

3.2 Properties of Solids

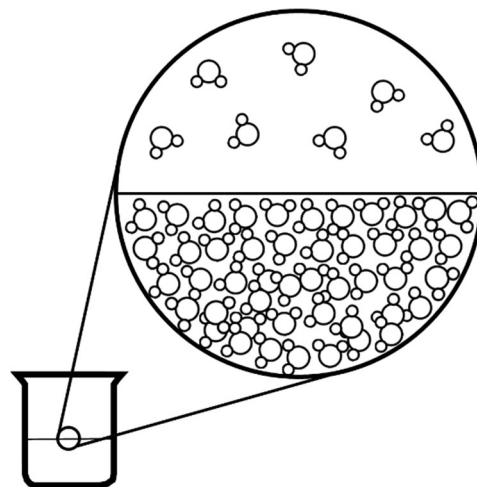
Essential knowledge statements from the AP Chemistry CED:

- Many properties of liquids and solids are determined by the strengths and types of intermolecular forces present. Because intermolecular interactions are broken when a substance vaporizes, the vapor pressure and boiling point are directly related to the strength of those interactions. Melting points also tend to correlate with interaction strength, but because the interactions are only rearranged, in melting, the relations can be more subtle.
- Particulate-level representations, showing multiple interacting chemical species, are a useful means to communicate or understand how intermolecular interactions help to establish macroscopic properties.
- Due to strong interactions between ions, ionic solids tend to have low vapor pressures, high melting points, and high boiling points. They tend to be brittle due to the repulsion of like charges caused when one layer slides across another layer. They conduct electricity only when the ions are mobile, as when the ionic solid is melted or dissolved in water or another solvent.
- In covalent network solids, the atoms are covalently bonded together into a three-dimensional network (e.g., diamond) or layers of two-dimensional networks (e.g., graphite). These are only formed from nonmetals: elemental (e.g., diamond, graphite) or binary compounds of two nonmetals (e.g., silicon dioxide and silicon carbide). Due to the strong covalent interactions, covalent solids have high melting points. Three-dimensional network solids are also rigid and hard, because the covalent bond angles are fixed. However, graphite is soft because adjacent layers can slide past each other relatively easily.
- Molecular solids are composed of distinct, individual units of covalently-bonded molecules attracted to each other through relatively weak intermolecular forces. Molecular solids generally have a low melting point because of the relatively weak intermolecular forces present between the molecules. They do not conduct electricity because their valence electrons are tightly held within the covalent bonds and the lone pairs of each constituent molecule. Molecular solids are sometimes composed of very large molecules or polymers.
- Metallic solids are good conductors of electricity and heat, due to the presence of free valence electrons. They also tend to be malleable and ductile, due to the ease with which the metal cores can rearrange their structure. In an interstitial alloy, interstitial atoms tend to make the lattice more rigid, decreasing malleability and ductility. Alloys typically retain a sea of mobile electrons and so remain conducting.
- In large biomolecules or polymers, noncovalent interactions may occur between different molecules or between different regions of the same large biomolecule. The functionality and properties of such molecules depend strongly on the shape of the molecule, which is largely dictated by noncovalent interactions.

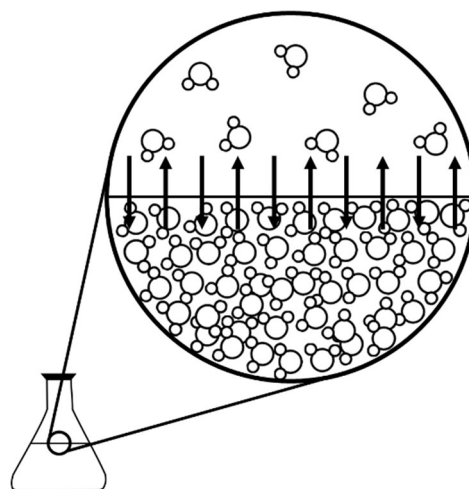
The first diagram shown at right represents a sample of pure water in a beaker at room temperature. The close-up view shows a particulate model of H₂O molecules near the surface of the liquid. The molecules in the liquid phase are moving at different speeds and have a range of values for kinetic energy.

