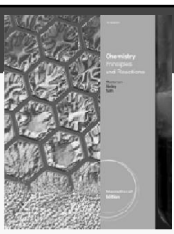

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Chapter 9
Liquids and Solids

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Outline

1. Liquid-vapor equilibrium
2. Phase diagrams
1. Comparing Solids, Liquids and Gases
3. Molecular substances; intermolecular forces
4. Network covalent, ionic and metallic solids
5. Crystal structures

Recall Gases

- At ordinary temperatures and pressures, all gases follow the ideal gas law
- There is no equivalent equation of state that can be written to correlate the properties of liquids and solids

Liquids and Solids Differ from Gases

1. Molecules are much closer together in liquids and solids than in gases
    - In gases, molecules are separated by ten or more molecular diameters
    - In liquids and solids, the molecules are in contact with each other
2. Intermolecular forces play a major role in the behavior of liquids and solids, whereas they are negligible in gases

Behavior of Liquids and Solids

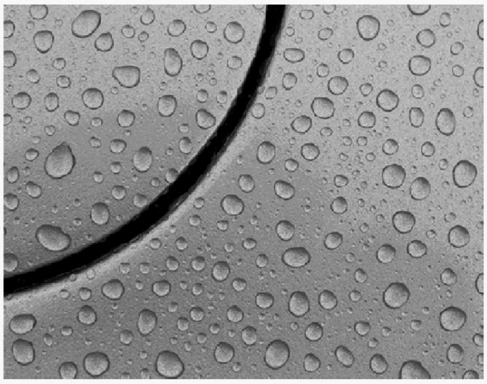
- Phase equilibria
    - Gas-liquid
        - Vapor pressure
        - Boiling point
        - Critical properties
- Relationships
    - Particle structure
    - Interparticle forces
    - Physical properties

Table 9.1: Phases

TABLE 9.1 Comparison of the Three Phases of Water

Phase	Molecular Spacing	Density	Volume of One Mole
Steam ($H_2O(g)$)		at 100°C, 1 atm 0.00059 g/mL	at 100°C, 1 atm 31 L
Water ($H_2O(l)$)		at 100°C, 1 atm 0.95 g/mL	19 mL
Ice ($H_2O(g)$)		at 0°C, 1 atm 0.92 g/mL	20 mL

Figure 9.1: Surface Tension of Water



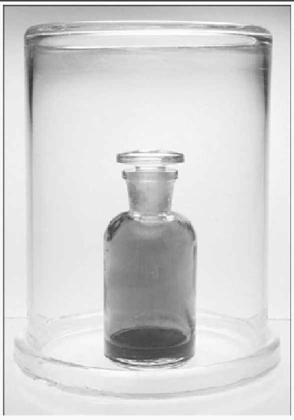
Liquid-Vapor Equilibrium

- Vaporization
  - Liquid is converted into a gas
  - In an open container, evaporation continues until all the liquid is converted into vapor
  - In a closed container, the process of vaporization is countered by the process of condensation:
    - Liquid ⇌ Vapor
    - The double arrow indicates a ***dynamic equilibrium***

Equilibrium

- When the rate at which the liquid vaporizes is equal to the rate at which the vapor condenses, a ***dynamic equilibrium is established***
- The ***liquid level in the container does not change***
- Molecules are entering the vapor phase from the liquid and condensing from the vapor phase to the liquid at the same rate

Equilibrium in Bromine



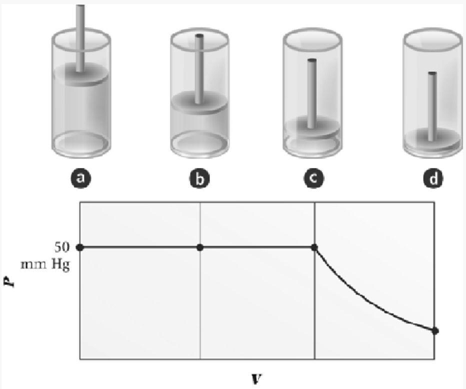
Vapor Pressure

- Once equilibrium between a liquid and its vapor is reached, the number of molecules per unit volume does not change with time
  - The pressure exerted by the vapor over the liquid remains constant
- The vapor pressure is temperature dependent

Pressure and Volume

- As long as both liquid and vapor are present, the vapor pressure is independent of the volume of the container

Figure 9.2



Example 9.1

EXAMPLE 9.1 GRADED

A "cool-mist" vaporizer with capacity 2.00 L is used to add moisture to dry air in a room at 25°C. The room has dimensions 12 ft by 12 ft by 8 ft. The vapor pressure of water at 25°C is 24 mm Hg. Take the density of water at 25°C to be 1.00 g/mL.

(a) If the vaporizer runs until it is empty, what is the vapor pressure of water in the room?

(b) How much water is required to completely saturate the air at 25°C?

(c) A relative humidity of 33% is desirable in heated space on wintry days. What volume of water is left in the vaporizer when the room's relative humidity reaches that level? (Relative humidity = 100 × P/P^0, where P is the actual pressure of water vapor and P^0 is the vapor pressure at saturation.)

continued

Example 9.1, (Cont'd)

(a)

ANALYSIS

Information given:	volume of vaporizer (2.00 L), T (25°C) room dimensions (12 ft × 12 ft × 8 ft) vapor pressure of water at 25°C (24 mm Hg) density of water (1.00 g/mL)
Information implied:	volume of water to be "vaporized" molar mass of H_2O ft^3 to L conversion factor R value
Asked for:	vapor pressure in the room when all the water is vaporized

STRATEGY

1. Assume that all the water in the vaporizer has been converted to vapor.
2. Find the volume of the room = volume of vapor (V).
3. Find the moles of water, n, from the vaporizer that will vaporize:

$$\text{Volume of water in vaporizer} \xrightarrow{\text{density}} \text{mass of water} \xrightarrow{\text{MM}} \text{mol water } (n)$$

4. Substitute into the ideal gas law and find P.
5. Check whether your assumption in (1) is correct.
   - Calculated P from (3) > vapor pressure at 25°C: assumption wrong.
     Vapor pressure is vapor pressure of water at 25°C.
   - Calculated P from (3) < vapor pressure at 25°C: assumption correct.
     Vapor pressure is calculated pressure from (3).

