# GENERAL CHEMISTRY

# GAS LAWS

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# OBJECTIVES

- **To become familiar with Gas Laws (Boyle, Charles and Ideal Gas Laws);**
- **To familiarize with Kinetic Molecular Theory;**
- **See some applications of Gas Laws.**

# TEXTBOOK

**Brown, Lemay & Bursten, *Chemistry: The Central Science*, 10th Ed. (Chapter 10)**

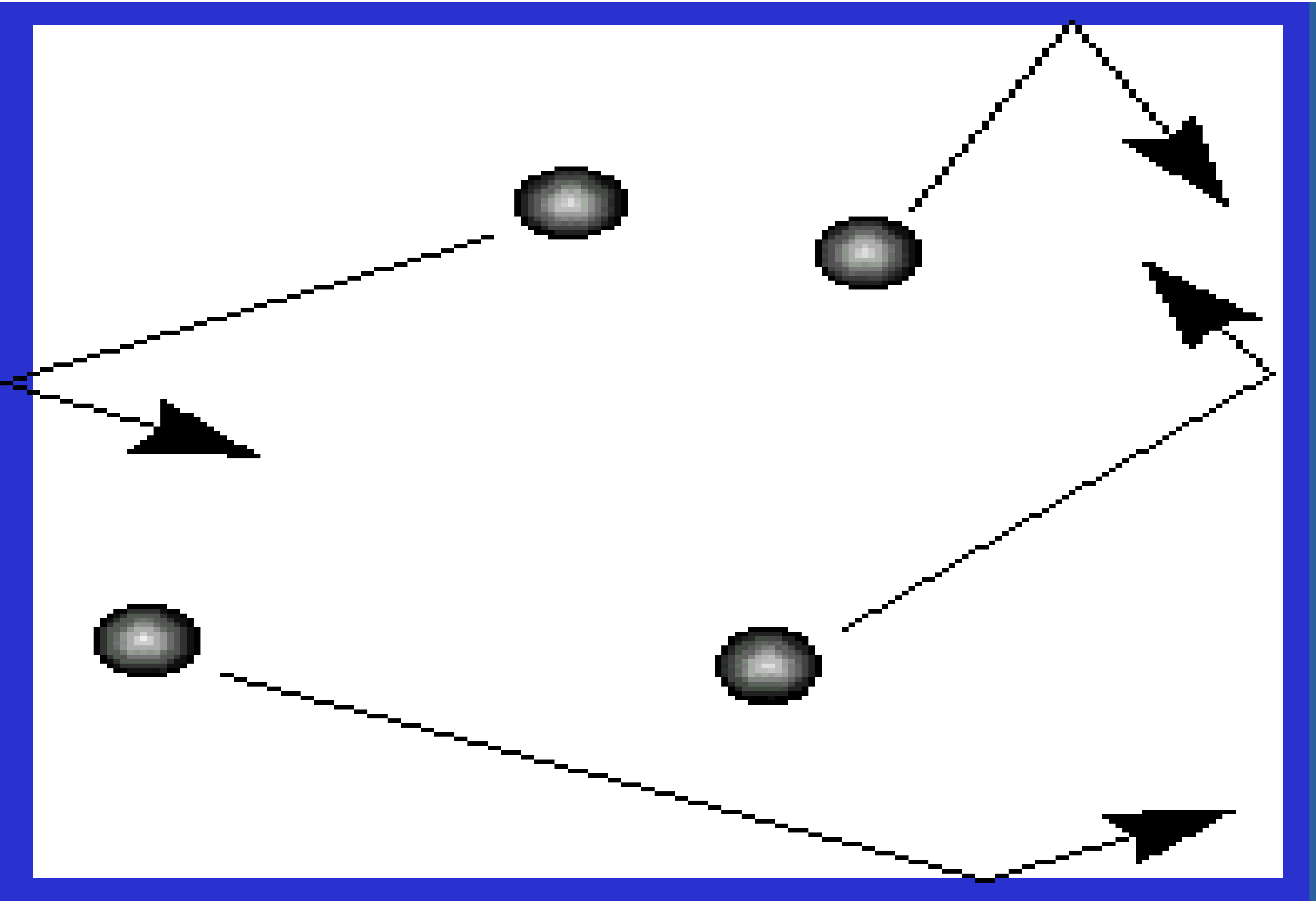
# GASES PROPERTIES

- **Gases are highly compressible and expand to occupy the full volume of their containers.**
- **Gases always form homogeneous mixtures with other gases.**
- **Gases only occupy about 0.1% of the volume of their containers.**

