Kinetic Molecular Theory, Vapor Pressure and Phase Diagrams

The Kinetic Molecular Theory of Gases

- The Kinetic Molecular Theory (KMT) is a model that attempts to explain the properties of an ideal gas.
- The KMT states:
  - The particles of an ideal gas are so small compared with the distances between them that the volume of individual particles can be assumed to be negligible (zero).
  - The particles of an ideal gas are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.
  - The particles of an ideal gas are assumed to exert no forces on each other; no attraction or repulsion between particles.
  - The average kinetic energy of gas particles of an ideal gas is assumed to be directly proportional to the Kelvin temperature of the gas.
- An ideal gas is a hypothetical concept. No gas exactly follows the ideal gas law, although many gases come very close at low pressures and/or high temperatures. (HoT LiPs). The ideal gas behavior can best be thought of as the behavior approached by real gases under certain conditions.

Vapor Pressure

- The water level in a glass of water left out will gradually decrease until all of the water has evaporated. This vaporization of water molecules occurs as water molecules gain enough kinetic energy to overcome the attractive forces keeping them in the liquid. Remember that as one molecule evaporates, the particles left behind cool. In order to evaporate a particle must absorb energy. Once this happens, it changes state and the particles left behind have a lower average kinetic energy.
- When a liquid is placed in a sealed container, the amount of liquid at first decreases but eventually becomes constant. The decrease occurs because there is an initial net transfer of molecules from liquid to the vapor state. This evaporation process occurs at a constant rate at a given temperature.
- The process by which vapor molecules re-form a liquid is called condensation. Eventually, enough vapor molecules are present above the liquid so that the rate of condensation equals the rate of evaporation. At this point no further net change occurs in the amount of liquid or vapor because the two processes exactly balance each other; the system is at equilibrium. This process is highly dynamic.
- Liquids with high vapor pressure are said to be volatile. The vapor pressure of a liquid is principally determined by the size of the intermolecular forces in the liquid.
- In general, substances with large molar masses have relatively low vapor pressures, mainly because of the large dispersion forces. The more electrons a substance has, the more polarizable it is, and the greater are the dispersion forces.
- Vapor pressure increases significantly with temperature. The diagram to the right shows how vapor pressure increases with temperature for 4 different substances.
- Like liquids, solids have vapor pressures. Under normal conditions iodine and dry ice (solid CO₂) sublime; they go directly from the solid to the gaseous state without passing through the liquid state.
- Scientists use an instrument called a manometer (pictured below) in order to measure the pressure exerted by a gas. By comparing the heights of the mercury in the U-tube, scientists can calculate a substance’s vapor pressure. In the diagrams below, the first graphic shows a higher vapor pressure than the second. As temperature increases, the vapor pressure of a liquid also increases, so you can assume that the first liquid is at a higher temperature than the second.

The images to the left show two manometers in which liquid A has a higher vapor pressure than liquid B.
Phase Diagrams

A phase diagram is a graphic representation of the relationship between the physical state of a substance and its pressure and temperature. A phase diagram describes conditions and events in a closed system. The phase diagram for water is shown to the right. A line that separates any two regions gives the conditions at which those two phases exist at equilibrium. The point at which the three segments meet is called the **triple point**. The triple point is the point on a phase diagram where all three states of a substance are present. For water, the triple point occurs when the pressure is 0.60 kPa and the temperature is 0.0098 °C. **Critical temperature** is defined as the temperature above which vapor cannot be liquefied no matter what pressure is applied. The **critical pressure** is the pressure required to produce liquefaction at the critical temperature. Together the critical pressure and the critical temperature define the **critical point**.

A phase diagram can be used to determine the melting point and boiling point for a substance at various temperatures and pressures. The **normal melting point** of a substance is the temperature at which the solid and liquid states have the same vapor pressure under conditions at standard pressure (1 atm or 101.3 kPa). For water, the normal melting point is 0°C. The **normal boiling point** is the temperature at which the vapor pressure of the liquid is equal to standard pressure (1 atm or 101.3 kPa). For water, the normal boiling point is 100°C. **Boiling point** is the temperature at which the vapor pressure of a liquid is just equal to the external pressure. As you can see from the diagram above, water can be made to melt or boil at temperature other than its normal melting and normal boiling points. Note that the solid/liquid boundary on the phase diagram for water has a negative slope. This means that the melting point of ice decreases as the external pressure increases. This behavior, which is opposite of most substances, occurs because the density of ice is less than that of the liquid water at its melting point. When water freezes it expands. The low density of ice means that ice formed on rivers and lakes will float, providing a layer of insulation that helps prevent bodies of water from freezing solid in the winter. Aquatic life can therefore continue to live through periods of freezing temperatures. The phase diagram for carbon dioxide is shown to the right. The solid/liquid line has a positive slope, since solid CO₂ is denser than liquid CO₂.