Some of the molecules near the surface have sufficient energy to overcome the intermolecular forces between them. They can escape from the liquid phase and enter the space above the liquid surface.

Eventually the beaker will become dry when the sample of water evaporates completely.



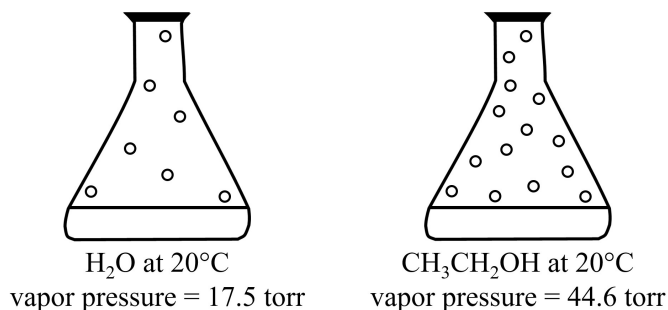
The second diagram shown at right represents a sample of pure water in a sealed flask at room temperature. The arrows in the close-up view indicate that molecules undergo both evaporation and condensation. A point is reached in this sealed container in which the rate of evaporation is equal to the rate of condensation. This is a state of dynamic equilibrium. As long as the temperature remains constant, the number of water molecules in the gas phase remains constant.



The **vapor pressure** of a liquid is defined as the pressure exerted by a gas in equilibrium with its liquid phase at a given temperature.

| Temp. (°C) | VP (torr) | Temp. (°C) | VP (torr) | Temp. (°C) | VP (torr) |
|------------|-----------|------------|-----------|------------|-----------|
| 10 | 9.21 | 40 | 55.3 | 70 | 233.7 |
| 20 | 17.54 | 50 | 92.5 | 80 | 355.1 |
| 30 | 31.82 | 60 | 149.4 | 90 | 525.8 |

1. The table above shows the vapor pressure of H₂O at various temperatures. Explain why the vapor pressure of water (or any liquid, for that matter) will increase when the temperature of the liquid increases. Discuss the kinetic energy of the particles in your answer.



The diagram above shows two sealed flasks at 20°C . The flask on the left contains a sample of pure H_2O , and the flask on the right contains a sample of pure ethanol ($\text{CH}_3\text{CH}_2\text{OH}$).

2. Answer the following questions based on the information in the diagram.
 - (a) Which substance, water or ethanol, appears to evaporate more easily at 20°C ?
 - (b) Which substance, water or ethanol, is more likely to experience stronger intermolecular attractive forces in the liquid phase?
 - (c) Which substance, water or ethanol, is more likely to have the higher boiling point?

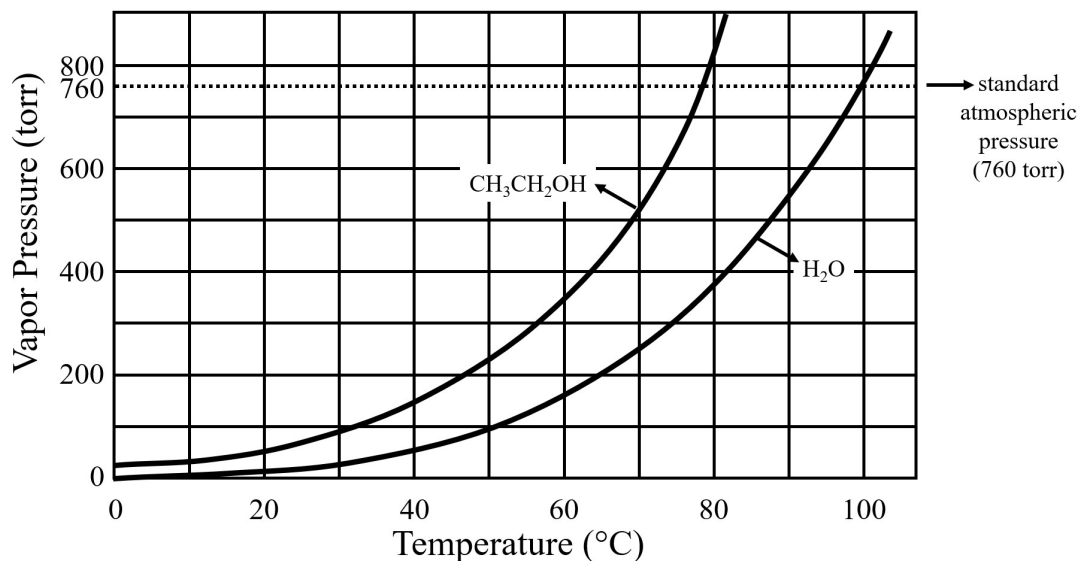
3. When comparing two different liquids at the same temperature, the liquid that has a