SOLUTION

$V_{room} = V_{gas}$	$(12 \times 12 \times 8)\ ft^3 \times \frac{28.32\ L}{1\ ft^3} = 3.3 \times 10^4\ L$
n_{steam}	$2.00\ L \times \frac{1000\ mL}{1\ L} \times \frac{1.00\ g}{1\ mL} \times \frac{1\ mol}{18.02\ g} = 111\ mol$
P_{calc}	$P_{calc} = \frac{nRT}{V} = \frac{(111\ mol)(0.0821\ L\cdot atm/mol\cdot K)(298\ K)}{3.3 \times 10^4\ L} = 0.082\ atm = 62\ mm\ Hg$
Check assumption	vapor pressure of water at 25°C = 24 mm Hg; P_{calc} = 62 mm Hg P_{calc} > 24 mm Hg; the assumption is wrong. The vapor pressure of water in the room is 24 mm Hg.

Example 9.1, (Cont'd)

(b)

ANALYSIS

Information given:	From part (a): P_{vapor} (24 mm Hg), V_{vapor} (3.3×10^4 L) T(25°C)
Information implied:	molar mass of H_2O R value
Asked for:	volume of water required to saturate the room *continued*

STRATEGY

1. Substitute into the ideal gas law to find n_{steam}.
2. Moles of vapor = moles of water. Convert to mass of water.

SOLUTION

n_{H_2O}	$n_{H_2O} = \frac{PV}{RT} = \frac{(24/760\ atm)(3.3 \times 10^4\ L)}{(0.0821\ L\cdot atm/mol\cdot K)(298\ K)} = 43\ mol$
$mass_{H_2O}$	$(43\ mol)(18.02\ g/mol) = 7.7 \times 10^2\ g$

Example 9.1, (Cont'd)

(c)

ANALYSIS

Information given:	From part (a): V_{vapor} (3.3×10^4 L), P^0 (24 mm Hg) T(25°C) volume of water in the vaporizer (2.00 L) density of water (1.00 g/mL)
Information implied:	molar mass of H_2O R value
Asked for:	volume of water in the vaporizer after 33% humidity is reached

STRATEGY

1. Find the pressure of vapor in the room at 33% humidity by substituting into

$$P = \frac{\text{relative humidity}}{100} \times P^0$$

where P^0 is the vapor pressure of water at 25°C = 24 mm Hg

2. Substitute into the ideal gas law to find n to reach P calculated in (1). V is the volume of the room.
3. Convert moles of water to mass of water (use MM) and then to volume of water (use density).
4. Water left in the vaporizer = (volume of water in the vaporizer initially) − (volume of water required to vaporize to reach 33% relative humidity)

SOLUTION

P_{steam} at 33% humidity	$P = \frac{\text{relative humidity}}{100} \times P^0 = \frac{33\%}{100\%} \times 24\ mm\ Hg = 7.9\ mm\ Hg$
n_{H_2O}	$n_{H_2O} = \frac{PV}{RT} = \frac{(7.9/760\ atm)(3.3 \times 10^4\ L)}{(0.0821\ L\cdot atm/mol\cdot K)(298\ K)} = 14\ mol$
Volume of water vaporized	$(14\ mol)(18.02\ g/mol) = 2.50 \times 10^2\ g = 2.50 \times 10^2\ mL = 0.25\ L$
V_{H_2O} in vaporizer	$2.00\ L - 0.25\ L = 1.75\ L$

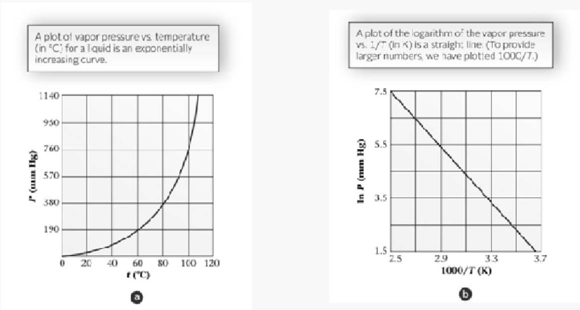
END POINTS

1. The volume of the room is the volume of the water vapor obtained from the vaporizer.
2. The volume of the water in the vaporizer cannot be used as V in the ideal gas law because it is the volume of a liquid, not a gas.
3. The calculations in part (b) show that about 770 grams (0.77 L) are required for saturation (100% relative humidity). To get 33% relative humidity, you would expect to need about a third of that amount (≈0.25 L), which is what the calculations in part (c) do give.

