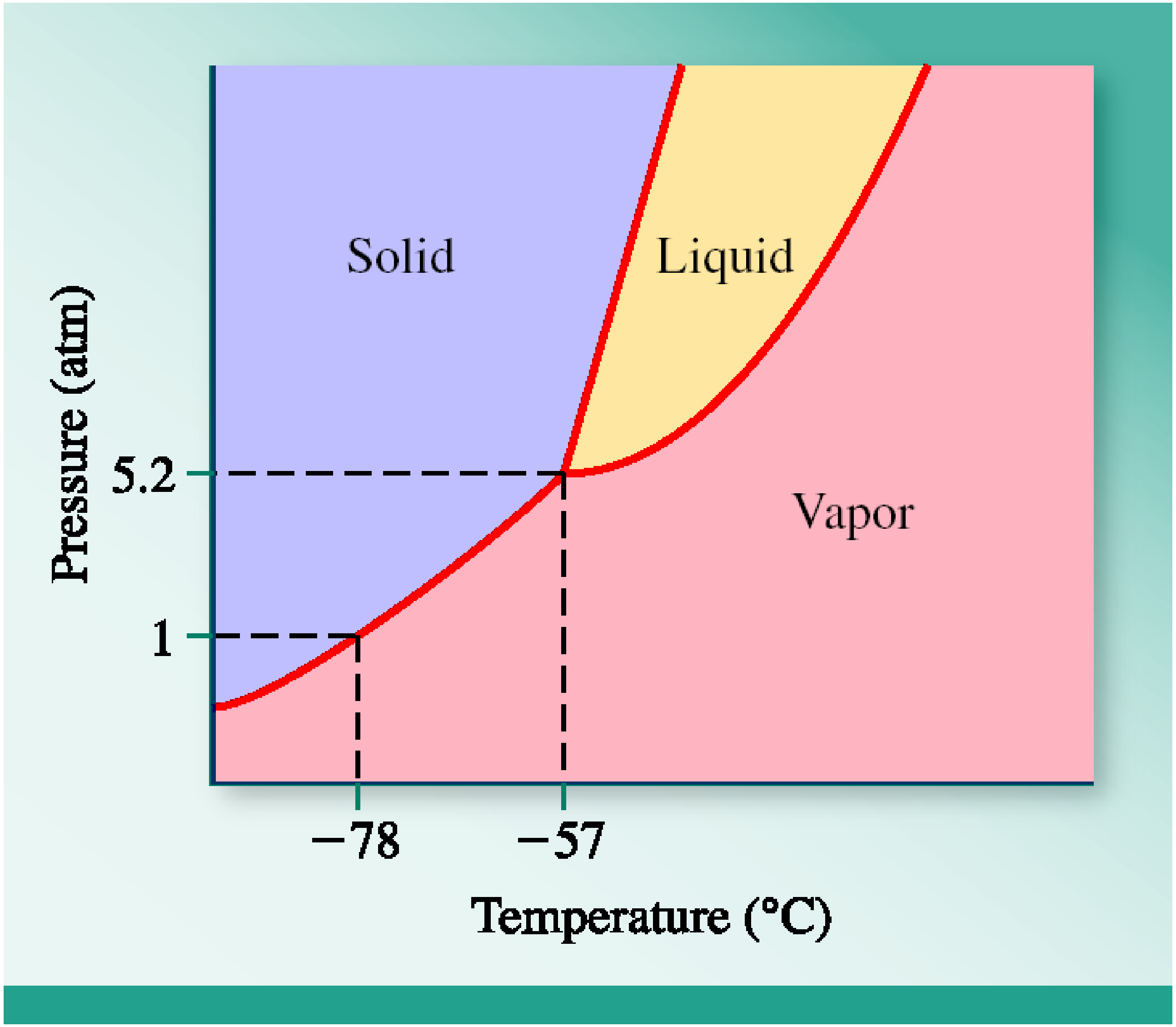
Total energy required

$$2.563\ \text{kJ} + (4.169 \times 10^{1}\ \text{kJ}) + (5.230 \times 10^{1}\ \text{kJ}) = 96.6\text{kJ}$$