# PRESSURE

- **The pressure of a gas is causes by collisions of the molecules with the walls of the container.**
- **The magnitude of the pressure is related to how hard and how often the molecules strike the wall.**
- **The "hardness" of the impact of the molecules with the wall will be related to the velocity of the molecules times the mass of the molecules.**

# PRESSURE



# MEASURING GAS PRESSURE

- **Pressure is the force acting on an object per unit area:**

$$P = \frac{F}{A}$$

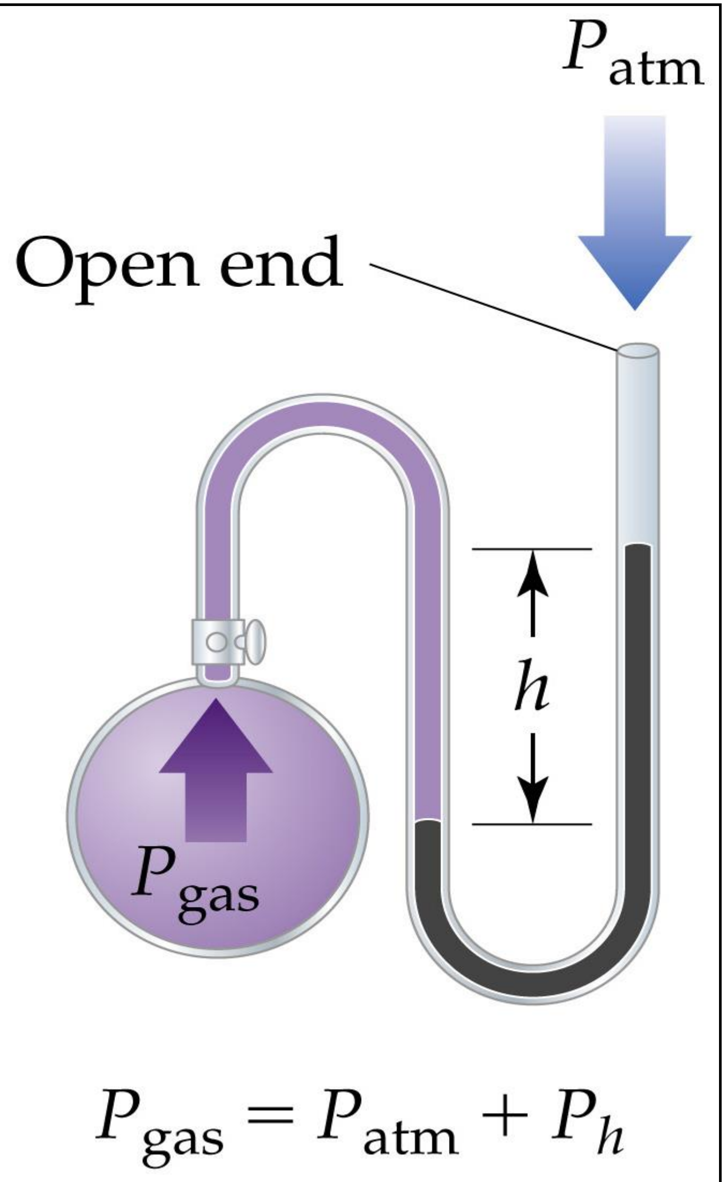
- **The gravity pulling down on a $1m^2$ column of the atmosphere causes a force of $10^5$ N. This is air pressure.**