(lower higher) vapor pressure should also be the liquid that has a

(lower higher) boiling point.

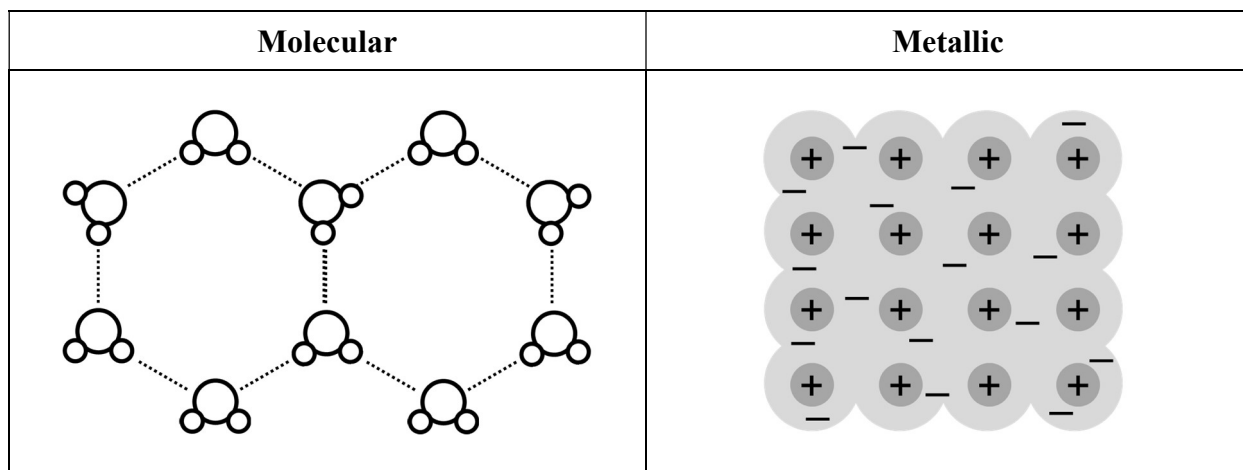
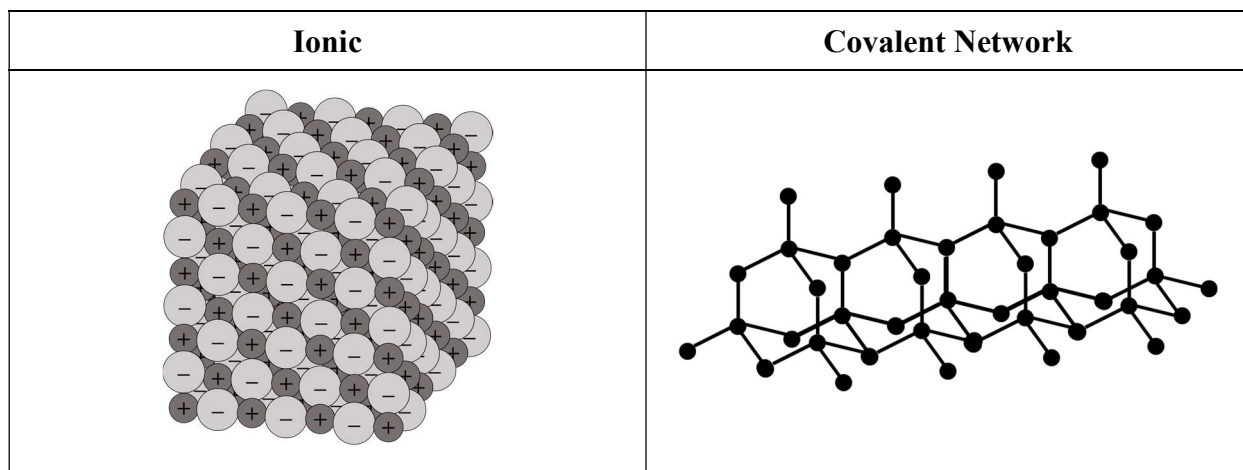
The **boiling point** of a liquid is defined as the temperature at which the vapor pressure of the liquid is equal to the external pressure surrounding the liquid.