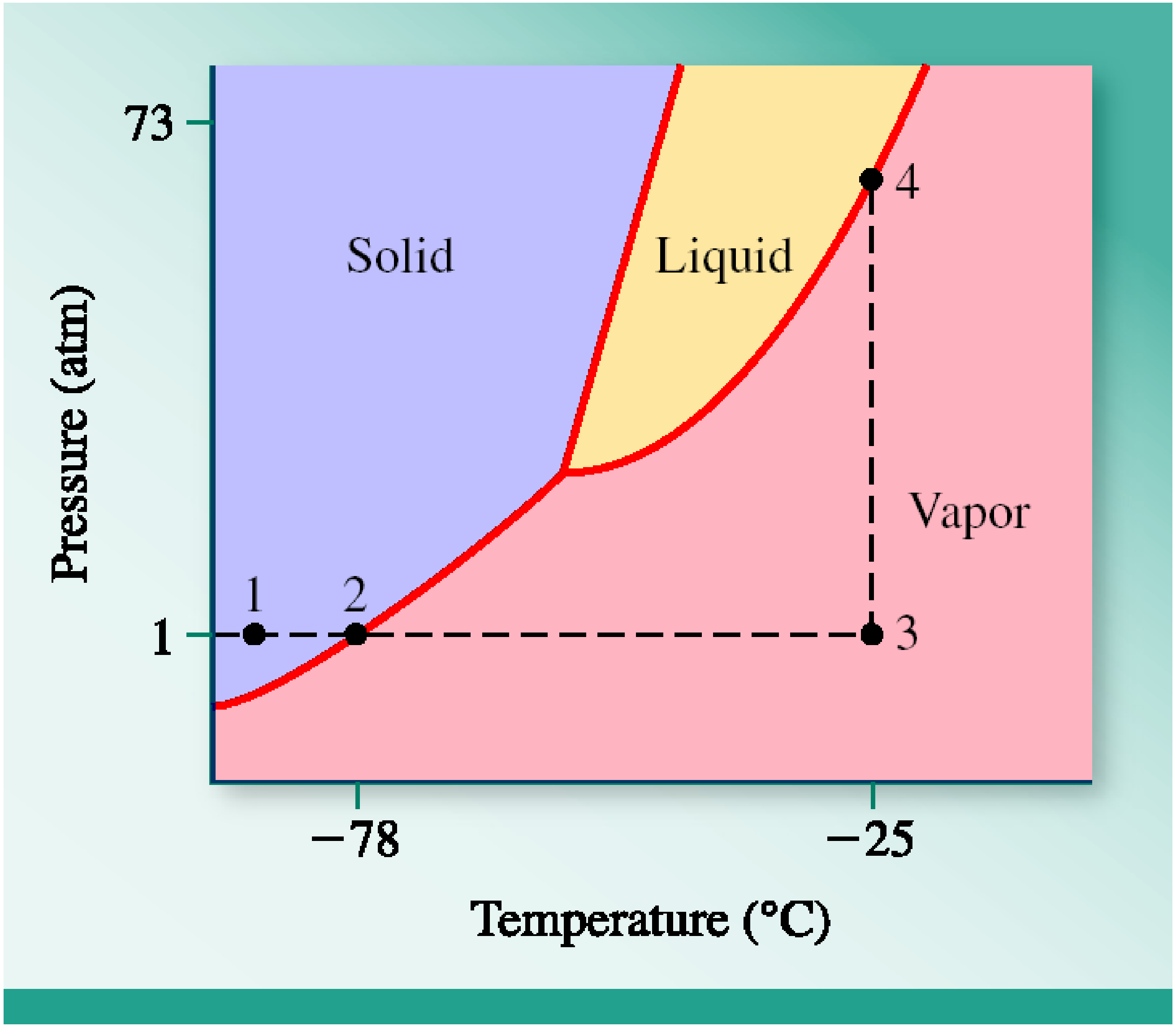
12.7 Phase Diagrams

- ***Phase diagram*** – summarizes the conditions (temperature and pressure) at which a substance exists as a solid, liquid or gas
  - Divided into three regions (solid, liquid, gas)
  - ***Phase boundary line*** – line separating any two regions
  - ***Triple point*** – the point at which all three phase boundary lines meet