- **SI Units for Pressure: 1 Pascal (Pa) = 1 $N/m^2$.**

## <u>Common Standard Pressure Units</u>

**1 atm = 760 mmHg = 760 torr = 101.3 kPa**

# ATMOSPHERIC PRESSURE AND THE MANOMETER




- **The pressures of gases not open to the atmosphere are measured in manometers.**
- **A manometer consists of a bulb of gas attached to a U-tube containing Hg.**

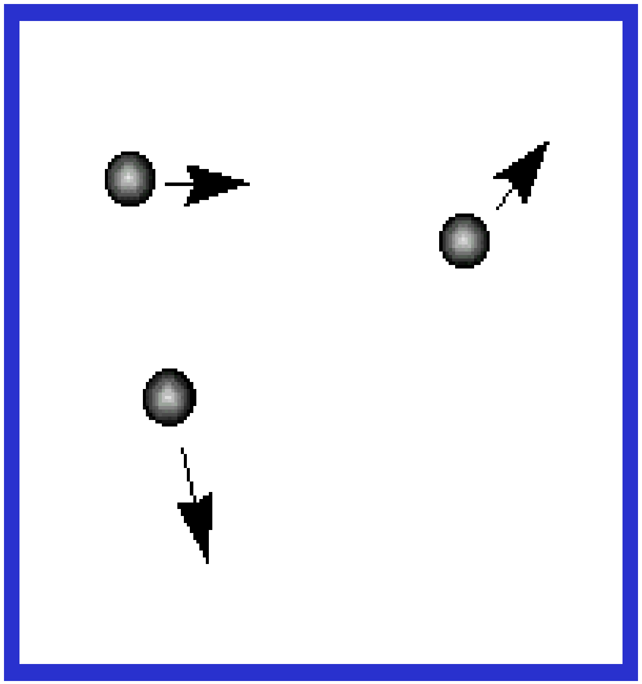
**If $P_{gas} < P_{atm}$ then $P_{gas} = P_{atm} - P_h$**

**If $P_{gas} > P_{atm}$ then $P_{gas} = P_{atm} + P_h$**

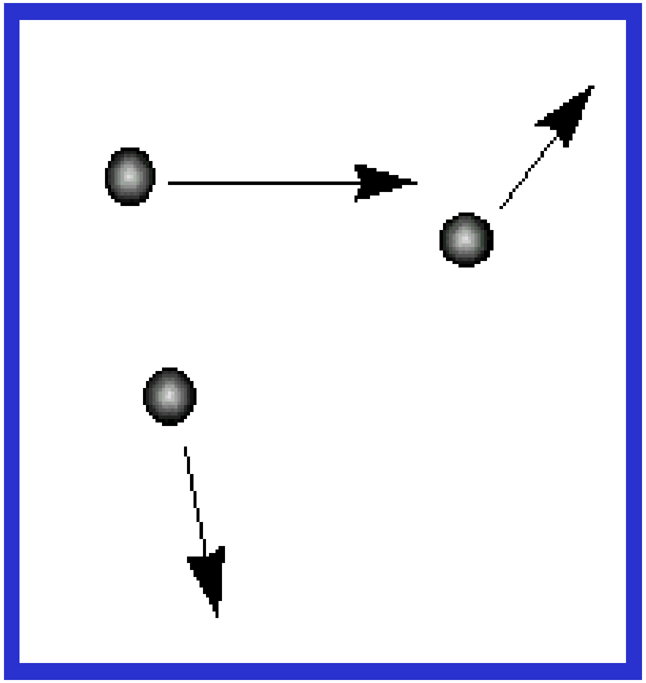
# ABSOLUTE TEMPERATURE

- **The absolute temperature is a measure of the *average kinetic energy* of its molecules.**
- **If two different gases are at the same temperature, their molecules have the same average kinetic energy.**
- **If the temperature of a gas is *doubled*, the average kinetic energy of its molecules is *doubled.***