The **normal boiling point** of a liquid refers to the situation in which the vapor pressure of the liquid is equal to standard atmospheric pressure at sea level, which is usually defined as 1 atmosphere (1 atm) or 760 torr.



4. The diagram above is a graph of vapor pressure versus temperature for water and ethanol. The normal boiling point of water is 100°C. Use the information in the diagram to estimate the normal boiling point of ethanol. _____

Particulate-level Representations of Four Different Types of Solid



There are four different types of solids that you should be familiar with in AP Chemistry. Descriptions of each type of solid are shown in the table below.

| Type | Ionic | Covalent Network | Molecular | Metallic |
|--------------------------------------|--|--|---|---|
| Particles | positive and negative ions | atoms | molecules | positive metal cations (nucleus plus core electrons) and valence electrons |
| Attractions Between Particles | electrostatic attractions between oppositely charged ions | covalent bonds between atoms in a large, extended network | intermolecular attractions between molecules | attractions between positive metal cations and a "sea" of delocalized, mobile valence electrons |
| Electrical Conductivity | does not conduct as a solid because ions cannot move freely; conducts when melted or dissolved in a solvent because ions can move freely | does not conduct because valence electrons are localized in covalent bonds | does not conduct because the electrons are localized in covalent bonds; the particles are neutral molecules | conducts electricity as a solid because of the mobile valence electrons |
| Melting Point | relatively high | relatively high | relatively low | varies over a wide range |
| Other Properties | hard, brittle solid | hard, rigid solid | soft solid | malleable and ductile |
| Examples | LiBr NaNO ₃ MgO KCl CuSO ₄ PbI ₂ | diamond (C) graphite (C) silicon (Si) quartz (SiO ₂) silicon carbide (SiC) boron nitride (BN) | I ₂ CO ₂ CH ₂ Cl ₂ H ₂ O C ₁₀ H ₈ C ₆ H ₁₂ O ₆ | Na Mg Al Ni Cu Zn |

5. When a sample of solid diamond (C) melts, covalent bonds are broken. However, when a sample of solid H₂O melts, covalent bonds are not broken. Explain.

6. The following information was collected for four different solids, labeled A through D.

| Solid | Physical Appearance | Melting Point | Conductivity | Solubility |
|-------|---------------------|---------------|--|--|
| A | white solid | 80°C | nonelectrolyte | slightly soluble in H ₂ O (30 mg/L) |
| B | gray solid | 1414°C | nonelectrolyte | insoluble in H ₂ O |
| C | white solid | 770°C | conducts electricity when dissolved in water | very soluble in H ₂ O (344 g/L) |
| D | silvery-white solid | 1455°C | conducts electricity as a solid | insoluble in H ₂ O |

(a) Based on this information, classify each of the four solids into one of the following types: metallic, ionic, covalent network, and molecular

A _____ C _____

B _____ D _____

(b) The identity of the four solids are (in no particular order):

silicon (Si), nickel (Ni), naphthalene (C₁₀H₈), and potassium chloride (KCl)

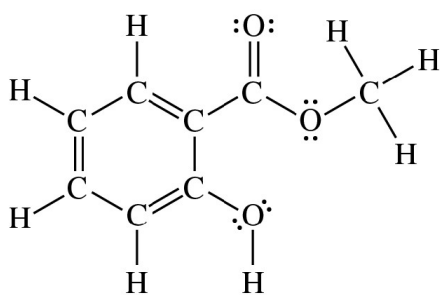
Make a prediction for the most likely identity of each solid.