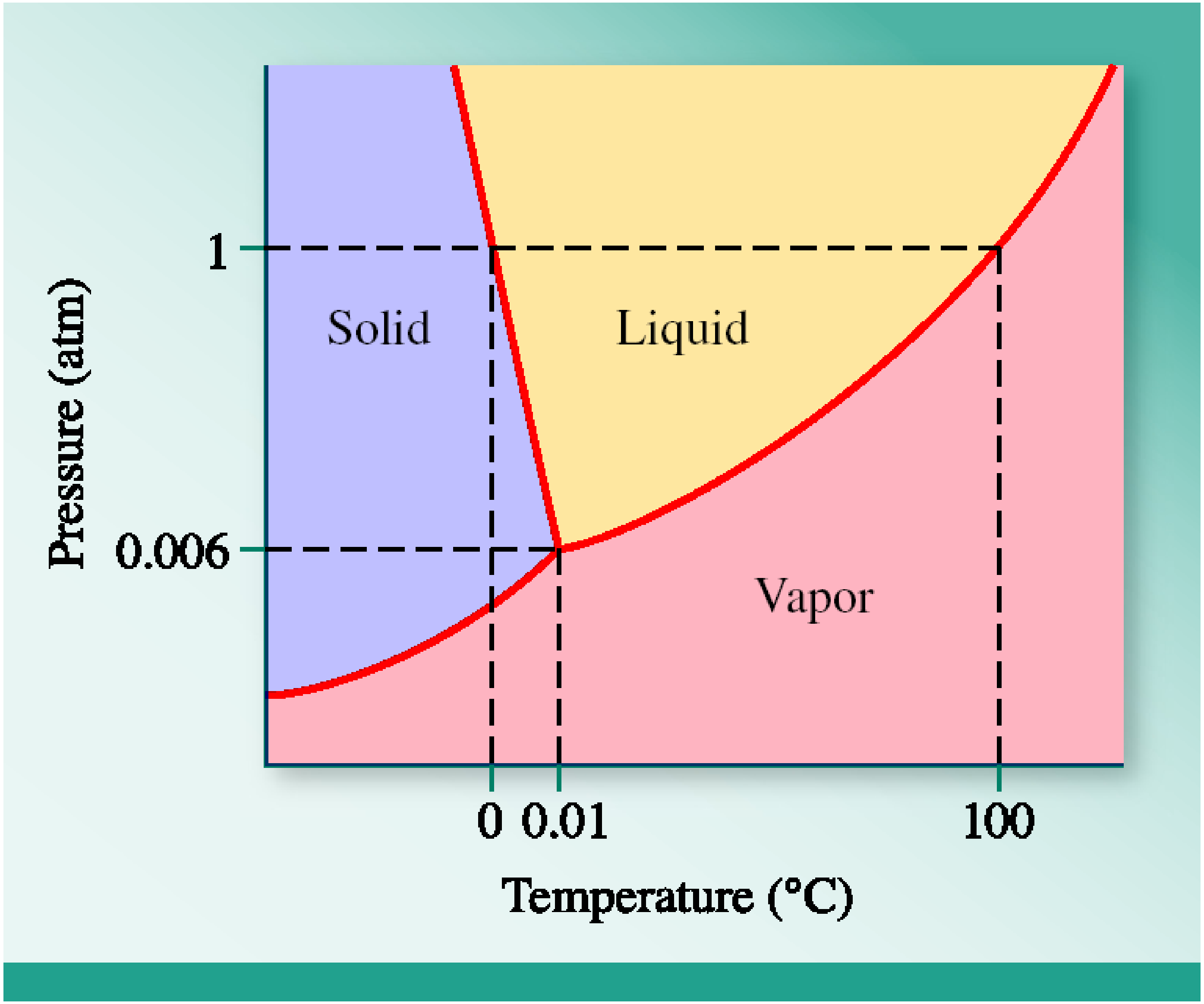
Phase Diagram of CO_2