Vapor Pressure and Temperature

- The vapor pressure of a liquid increases as the temperature rises
  - Increase in P is not linear with temperature
  - Water
    - VP is 24 mmHg at 25 ° C
    - VP is 92 mmHg at 50 ° C
- To make a linear plot, the natural logarithm is required

Figure 9.3 – Exponential and Logarithmic Plots



Vapor Pressure Equation

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

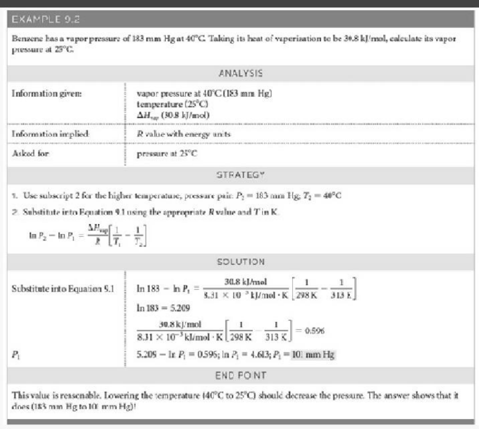
The Clausius-Clapeyron Equation

- For many purposes, a two-point equation is useful
  - Two pressures
  - Two temperatures

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

- Notes:
  - Temperatures must be in Kelvin
    - R = 8.31 J/mol·K
    - ΔH_{vap} must be in J for use with this value for R

Example 9.2



EXAMPLE 9.2

Benzene has a vapor pressure of 183 mm Hg at 40°C. Taking its heat of vaporization to be 30.8 kJ/mol, calculate its vapor pressure at 25°C.

ANALYSIS

Information given:	vapor pressure at 40°C (183 mm Hg) temperature (25°C) ΔH_{vap} (30.8 kJ/mol)
Information implied:	R value with energy units
Asked for:	pressure at 25°C

STRATEGY

1. Use subscript 2 for the higher temperature, pressure pair: P_2 = 183 mm Hg; T_2 = 40°C
2. Substitute into Equation 9.1 using the appropriate R value and T in K.

$$\ln P_2 - \ln P_1 = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

SOLUTION

Substitute into Equation 9.1	$\ln 183 - \ln P_1 = \frac{30.8 \text{ kJ/mol}}{8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}}\left[\frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}}\right]$ $\ln 183 = 5.209$ $\frac{30.8 \text{ kJ/mol}}{8.31 \times 10^{-3} \text{ kJ/mol} \cdot \text{K}}\left[\frac{1}{298 \text{ K}} - \frac{1}{313 \text{ K}}\right] = 0.596$
P_1	$5.209 - \ln P_1 = 0.596$; $\ln P_1 = 4.613$; P_1 = 101 mm Hg

END POINT

This value is reasonable. Lowering the temperature (40°C to 25°C) should decrease the pressure. The answer shows that it does (183 mm Hg to 101 mm Hg)!

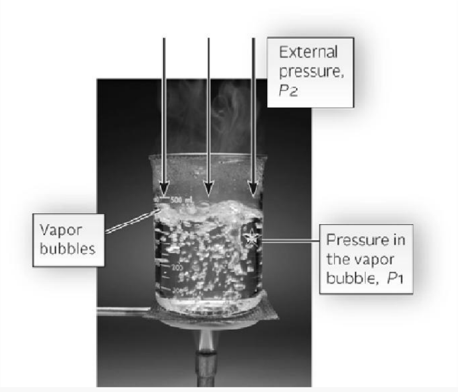
Boiling Point

- When heat is applied to a liquid in an open container, bubbles eventually form at the bottom
  - At a certain temperature, large bubbles form throughout the liquid; i.e., the liquid boils
  - The temperature at which a liquid boils depends on the pressure above it
    - If the ***pressure is 1 atm, the temperature at which the liquid boils is called the normal boiling point***
    - When the term ***boiling point is used, the normal boiling point is implied***
  - ***The boiling point is the temperature at which the vapor pressure equals the prevailing pressure***

Boiling Point and Prevailing Pressure

- Variation on atmospheric pressure will change the boiling point
  - At high elevation, atmospheric pressure is lower, so the boiling point is lower
  - To elevate the boiling point and allow food to cook more quickly, a pressure cooker can be used

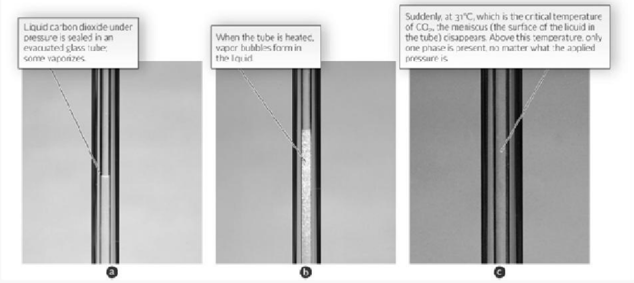
Figure 9.4 - Boiling



Carbon Dioxide

- Consider carbon dioxide
  - CO_2 as a liquid is sealed into an evacuated glass tube
  - As the tube is heated, some liquid is converted to vapor, and the pressure rises to 44 atm at 10 °C
  - At 31 °C, the pressure is 73 atm
  - Suddenly, the meniscus between liquid and vapor disappears and only vapor is present

Figure 9.5



Critical Temperature and Pressure

- For every liquid, there is a temperature above which only vapor can exist
  - This is the ***critical temperature***
- At this temperature, the pressure is called the ***critical pressure***
  - Together, the critical temperature and pressure are called the ***critical point***

Table 9.2: Critical Temperatures

TABLE 9.2 Critical Temperatures (°C)

Permanent Gases		Condensable Gases		Liquids	
Helium	−268	Carbon dioxide	31	Ethyl ether	194
Hydrogen	−240	Ethane	32	Ethyl alcohol	243
Nitrogen	−147	Propane	97	Benzene	289
Argon	−122	Ammonia	132	Bromine	311
Oxygen	−119	Chlorine	144	Water	374
Methane	−82	Sulfur dioxide	158		

Permanent Gases

- Permanent gases are substances with critical temperatures below 25 °C.
  - Usually stored in cylinders at 150 atm or greater
  - Only vapor is present in the tank
  - Pressure in the tank drops as the gas is released