A _____ C _____

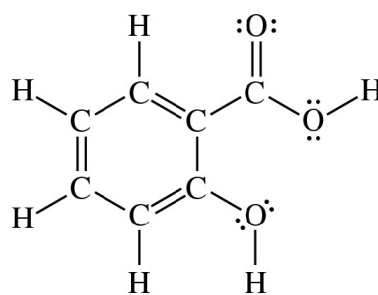
B _____ D _____

| Substance | Melting Point (K) | Boiling Point (K) |
|------------------|-------------------|-------------------|
| SiH ₄ | 88 | 161 |
| SiO ₂ | 1986 | 3220 |

7. Use principles of interparticle forces to explain the difference in the properties of the two substances shown in the table above.



Methyl Salicylate
Melting Point: -9°C



Salicylic Acid
Melting Point: 159°C

8. The structures and melting points for methyl salicylate and salicylic acid are shown above. The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

3.3 Solids, Liquids, and Gases

Essential knowledge statements from the AP Chemistry CED:

- Solids can be crystalline, where the particles are arranged in a regular three-dimensional structure, or they can be amorphous, where the particles do not have a regular, orderly arrangement. In both cases, the motion of the individual particles is limited, and the particles do not undergo overall translation with respect to each other. The structure of the solid is influenced by interparticle interactions and the ability of the particles to pack together.
 - The constituent particles in liquids are in close contact with each other, and they are continually moving and colliding. The arrangement and movement of particles are influenced by the nature and strength of the forces (e.g., polarity, hydrogen bonding, and temperature) between the particles.
 - The solid and liquid phases for a particular substance typically have similar molar volume because, in both phases, the constituent particles are in close contact at all times.
 - In the gas phase, the particles are in constant motion. Their frequencies of collision and the average spacing between them are dependent on temperature, pressure, and volume. Because of this constant motion, and minimal effects of forces between particles, a gas has neither a definite volume nor a definite shape.
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3.4 Ideal Gas Law

Essential knowledge statements from the AP Chemistry CED:

- The macroscopic properties of ideal gases are related through the ideal gas law.
 - Equation: $PV = nRT$
 - In a sample containing a mixture of ideal gases, the pressure exerted by each component (the partial pressure) is independent of the other components. Therefore, the total pressure of the sample is the sum of the partial pressures.
 - Equation: $P_A = P_{\text{total}} \times X_A$ where $X_A = \frac{\text{moles A}}{\text{total moles}}$
 - Equation: $P_{\text{total}} = P_A + P_B + P_C + \dots$
 - Graphical representations of the relationships between P , V , T , and n are useful to describe gas behavior.
-

Properties of an Ideal Gas

- Gas particles are in constant random, rapid motion.
- Gases expand to fill their container completely.
- Two or more gases will form a homogeneous mixture when they are combined together.
- Gases are highly compressible.
- The volume of the gas particles themselves is negligible compared to the volume occupied by the gas.
- Collisions of gas particles are perfectly elastic, meaning that energy is transferred but not lost during collisions.
- There are no attractive or repulsive forces between the gas particles.

Here is a portion of the AP Chemistry Equations and Constants Sheet that includes information about gases.

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE_{\text{molecule}} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = \epsilon bc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

ϵ = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$

$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr}$

STP = 273.15 K and 1.0 atm

Ideal gas at STP = 22.4 L mol⁻¹

Relationships Between Gas Variables (P, V, n, and T)

| Variable #1 | Relationship | Variable #2 | Constant Variables | Equation |
|-------------|------------------------------|-------------|--------------------|-------------------------------------|
| P | is inversely proportional to | V | n, T | $P_1V_1 = P_2V_2$ |
| P | is directly proportional to | T | n, V | $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ |
| P | is directly proportional to | n | V, T | $\frac{P_1}{n_1} = \frac{P_2}{n_2}$ |
| V | is directly proportional to | n | P, T | $\frac{V_1}{n_1} = \frac{V_2}{n_2}$ |
| V | is directly proportional to | T | n, P | $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ |

9. A student was assigned the task of determining the molar mass of an unknown gas. The student measured the mass of a sealed 843 mL rigid flask that contained dry air. The student then flushed the flask with the unknown gas, resealed it, and measured the mass again. Both the air and the unknown gas were at 23.0°C and 750. torr. The data for the experiment are shown in the table below.

| | |
|--------------------------------------|----------|
| Volume of sealed flask | 843 mL |
| Mass of sealed flask and dry air | 157.70 g |
| Mass of sealed flask and unknown gas | 158.08 g |

- (a) Calculate the mass, in grams, of the dry air that was in the sealed flask.
(The density of dry air is 1.18 g L^{-1} at 23.0°C and 750. torr.)
- (b) Calculate the mass, in grams, of the sealed flask itself (i.e., if it had no air in it.)
- (c) Calculate the mass, in grams, of the unknown gas that was added to the sealed flask.
- (d) Using the information above, calculate the value of the molar mass of the unknown gas.
- (e) After the experiment was completed, the instructor informed the student that the unknown gas was carbon dioxide (44.0 g/mol). Calculate the percent error in the value of the molar mass calculated in part (d).

9. (continued)

- (f) For each of the following two possible occurrences, indicate whether it by itself could have been responsible for the error in the student's experimental result. You need not include any calculations with your answer. For each of the possible occurrences, justify your answer.

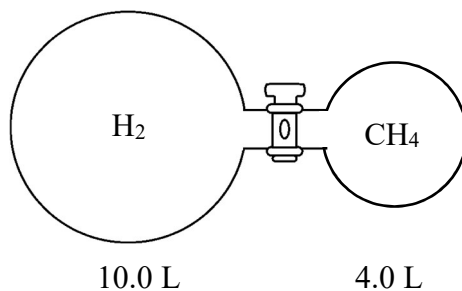
Occurrence 1: The flask was incompletely flushed with $\text{CO}_2(g)$, resulting in some dry air remaining in the flask.

Occurrence 2: The temperature of the air was 23.0°C , but the temperature of the $\text{CO}_2(g)$ was lower than the reported 23.0°C .

- (g) Describe the steps of a laboratory method that the student could use to verify that the volume of the rigid flask is 843 mL at 23.0°C . You need not include any calculations in your answer.

10. A pure sample of a gas has a density of 1.31 g/L at 1.00 atm and 25.0°C . What is the molar mass of this gas? Propose a possible identity of this gas.

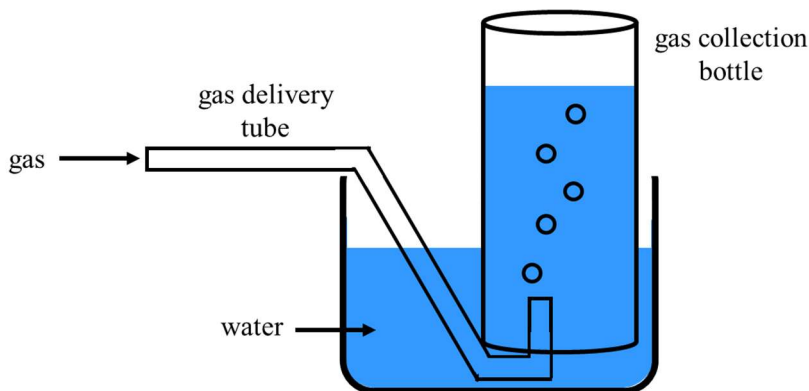
11. A gas mixture contains 14.0 g $\text{N}_2(\text{g})$ and 32.0 g $\text{O}_2(\text{g})$. The total pressure of the gas mixture is equal to 1200 torr. Calculate the partial pressure of each gas in the mixture.



12. In the diagram above, two flasks are connected by a valve that is closed. The flask on the left contains 10.0 L of $\text{H}_2(\text{g})$ at a pressure of 3.0 atm. The flask on the right contains 4.0 L of $\text{CH}_4(\text{g})$ at a pressure of 2.0 atm.
- (a) Calculate the total pressure of the system after the valve is opened and the two gases are mixed completely. Assume that the temperature remains constant and that the total volume of the gas mixture is equal to 14.0 L.

$$\text{mole fraction of A } (X_A) = \frac{\text{moles of A}}{\text{total moles in mixture}}$$

- (b) The definition of mole fraction (X) is shown above. Calculate the mole fraction of H_2 and CH_4 in this gas mixture.