# ABSOLUTE TEMPERATURE



Lower average kinetic energy
Lower absolute temperature



Higher average kinetic energy
Higher absolute temperature

# GAS LAWS

Robert Boyle

**Relationship between P and V (T constant)**

Jacques Charles

**Relationship between T and V (P constant)**

# BOYLE'S LAW

**Robert Boyle was another man with a dream. He wanted to be the first man to eat 100 hard boiled eggs in a 24-hour period. Unfortunately, some of the other chemists got jealous - let's just say that considerable ugliness ensued and Boyle's dream was permanently derailed. However, Boyle was a man of many talents, and was able to come back from his humiliating egg fiasco* to come up with a gas law of his own.**

# BOYLE'S LAW

**Here's what Boyle did: He put a gas into a container in which he could change the volume and measure the pressure. When he multiplied the volume of the gas times it's pressure, he found it was equal to some arbitrary number (let's call it k, because he did). If he changed the pressure of the gas, he found that the volume also changed, which isn't really surprising (if you push on something, it gets smaller). What is surprising is that if you multiply the new pressure by the new volume, the answer is the same arbitrary number that you had in the first place (k!). From this, we can make the following statement:**

$$P_1V_1 = P_2V_2$$

# CHARLES' LAW

**Jaques Charles was a disturbing and scary guy. Though he came up with a really handy law for determining what the relationships between the volume and temperature of a gas are, his private life was far more bizarre. Some say that if you go by the old Charles mansion at the edge of town, you can still hear the moaning and wailing of his ghost, forever roaming the night.**

# CHARLES' LAW

**What Charles determined through his studies was that when you change the temperature of a gas, the volume changes. Not surprising - you probably know already that if you heat something, it tends to get bigger. What he found, though, was that if you divide the volume by the temperature of a gas at one temperature, you get a constant. Just like Boyle found, if you change the volume or temperature of this gas, you get the same constant. From this, Charles came up with this statement:**