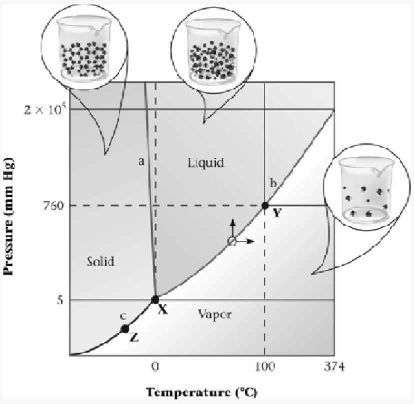
Condensable Gases

- Condensable gases have critical temperatures above 25 ° C.
  - Carbon dioxide
  - Hydrocarbon gases
  - Ammonia
  - Chlorine
  - Sulfur dioxide
- For these substances, the liquid-vapor equilibrium accounts for the pressure in the tank
  - Pressure will not change until all the liquid is gone

Phase Diagrams

- Phase diagrams are graphical representations of the pressure and temperature dependence of a pure substance
  - Pressure on the y-axis
  - Temperature on the x-axis
- Three places to consider
  - In a region, one phase exists
  - On a line, two phases exist in equilibrium
  - At a point, three phases exist in equilibrium

Figure 9.6: A Phase Diagram



Phase Diagram of Water

- Curve b (green) is the vapor pressure-temperature curve of liquid water
- Curve c (red) is the vapor pressure curve of ice
- Line a (blue) gives the temperature-pressure dependence for ice in equilibrium with water
- Point X is the ***triple point***
  - All three phases are in equilibrium
  - There is only one triple point for a pure substance
  - For water, the triple point is at 0.01 ° C and 4.56 mmHg

Example 9.3

EXAMPLE 9.3 CONCEPTUAL

Consider a sample of H_2O at point X in Figure 9.6.

(a) What phase(s) is (are) present?

(b) If the temperature of the sample were reduced at constant pressure, what would happen?

(c) How would you convert the sample to vapor without changing the temperature?

STRATEGY

1. Use the phase diagram in Figure 9.6.
2. Note that P increases moving up vertically; T increases moving to the right.

SOLUTION

(a) X is the triple point. Ice, liquid water, and water vapor are present.

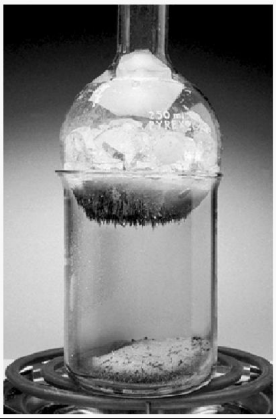
(b) Move to the left to reduce T. This penetrates the solid area, which implies that the sample freezes completely.

(c) Reduce the pressure to below the triple point value, perhaps to 4 mm Hg.

Sublimation

- Sublimation is the process by which a solid passes directly into the vapor phase without first being converted to a liquid
  - Sublimation can happen only at a temperature below the triple point
  - Water can sublime if the pressure is reduced
    - Freeze drying
    - Cold winter days
  - Iodine sublimes readily because its triple point pressure is much higher than that of water

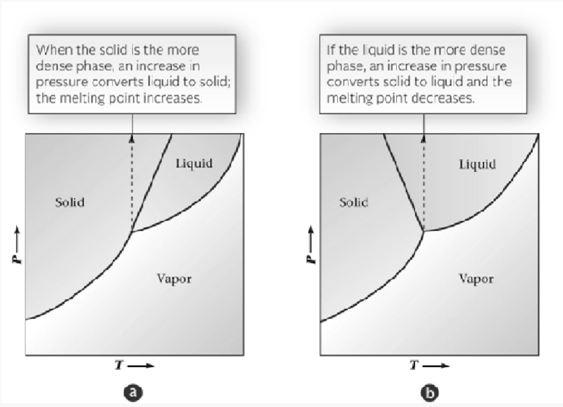
Figure 9.7: Sublimation of I_2



Melting Point

- For a pure substance, the melting point and freezing point are identical
  - The effect of pressure on the freezing point is very small
  - An increase in pressure favors the more dense phase
    - This is usually the solid phase
    - Water is denser than ice, so water is anomalous
    - The slope of the solid-liquid line depicts the behavior of the freezing point as pressure is increased or decreased
      - Positive slope: solid is denser than liquid
      - Negative slope: liquid is denser than solid

Figure 9.8



Molecular Substances; Intermolecular Forces

- Many gases, most liquids and many solids are molecular
  - Molecules are the structural units of such matter
  - Properties of molecular substances include
    - They are nonconductors of electricity when pure
    - They are insoluble in water but soluble in nonpolar solvents such as CCl_4 or benzene
    - They have low melting points
  - These properties depend on the intermolecular forces between the molecules of the substance

Dispersion Forces

- All substances have dispersion forces
  - Also called London or van der Waals forces
  - Stem from induced dipoles in molecules
  - Motion of electrons in the molecule causes transient dipoles to form
  - Increase with the number of electrons in the molecule
  - As molar mass increases, dispersion forces become stronger

Figure 9.9 and Table 9.3

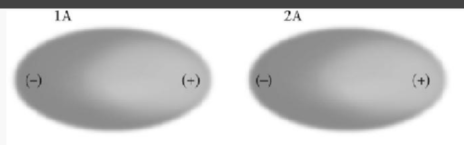


TABLE 9.3 Effect of Molar Mass on Boiling Points of Molecular Substances

Noble Gases*			Halogens			Hydrocarbons		
	MM (g/mol)	bp (°C)		MM (g/mol)	bp (°C)		MM (g/mol)	bp (°C)
He	4	−269	F_2	38	−188	CH_4	16	−161
Ne	20	−246	Cl_2	71	−34	C_2H_6	30	−88
Ar	40	−186	Br_2	160	59	C_3H_8	44	−42
Kr	84	−152	I_2	254	184	n-C_4H_{10}	58	0

*Strictly speaking, the noble gases are "atomic" rather than molecular. However, like molecules, the noble-gas atoms are attracted to one another by dispersion forces.