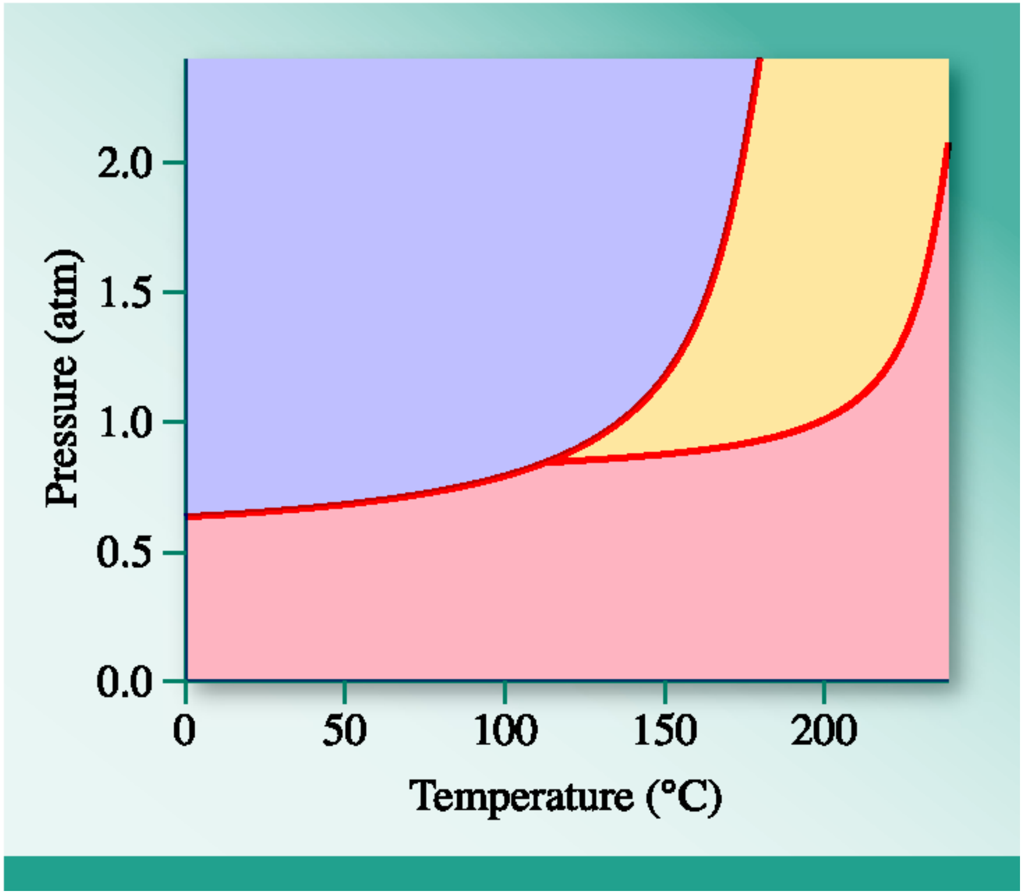
Heating CO_2 Starting at –100ºc and 1 atm