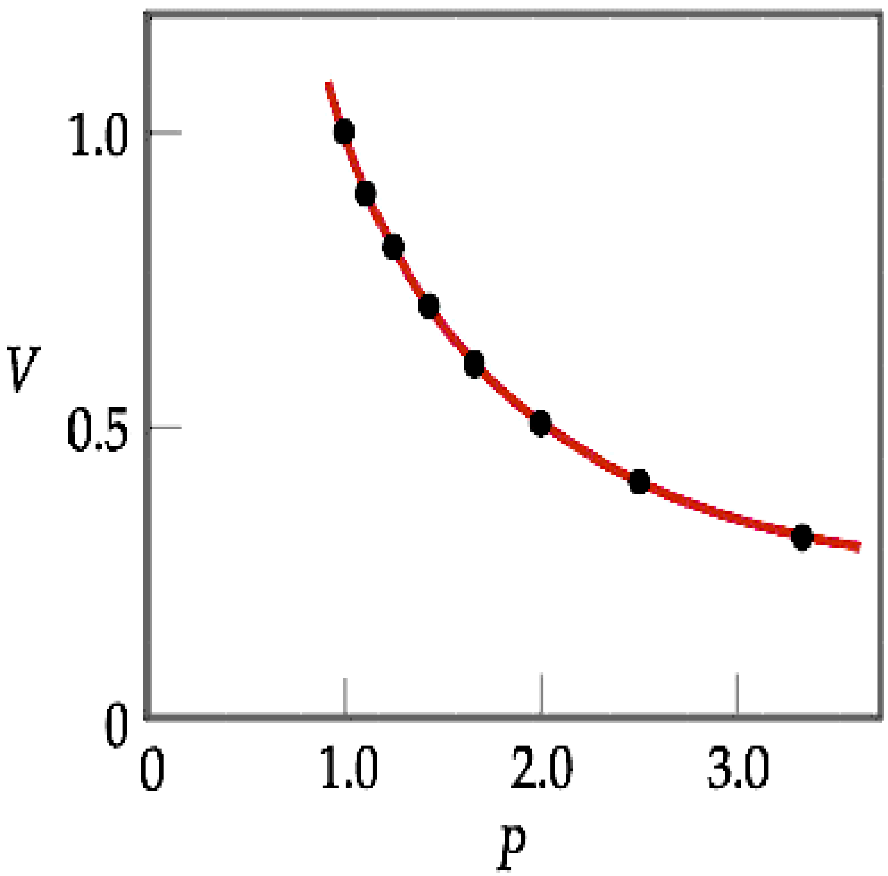
$$V_1/T_1 = V_2/T_2$$

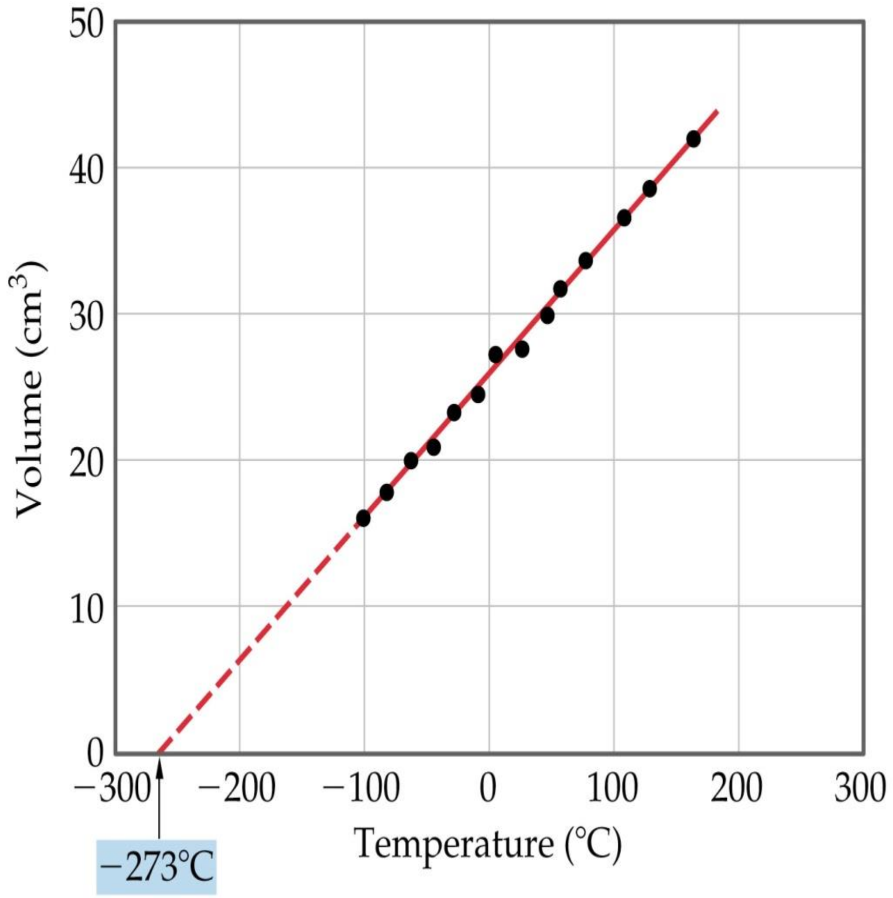
# GAS LAWS

**Quick Review: (PTV)**

- **Boyle's Law: P↓, V↑ (at constant T)**
  - **Common Example: Put a balloon in a vacuum and it will expand. ($P_1V_1 = P_2V_2$)**
- **Charles's Law: T↑, V↑ (at constant P)** $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$
  - **Common Example: Heat a balloon and it expands. Cool the balloon, and it shrinks.**