Dipole Forces

- Molecules with permanent dipoles display dipole forces
  - Dispersion forces are also present but are much weaker
  - Adjacent molecules line up so that the negative pole of one molecule is as close as possible to the positive pole of another molecule
  - Result is an electrostatic attractive force that causes molecules to associate with each other

Figure 9.10

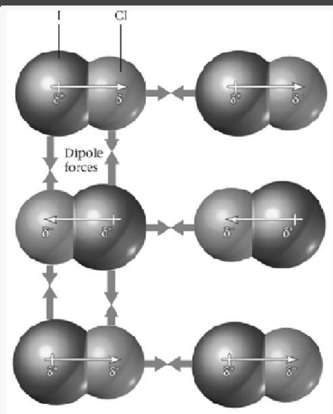


Table 9.4

TABLE 9.4 Boiling Points of Nonpolar Versus Polar Substances

Nonpolar			Polar		
Formula	MM (g/mol)	bp (°C)	Formula	MM (g/mol)	bp (°C)
N_2	28	−196	CO	28	−192
SiH_4	32	−112	PH_3	34	−88
GeH_4	77	−90	AsH_3	78	−62
Br_2	160	59	ICl	162	97

Example 9.4

EXAMPLE 9.4 CONCEPTUAL

Explain, in terms of intermolecular forces, why
(a) the boiling point of O_2 (−183°C) is higher than that of N_2 (−196°C).
(b) the boiling point of NO (−151°C) is higher than that of either O_2 or N_2.

STRATEGY

1. Draw the Lewis structure of the molecule.
2. Determine its polarity.
3. Identify the intermolecular forces present.
4. Remember that dispersion forces are always present and increase with molar mass.

SOLUTION

(a)	
1. Lewis structures	Ö=Ö: vs :N≡N:
2. Polarity	Both are nonpolar.
3. Intermolecular forces	Only dispersion forces for both O_2 and N_2
4. Strength of forces	MM_{O_2} = 32 g/mol; MM_{N_2} = 28 g/mol
	Dispersion forces of O_2 are larger.
(b)	
1. Lewis structures	N̈=Ö; see part (a) for O_2 and N_2
2. Polarity	NO is polar, O_2 and N_2 are nonpolar.
3. Intermolecular forces	NO: dispersion and dipole forces;
	O_2 and N_2 only have dispersion forces.
4. Strength of forces	MM_{O_2} = 32 g/mol; MM_{N_2} = 28 g/mol; MM_{NO} = 30 g/mol
	All have similar dispersion force strength.
	Only NO has dipole forces in addition to the dispersion forces.

Hydrogen Bonding

- Unusually strong type of dipole force
  - H attached to a(n) N, O, or F
  - The H from one molecule can associate itself with the negative end of the dipole of another
    - Dipole arises from the difference in the electronegativity between H and (N, O, or F)
    - Small size of H allows the unshared pair from the negative end of the dipole to approach the H closely
  - HF, H_2O and NH_3: unusually high boiling points as a result of hydrogen bonding

Table 9.5

TABLE 9.5 Effect of Hydrogen Bonding on Boiling Point

	bp (°C)		bp (°C)		bp (°C)
NH_3	−33	H_2O	100	HF	19
PH_3	−88	H_2S	−60	HCl	−85
AsH_3	−63	H_2Se	−42	HBr	−67
SbH_3	−18	H_2Te	−2	HI	−35

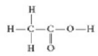
Note: Molecules in blue show hydrogen bonding.

Example 9.5

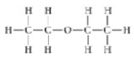
EXAMPLE 9.5

Would you expect to find hydrogen bonds in

(a) acetic acid?



(b) diethyl ether?



(c) hydrazine, N_2H_4?

STRATEGY

1. Lewis structures for (a) and (b) are given; draw the Lewis structure for hydrazine.
2. For H-bonding to occur, one of the following bonds has to be present in the molecule: H—F, H—O, or H—N

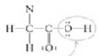
continued

Example 9.5, (Cont'd)

SOLUTION

(a)

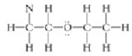
1. Lewis structure: Given:



2. H—F, H—O, or H—N? Yes; hydrogen bonding is present.

(b)

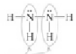
1. Lewis structure: Given:



2. H—F, H—O, or H—N? No. The presence of O and H atoms in the molecule does not mean that H-bonding can occur.

(c)

1. Lewis structure:



2. H—F, H—O, or H—N? Yes. H-bonding can occur.

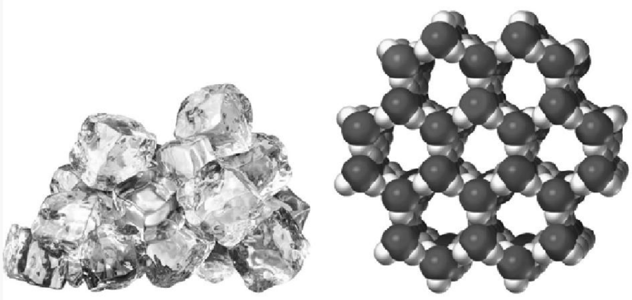
END POINT

In acetic acid, the H atom bonded to oxygen in one molecule forms a hydrogen bond with an oxygen in an adjacent molecule. The same situation applies in hydrazine if you substitute nitrogen for oxygen.

Water

- Hydrogen bonding in water accounts for
  - High specific heat
  - High boiling point
  - Higher density of the liquid phase relative to the solid

Figure 9.11



Example 9.6

EXAMPLE 9.6 CONCEPTUAL

What types of intermolecular forces are present in

(a) nitrogen, N_2? (b) chloroform, $CHCl_3$? (c) carbon dioxide, CO_2? (d) ammonia, NH_3?