Carbon dioxide is often used in fire extinguishers, where it exists as a liquid at 25°C under high pressures. Liquid CO₂ released from the extinguisher into the environment at 1 atm immediately changes to a vapor. Being heavier than air, this vapor smothers the fire by keeping oxygen away from the flame. The liquid/vapor transition is highly endothermic, so cooling also results, which helps to put out the fire.

**Homework:**

1. List the four properties assumed by the kinetic molecular theory.

2. What is vapor pressure?

3. What is meant when a liquid is said to be volatile?

4. Which of the following substances would have the lowest vapor pressure, CH₄, C₂H₆, C₃H₈ or C₄H₁₀? Explain!

5. What happens to vapor pressure as temperature increases?

6. Do solids exert a vapor pressure?
7. Draw a graph that shows the relationship between vapor pressure and temperature.

8. What is a manometer?

9. Equal quantities of different liquids are placed in an open manometers at 20°C. Which liquid has the highest vapor pressure?

10. Define triple point.

11. What are the triple point values of pressure and temperature for water?

12. Define critical temperature.

13. Define critical pressure.


15. Define normal melting point.

16. Define normal boiling point.

17. Define boiling point.

18. What is the difference between boiling point and normal boiling point? (Don’t just tell me the definitions!)

19. What can be done to get water to boil below its normal boiling point?

20. What characteristic of water’s triple point graph indicates that solid water is less dense than liquid water?

21. On the diagram to the right, label all of the following: normal melting point, normal boiling point, solid, liquid, gas, triple point, the solid-vapor border, the liquid-vapor border and the solid-liquid border.
Gas Laws Multiple Choice Review

1. When a sample of oxygen gas in a closed container of constant volume is heated until its absolute temperature is doubled, which of the following is also doubled?
   (A) The density of the gas  
   (B) The pressure of the gas  
   (C) The average velocity of the gas molecules  
   (D) The number of molecules per cm³  
   (E) The potential energy of the molecules

2. Equal masses of three different ideal gases, X, Y, and Z, are mixed in a sealed rigid container. If the temperature of the system remains constant, which of the following statements about the partial pressure of gas X is correct?
   (A) It is equal to 1/3 the total pressure  
   (B) It depends on the intermolecular forces of attraction between molecules of X, Y, and Z.  
   (C) It depends on the relative molecular masses of X, Y, and Z.  
   (D) It depends on the average distance traveled between molecular collisions.  
   (E) It can be calculated with knowledge only of the volume of the container.

3. The system shown to the right is at equilibrium at 28°C. At this temperature, the vapor pressure of water is 28 millimeters of mercury. The partial pressure of O₂(g) in the system is:
   (A) 28 mm Hg  
   (B) 56 mm Hg  
   (C) 133 mm Hg  
   (D) 161 mm Hg  
   (E) 189 mm Hg

4. What is the volume of 3.00 mol of gas @ STP?
   (A) 22.4 L  
   (B) 3 x 22.4 L  
   (C) 3 x 22.4 L x 760  
   (D) 3 x 22.4 L x 273 / 760  
   (E) It cannot be determined without knowing which gas is involved.

5. An ideal gas of volume 189 mL is collected over water at 30°C and 777 torr. The vapor pressure of water is 32 torr @ 30°C. What pressure is exerted by the dry gas under these conditions?
   (A) 320 torr  
   (B) 745 torr  
   (C) 777 torr  
   (D) 32 / 77 torr  
   (E) 32 x 777 torr

6. Two flexible containers for gases are at the same temperature and pressure. One holds 0.50 gram of hydrogen and the other holds 8.0 grams of oxygen. Which of the following statements regarding these gas samples is FALSE?
   (A) The volume of the hydrogen container is the same as the volume of the oxygen container.  
   (B) The number of molecules in the hydrogen container is the same as the number of molecules in the oxygen container.  
   (C) The density of the hydrogen sample is less than that of the oxygen sample.  
   (D) The average kinetic energy of the hydrogen molecules is the same as the average kinetic energy of the oxygen molecules.  
   (E) The average speed of the hydrogen molecules is the same as the average speed of the oxygen molecules.

7. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of
   (A) ½  
   (B) (313/293)½  
   (C) 313/293  
   (D) 2  
   (E) 4

8. Which of the following is the same for one mole samples of ideal monatomic gases at standard temperature and pressure?
   (A) The total kinetic energy of the molecules  
   (B) The density of the sample  
   (B) The number of collisions per second of molecules with the wall  
   (D) The average speed of the molecules  
   (E) The root-mean-square speed of the molecules

9. At 25 °C, a sample of NH₃ (molar mass 17 grams) effuses at the rate of 0.050 mole per minute. Under the same conditions, which of the following gases effuses at approximately one-half that rate?
   (A) O₂ (molar mass 32 grams)  
   (B) He (molar mass 4.0 grams)  
   (C) CO₂ (molar mass 44 grams)  
   (D) Cl₂ (molar mass 71 grams)  
   (E) CH₄ (molar mass 16 grams)

10. A sample of an ideal gas is cooled from 50.0 °C to 25.0 °C in a sealed container of constant volume. Which of the following values for the gas will decrease?
    I. The average molecular mass of the gas  
    II. The average distance between the molecules  
    III. The average speed of the molecules
    (A) I only  
    (B) II only  
    (C) III only  
    (D) I and III  
    (E) II and III
11. A rigid metal tank contains oxygen gas. Which of the following applies to the gas in the tank when additional oxygen is added at constant temperature?
   (A) The volume of the gas increase.
   (B) The pressure of the gas decreases.
   (C) The average speed of the gas molecules remains the same.
   (D) The total number of gas molecules remains the same.
   (E) The average distance between the gas molecules increases.

12. Equal numbers of moles of He(g), Ar(g), and Ne(g) are placed in a glass vessel at room temperature. If the vessel has a pinhole-sized leak, which of the following will be true regarding the relative values of the partial pressures of the gases remaining in the vessel after some of the gas mixture has effused?
   (A) \( P_{\text{He}} < P_{\text{Ne}} < P_{\text{Ar}} \)
   (B) \( P_{\text{He}} < P_{\text{Ar}} < P_{\text{Ne}} \)
   (C) \( P_{\text{Ne}} < P_{\text{Ar}} < P_{\text{He}} \)
   (D) \( P_{\text{Ar}} < P_{\text{He}} < P_{\text{Ne}} \)
   (E) \( P_{\text{He}} = P_{\text{Ar}} = P_{\text{Ne}} \)

13. Argon gas initially at 25°C is heated to 50°C in a closed container. Which statement is correct?
   (A) The average kinetic energy of the argon atoms does not change.
   (B) The average kinetic energy of the argon atoms doubles.
   (C) The pressure of the gas decreases by about 50 percent.
   (D) The pressure of the gas doubles.
   (E) The pressure of the gas increases by about 8 percent.

14. 100 grams of O\(_2\)(g) and 100 grams of He(g) are in separate containers of equal volume. Both gases are at 100°C. Which of the following statements is true?
   (A) Both gases would have the same pressure.
   (B) The average kinetic energy of the O\(_2\) molecules is greater than that of the He molecules.
   (C) The average kinetic energy of the He molecules is greater than that of the O\(_2\) molecules.
   (D) There are equal numbers of He molecules and O\(_2\) molecules.
   (E) The pressure of the He(g) would be greater than that of the O\(_2\)(g).

15. Which one of the following is NOT an assumption of the kinetic theory of gases?
   (A) Gas particles are negligibly small.
   (B) Gas particles are in constant motion.
   (C) Gas particles don’t attract each other.
   (D) Gas particles undergo elastic collisions.
   (E) Gas particles undergo a decrease in kinetic energy when passed from a region of high pressure to a region of low pressure.

16. Which of the following would express the approximate density of carbon dioxide gas at 0°C and 2.00 atm pressure (in grams per liter)?
   (A) 2 g/L
   (B) 4 g/L
   (C) 6 g/L
   (D) 8 g/L
   (E) none of the above

17. At 25°C, a sample of NH\(_3\) (molar mass 17 grams) effuses at the rate of 0.050 mole per minute. Under the same conditions, which of the following gases effuses at approximately double that rate?
   (A) O\(_2\) (molar mass 32 grams)
   (B) He (molar mass 4.0 grams)
   (C) CO\(_2\) (molar mass 44 grams)
   (D) Cl\(_2\) (molar mass 71 grams)
   (E) CH\(_4\) (molar mass 16 grams)

18. A sample of 0.0100 mole of oxygen gas is confined at 37°C and 0.216 atmosphere. What would be the pressure of this sample at 15°C and the same volume?
   (A) 0.0876 atm
   (B) 0.175 atm
   (C) 0.201 atm
   (D) 0.233 atm
   (E) 0.533 atm