# GRAPHS




**Boyle's Law (inverse)**

**Charles's Law (direct)**

# ABSOLUTE TEMPERATURE SCALE

- **From reading the graph of Charles's Law, one can see that at a temp. of -273 $^{o}$C the volume of a gas would ideally become zero (if it didn't condense into a liquid.)**
- **In 1848, William Thomson (a.k.a. "Lord Kelvin") proposed a new temperature scale based on this fact.**

**Absolute zero (Zero Kelvin) = -273.15 $^{o}$C**

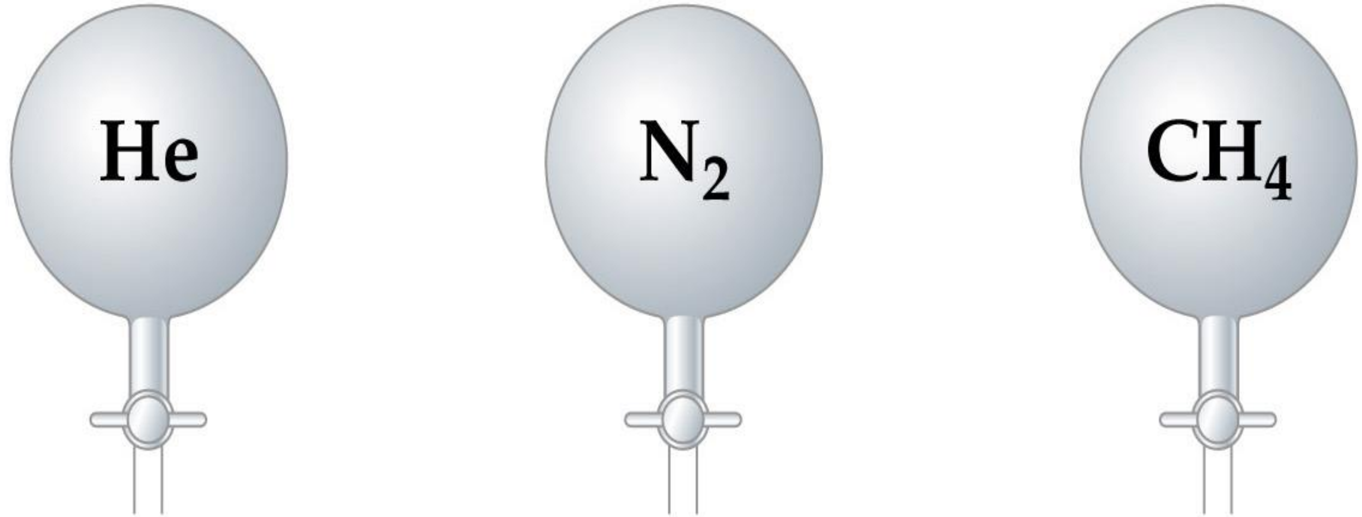
- **All temperatures used in gas law equations MUST be in units of Kelvin!**

# AVOGADRO AND GASES

- **Avogadro's Hypothesis: equal volumes of gas at the same temperature and pressure will contain the same number of molecules.**

- **Avogadro's Law: the volume of gas at a given temperature and pressure is directly proportional to the number of moles of gas.**
  - **Doubling the moles of gas in a balloon would double the volume of a balloon.**

# THE QUANTITY-VOLUME RELATIONSHIP: AVOGADRO'S LAW




| | He | $N_2$ | $CH_4$ |
|---|---|---|---|
| Volume | 22.4 L | 22.4 L | 22.4 L |
| Pressure | 1 atm | 1 atm | 1 atm |
| Temperature | 0°C | 0°C | 0°C |
| Mass of gas | 4.00 g | 28.0 g | 16.0 g |
| Number of gas molecules | $6.02 \times 10^{23}$ | $6.02 \times 10^{23}$ | $6.02 \times 10^{23}$ |