STRATEGY

1. Write the Lewis structure for each molecule.
2. Determine polarity. Polar molecules have dipole forces.
3. Check for the presence of H—N, H—O, and H—F bonds. The presence of these bonds indicates hydrogen bonding.
4. All molecules have dispersion forces.

SOLUTION

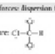
(a) N_2

1. Lewis structure: N≡N
2. Polarity: nonpolar—no dipole forces present
3. H—N, H—O, and H—F? No. Hydrogen bonding not possible

Intermolecular forces: dispersion forces

(b) $CHCl_3$

1. Lewis structure:



2. Polarity: polar—dipole forces present
3. H—N, H—O, and H—F? No. Hydrogen bonding not possible

Intermolecular forces: dispersion and dipole forces

(c) CO_2

1. Lewis structure: O=C=O
2. Polarity: nonpolar—no dipole forces present
3. H—N, H—O, and H—F? No. Hydrogen bonding not possible

Intermolecular forces: dispersion forces

(d) NH_3

1. Lewis structure: H—N—H (with H below N)
2. Polarity: polar—dipole forces present
3. H—N, H—O, and H—F? Yes. Hydrogen bonding possible

Intermolecular forces: dispersion, hydrogen bonds, and dipole forces

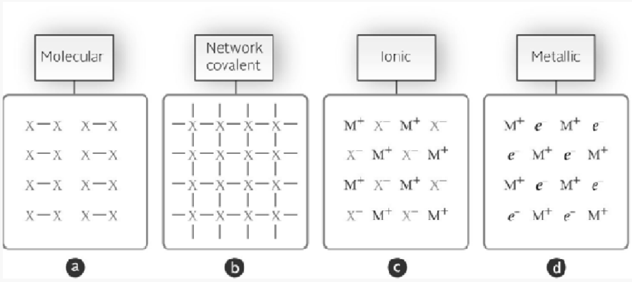
Covalent Bonds vs. Intermolecular Forces

- Three types of intermolecular forces
  - Dispersion
  - Dipole
  - Hydrogen bond
- All three intermolecular forces are weak relative to the strength of a covalent bond
  - Attractive energy in ice is 50 kJ/mol
  - Covalent bond in water is 928 kJ/mol

Solids: Network Covalent, Ionic and Metallic

- Network covalent solids
  - Continuous network of covalent bonds
  - Crystal is one large molecule
- Ionic solids
  - Oppositely-charged ions held together by strong electrical forces
- Metallic solids
  - Structural unit are +1, +2 and +3 metals with associated electrons

Figure 9.12



Network Covalent Solids

- Characteristics
  - High melting points, often above $1000\ ^\circ C$
  - Covalent bonds must be broken to melt the substance
- Examples
  - Graphite and diamond: allotropes
    - Diamond is three-dimensional and tetrahedral
    - Graphite is two-dimensional and planar

Figure 9.13

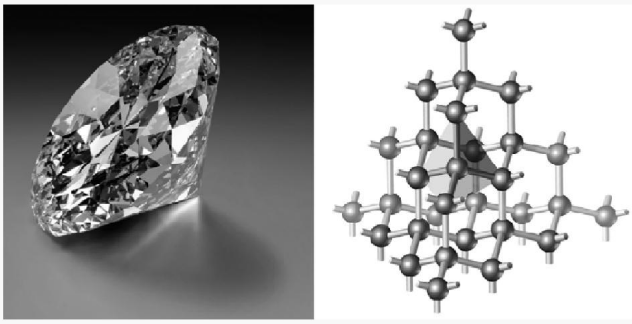
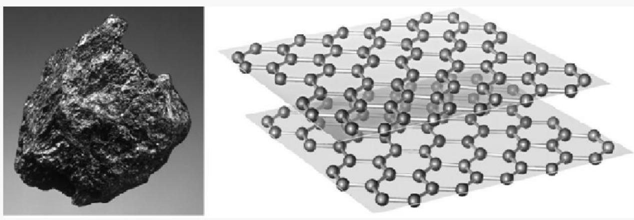


Figure 9.14



Compounds of Silicon

- Quartz
  - SiO_2
    - Major component of sand
    - Glass
  - Layered structures
    - Talc
  - Silicate lattices
    - Chains in 1, 2 and 3 dimensions
    - Zeolites

Figure 9.15

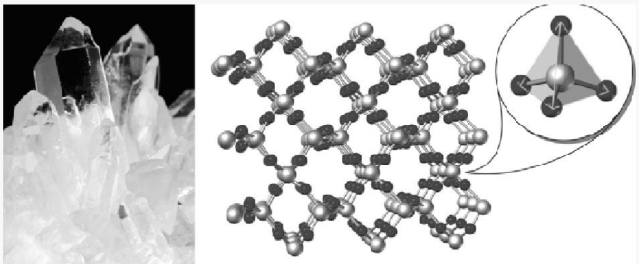
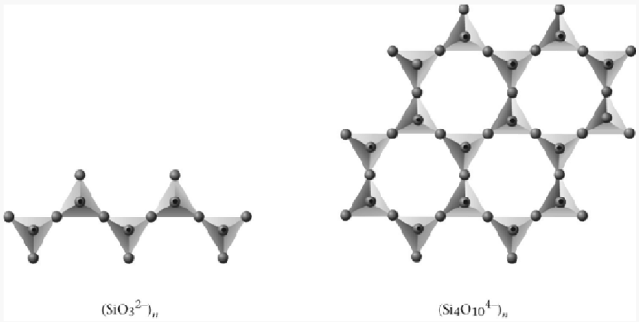


Figure 9.16



Ionic Solids

- Characteristics
  - Nonvolatile; high melting points (600-2000 °C)
  - Nonconductors of electricity in the solid state
    - Conduct when melted or dissolved in water
  - Many are soluble in water but not in nonpolar solvents