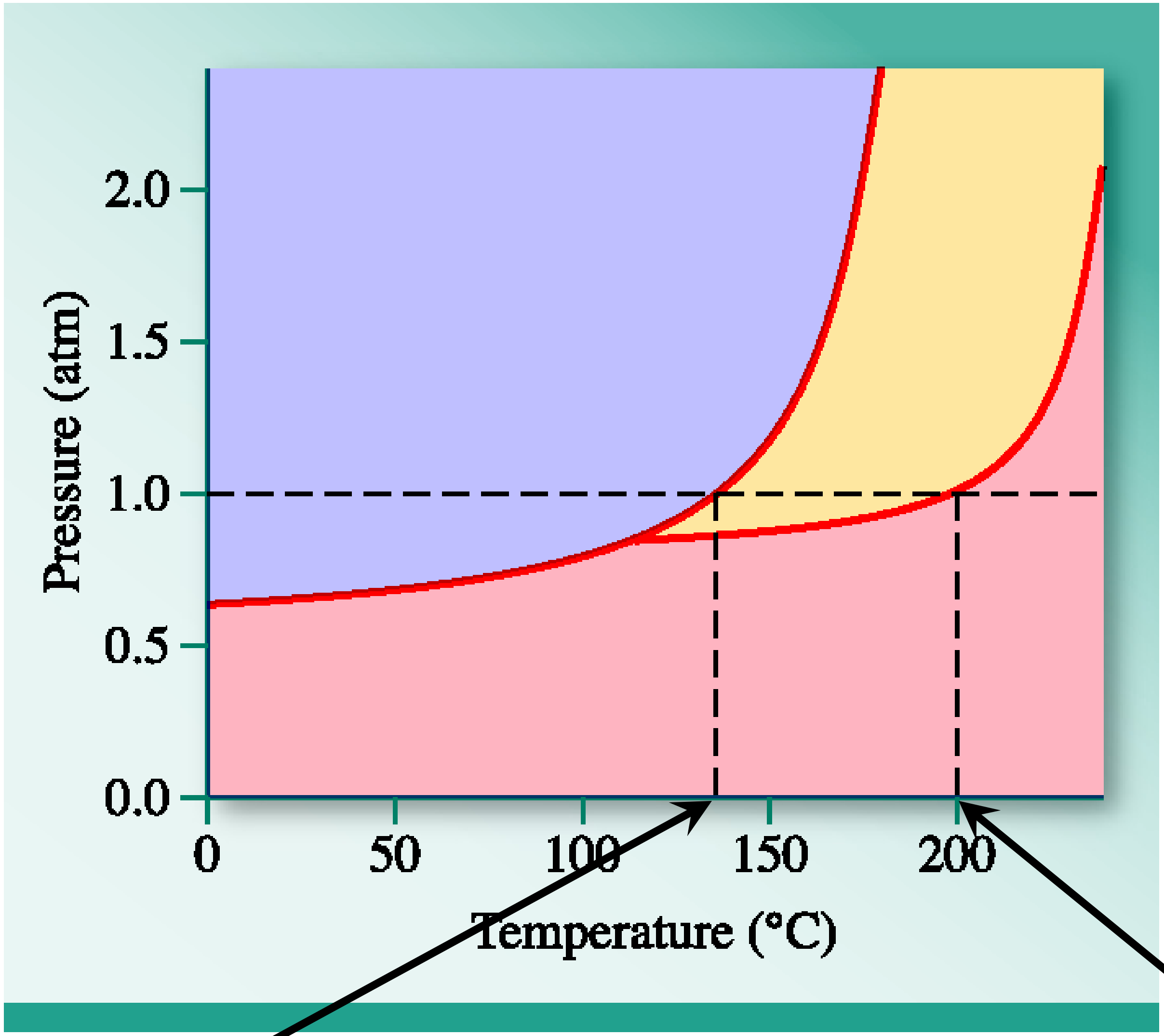
Phase Diagram of H_2O



What is a) the normal* melting point, b) the normal* boiling point and c) the physical state of the substance at 2.0 atm and 110^{o} C?