In the laboratory, water displacement can be used to collect a sample of gas. This technique is appropriate to collect a gas that does not react with water or dissolve (very much) in water. A collection bottle is prepared that is initially filled with water and inverted in a container of water. Once the gas has been collected, the collection bottle is raised or lowered so that the water level inside the bottle is the same as the water level outside the bottle. This ensures that the gas pressure inside the bottle is equal to the atmospheric pressure outside the bottle.

The total pressure inside the collection bottle is equal to the sum of the partial pressure of the gas collected (P_{gas}) and the vapor pressure of the water (P_{H_2O}). Values for the vapor pressure of water at various temperatures can be found in a reference table.

$$P_{total} = P_{atmosphere} = P_{gas} + P_{H_2O}$$

13. A sample of butane gas was collected by the method of water displacement. The initial mass of a butane lighter is recorded as 22.24 g. The temperature of the water bath is 22°C. The barometric pressure in the laboratory is 755.0 torr. After the gas is collected, the mass of the butane lighter is recorded as 22.02 g. At the end of the experiment, the height of the collection tube is adjusted so that the water levels inside and outside the tube are the same.

| Vapor Pressure of Water at Different Temperatures (torr) | | | | |
|--|-------|-------|-------|-------|
| Temperature (°C) | 20 | 21 | 22 | 23 |
| Vapor Pressure (torr) | 17.54 | 18.65 | 19.83 | 21.07 |

- (a) Based on the information in the table above, what is the value of the vapor pressure of water under the conditions of this experiment?
- (b) Calculate the partial pressure of the dry butane gas that is collected in this experiment.

13. (continued)

- (c) The volume of butane gas collected in this experiment is recorded as 100.0 mL. Calculate the number of moles of butane gas collected in this experiment. Assume that the temperature of the butane gas is the same as the temperature of the water bath.

 - (d) Calculate the mass of butane gas collected in this experiment.

 - (e) Calculate the experimental value for the molar mass of butane.

 - (f) Calculate the percent error for the molar mass value obtained in this experiment. The chemical formula for butane is C_4H_{10} .
-

14. A sample of a pure, gaseous hydrocarbon is introduced into a previously evacuated rigid 1.00 L vessel. The pressure of the gas is 0.200 atm at a temperature of 127°C .

- (a) Calculate the number of moles of the hydrocarbon in the vessel.

- (b) $O_2(g)$ is introduced into the same vessel containing the hydrocarbon. After the addition of the $O_2(g)$, the total pressure of the gas mixture in the vessel is 1.40 atm at 127°C . Calculate the partial pressure of $O_2(g)$ in the vessel.

14. (continued)

The mixture of the hydrocarbon and $\text{O}_2(g)$ is sparked so that a combustion reaction occurs, producing $\text{CO}_2(g)$ and $\text{H}_2\text{O}(g)$. The reaction proceeds to completion so that all of the hydrocarbon is consumed. There is some $\text{O}_2(g)$ remaining in the reaction vessel after the reaction is complete. The temperature inside the reaction vessel is returned to 127°C , and the partial pressure of each gas in the reaction vessel at the end of the reaction are shown in the table below.

| Gas | Partial Pressure (atm) at 127°C |
|-------------------------|---|
| $\text{CO}_2(g)$ | 0.600 |
| $\text{H}_2\text{O}(g)$ | 0.800 |
| $\text{O}_2(g)$ | 0.200 |

(c) Calculate each of the following quantities.

$$\frac{\text{moles of } \text{CO}_2(g) \text{ produced}}{\text{moles of hydrocarbon consumed}}$$

$$\frac{\text{moles of } \text{H}_2\text{O}(g) \text{ produced}}{\text{moles of hydrocarbon consumed}}$$

(d) Determine the chemical formula of the hydrocarbon and write the balanced chemical equation for the combustion reaction that occurred in this experiment.

(e) Calculate the mass of the hydrocarbon that was consumed in this experiment.