Strengths of Ionic Bonds

- Coulomb's Law

$$E = \frac{k \times Q_1 \times Q_2}{d}$$

$$d = r_{cation} + r_{anion}$$

- Strength of ionic bond depends on
  - Charges of the ions (higher charges produce stronger bonds)
  - Sizes of the ions (smaller internuclear distances result in stronger bonds)

Metals

- Characteristics of metals
  - High electrical conductivity
    - Highly mobile electrons in structure
  - High thermal conductivity
    - Heat is carried through the structure by collision between electrons
  - Ductility and malleability
    - Can be drawn into wire or hammered into sheets
  - Luster
    - Polished metal surfaces reflect light
  - Insolubility in water and other common solvents

Solids with Different Structures

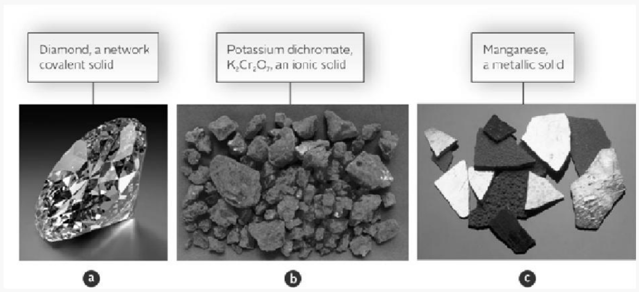


Table 9.6

TABLE 9.6 Structures and Properties of Types of Substances

Type	Structural Particles	Forces Within Particles	Forces Between Particles	Properties	Examples
Molecular	Molecules				
	(a) nonpolar	Covalent bond	Dispersion	Low mp, bp; often gas or liquid at 25°C; nonconductors; insoluble in water, soluble in organic solvents	H_2 CCl_4
	(b) polar	Covalent bond	Dispersion, dipole, H bond	Similar to nonpolar but generally higher mp and bp, more likely to be water-soluble	HCl NH_3
Network covalent	Atoms	—	Covalent bond	Hard solids with very high melting points; nonconductors; insoluble in common solvents	C SiO_2
Ionic	Ions	—	Ionic bond	High mp; conductors in molten state or water solution; often soluble in water, insoluble in organic solvents	NaCl MgO $CaCO_3$
Metallic	Cations, mobile electrons	—	Metallic bond	Variable mp; good conductors in solid; insoluble in common solvents	Na Fe

Example 9.7

EXAMPLE 9.7 CONCEPTUAL

For each species in column A, choose the description in column B that best applies.

A	B
(a) CO_2	(e) ionic, high-melting
(b) $CuSO_4$	(f) liquid metal, good conductor
(c) SiO_2	(g) polar molecule, soluble in water
(d) Hg	(h) ionic, insoluble in water
	(i) network covalent, high-melting
	(j) nonpolar molecule, gas at 25°C

STRATEGY

1. Characterize each species with respect to type, forces within and between particles, and if necessary, physical properties.
2. Find the appropriate matches.

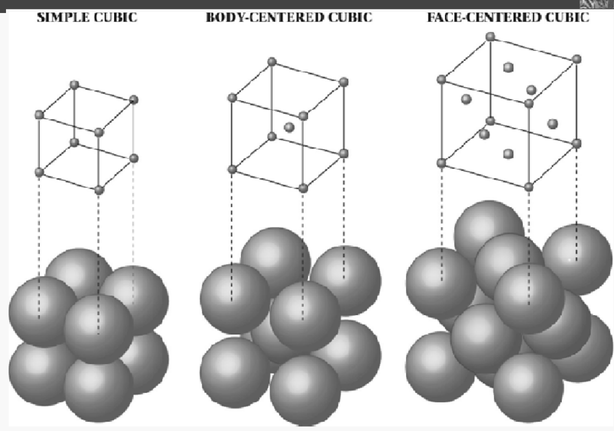
SOLUTION

(a) CO_2	molecule, nonpolar Only match is (j) even if you did not know that CO_2 is a gas at 25°C.
(b) $CuSO_4$	ionic, water soluble Only match is (e) even if you did not know that $CuSO_4$ has a high melting point.
(c) SiO_2	network covalent Only match is (i).
(d) Hg	metal, liquid at room temperature Only match is (f).

Crystal Structures

- Solids crystallize into definite geometric forms
  - Many times, the naked eye can see the crystal structure
  - NaCl forms cubic crystals

Figure 9.17



Crystal Building Blocks

- Crystals have definite geometric forms because the atoms or ions are arranged in definite, three-dimensional patterns
- Metals crystallize into one of three unit cells
  1. Simple cubic (SC): eight atoms at the corners
  2. Face centered cubic (FCC): simple cubic plus one atom in the center of each face
  3. Body-centered cubic (BCC): simple cubic plus one atom in the center of the cube

Crystal Building Blocks, Cont'd

- Three other ways to look at the crystalline unit cells:
  1. Number of atoms per unit cell
     - SC: 1 FCC: 4 BCC: 2
  2. Relation between side of cell (s) and radius of atom or ion (r)
     - SC: $2r = s$ FCC: $4r = s\sqrt{2}$ BCC: $4r = s\sqrt{3}$
  3. Percentage of empty space
     - SC: 47.5 FCC: 32.0 BCC: 26.0

Table 9.7

TABLE 9.7 Properties of Cubic Unit Cells

	Simple	BCC	FCC
Number of atoms per unit cell	1	2	4
Relation between side of cell, s, and atomic radius, r	$2r = s$	$4r = s\sqrt{3}$	$4r = s\sqrt{2}$
% of empty space	47.6	32.0	26.0

Example 9.8

EXAMPLE 9.8 GRADED

Silver is a metal commonly used in jewelry and photography. It crystallizes with a face-centered cubic (FCC) unit cell 0.407 nm on an edge.