*normal – measured at 1.00 atm

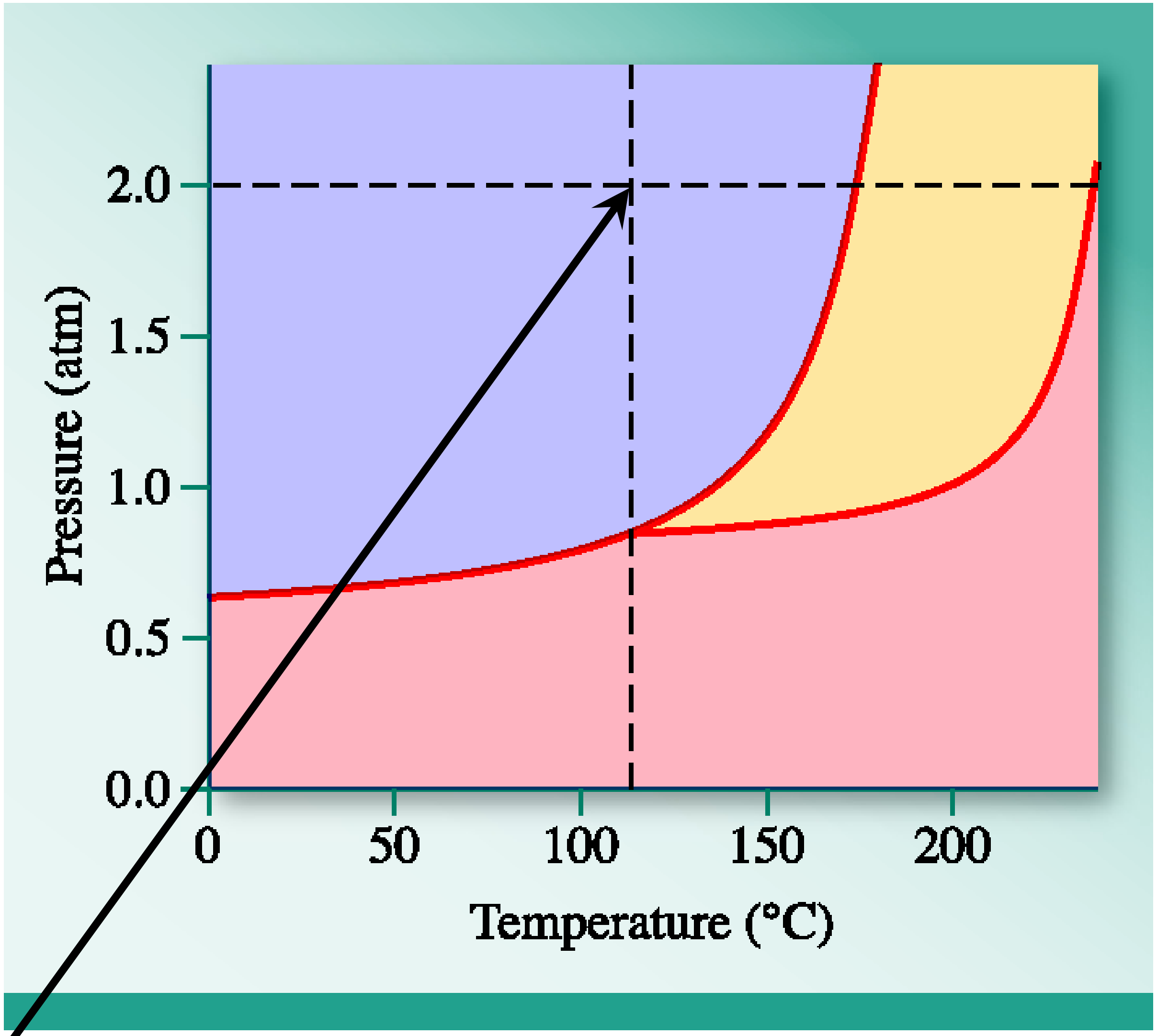


normal melting point

~135^{o}C

normal boiling point

~200^{o}C



solid physical state

Key Points

- Intermolecular forces
  - Dipole-dipole interactions
  - Hydrogen bonding
  - (London) dispersion forces
- Properties of liquids
  - Surface tension
  - Viscosity
  - Vapor pressure
    - Clausius-Clapeyron equation

- Crystal structure
  - Unit cells
    - Lattice point
  - Packing spheres
    - Coordination number
    - Cubic unit cells
  - Closest Packing
- Types of crystals
  - Ionic
  - Covalent
  - Molecular
  - Metallic

- Amorphous solids
- Phase changes
  - Liquid-vapor transitions
    - Boiling point
    - Heat of vaporization
    - Critical temperature and pressure
  - Solid-liquid transitions
    - Melting point
    - Heat of fusion
- Phase diagrams