(a) What is the atomic radius of silver in cm? ($1\ nm = 10^{-7}\ cm$)

(b) What is the volume of a single silver atom? (The volume of a spherical ball of radius r is $V = \frac{4}{3}\pi r^3$.)

(c) What is the density of a single silver atom?

(a)

ANALYSIS

Information given:	type of cubic cell (face-centered) length of side, s (0.407 nm) nm to cm conversion ($1\ nm = 1 \times 10^{-7}\ cm$)
Information implied:	side and atomic radius relationship in a face-centered cubic cell
Asked for:	atomic radius of silver in cm

STRATEGY

1. Relate the atomic radius, r, to the side of the cube, s, in a face-centered cubic cell (FCC). See Table 9.7.
2. Substitute into the equation $4r = s\sqrt{2}$.
3. Convert nm to cm.

SOLUTION

$4r = s\sqrt{2}$	$r = \frac{0.407\ nm\ (\sqrt{2})}{4} = 0.144\ nm \times \frac{1 \times 10^{-7}\ cm}{1\ nm} = 1.44 \times 10^{-8}\ cm$

Example 9.8, (Cont'd)

(b)

ANALYSIS

Information given:	from part (a); atomic radius, r (1.44×10^{-8} cm) formula for the volume of a sphere ($V = \frac{4}{3}\pi r^3$)
Asked for:	volume of a single Ag atom

continued

STRATEGY

Assume that the atom is a perfect sphere and substitute into the formula for the volume of a sphere.

SOLUTION

V	$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(1.44 \times 10^{-8}\ cm)^3 = 1.25 \times 10^{-23}\ cm^3$

Example 9.8, (Cont'd)

(c)

ANALYSIS

Information given:	from part (b): atomic volume, V ($1.25 \times 10^{-23}\ cm^3$) formula for the volume of a sphere ($V = \frac{4}{3}\pi r^3$)
Information implied:	molar mass of Ag Avogadro's number
Asked for:	density of a single Ag atom

STRATEGY

1. Recall that density = mass/volume.
2. Find the mass of a single Ag atom. Recall that there are 6.022×10^{23} atoms of silver in one molar mass of silver (107.9 g/mol). Use that as a conversion factor.

SOLUTION

mass of 1 Ag atom	$1\ Ag\ atom \times \frac{107.9\ g}{6.022 \times 10^{23}\ atoms} = 1.792 \times 10^{-22}\ g$
density	$density = \frac{mass}{volume} = \frac{1.792 \times 10^{-22}\ g}{1.25 \times 10^{-23}\ cm^3} = 14.3\ g/cm^3$

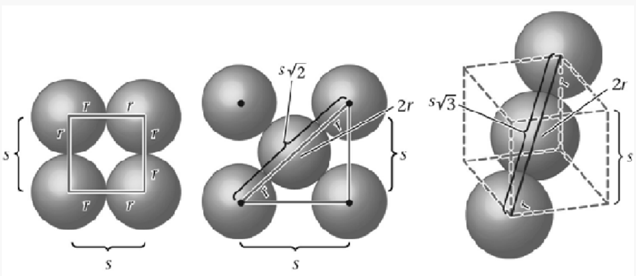
END POINTS

1. In face-centered cubic cells, the fraction of empty space is 0.26.
2. The calculated density in part (c) assumes no empty space. If empty space is factored in, [(0.26)(14.3) = 3.7], then 3.7 g/cm³ has to be subtracted from the density obtained in part (c). The calculated density is therefore [14.3 − 3.7] = 10.6 g/cm³. The experimentally obtained value is 10.5 g/cm³.

Ionic Crystals

- Geometry of ionic crystals is more difficult to describe than that of metals
  - LiCl
    - Larger Cl^- ions form a face-centered cube with Li^+ ions in the "holes" between the anions
  - NaCl
    - Larger Na^+ ions are slightly too large to fit into the holes between the anions, so the Cl^- ions are pushed apart slightly

Figure 9.18



Example 9.9

EXAMPLE 9.9

Consider Figure 9.19. The length of an edge of a cubic cell, *s*, is the distance between the center of an atom or ion at the "top" of the cell and the center of the atom or ion at the "bottom." Taking the ionic radii of Li^+, Na^+, and Cl^- to be 0.060 nm, 0.095 nm, and 0.181 nm, respectively, determine *s* for

(a) NaCl (b) LiCl

STRATEGY

Use Figure 9.19 to determine along which lines the ions touch.

SOLUTION

(a) NaCl

The atoms touch along a side.

$s = 1\ r \text{ of } Cl^- + 2\ r \text{ of } Na^+ + 1\ r \text{ of } Cl^-$

$= 0.181\text{ nm} + 2(0.095\text{ nm}) + 0.181\text{ nm} = 0.552\text{ nm}$

(b) LiCl

The chloride atoms touch along a face diagonal.

$s = 1\ r \text{ of } Cl^- + 2\ r \text{ of } Cl^- + 1\ r \text{ of } Cl^- = 4\ r \text{ of } Cl^-$

$= 4(0.181\text{ nm}) = 0.724\text{ nm}$

length of face diagonal $= s\sqrt{2} = (0.724\text{ nm})(\sqrt{2}) = 0.512\text{ nm}$

Key Concepts

1. Use the ideal gas law to determine whether a liquid will completely vaporize in a sealed container
2. Use the Clausius-Clapeyron equation to relate vapor pressure to temperature
3. Use a phase diagram to determine the phases present given the pressure and temperature
4. Identify the type of intermolecular forces in different substances
5. Classify substances as ionic, molecular, network covalent, or metallic
6. Relate unit cell dimensions to atomic or ionic radii