# STP

**Many times you will have to convert gases to a volume at standard temperature and standard pressure, STP. Use these values…**

**Standard Temperature**

**0 ºC or 273 Kelvin**

**Standard Pressure**

**1 atm = 760 mmHg = 101.3 kPa**

# THE COMBINED GAS LAW

- **The following equation can be used to determine the new temperature, pressure or volume of a gas when the conditions change….**

$$\frac{\mathbf{P}_1\ \mathbf{V}_1}{\mathbf{T}_1} = \frac{\mathbf{P}_2\ \mathbf{V}_2}{\mathbf{T}_2}$$

# THE COMBINED GAS LAW

**Imagine a world in which you didn't need to memorize the three laws above. Instead, there was one big law that covered both of them. Hey, that's the world you live in now, and the law you need to know is the combined gas law:**

$$\frac{\mathbf{P}_1\ \mathbf{V}_1}{\mathbf{T}_1} = \frac{\mathbf{P}_2\ \mathbf{V}_2}{\mathbf{T}_2}$$

# THE COMBINED GAS LAW

**In this equation, all of the terms are exactly the same as in the preceding equations. The way you can use this equation is that whenever you're changing the conditions of pressure, volume, and/or temperature for a gas, you just plug the numbers into this equation. However, let's imagine that the temperature of the gas didn't change while you were making your change. Since the first temperature term and the second are the same, they cancel out. As a result, if one of these variables isn't mentioned in the problem, just ignore it entirely.**

# THE IDEAL GAS EQUATION

- **The following equation is often used to determine the quantity of gas in a container when given the conditions of temperature, pressure and volume of the gas.**

$$PV = nRT$$

- ***R* is called the *gas constant*…**

  ***R* = 0.08206 L·atm/mol·K**

- **n= number of moles of gas**
- **Be careful of units!**

  **(P= atm, V= Liters, T=Kelvin)**

- **If P = kPa, then R = 8.31 L·kPa/mol·K**

# FURTHER APPLICATIONS OF PV=nRT

- **Gas Densities and Molar Mass**
  - **Density, (d), has units of mass over volume. The density of a gas varies directly with pressure and inversely with the Kelvin temp… P↑ density↑ ; T ↑ density↓**
  - **Rearranging the ideal-gas equation with *M* as molar mass (in units of grams/mole) we get…**

$$\frac{n}{V} = \frac{P}{RT} \longrightarrow \frac{nM}{V} = \mathrm{d} = \frac{PM}{RT}$$

**Solving for *M*…** **Molar Mass = dRT/P**

**This equation is not given on the AP equation sheet!**

# DALTON'S LAW OF PARTIAL PRESSURES

- **In a gas mixture the total pressure is given by the sum of partial pressures of each component:**

$$P_t = P_1 + P_2 + P_3 \ldots$$

- **If a gas is collected by water displacement, the water vapor pressure must be taken into account in order to find the pressure of the "dry gas"…**

$$P_{total} = P_{dry\ gas} + P_{H_2O}$$

# PARTIAL PRESSURES AND MOLE FRACTIONS

- Often you will have to calculate the partial pressure of a gas in a container when given the # of moles of each component.
- Let $n_1$ be the number of moles of gas 1 exerting a partial pressure $P_1$, then…

$$P_1 = X_1 P_t$$

Where $X_1$ is the mole fraction ($n_1/n_t$).

Note that a mole fraction is
a dimensionless number.

# KINETIC MOLECULAR THEORY

- **This theory explains *why* gases behave as they do.**

## ASSUMPTIONS

1) **Gases are composed of many tiny particles traveling in random straight-line motion.**
2) **The volume of the gas particles is negligible compared to the total volume of the container.**
3) **The attractive and repulsive forces between particles are negligible.**
4) **Collisions are perfectly elastic… i.e.-the total kinetic energy of the gas before and after a collision is the same.**
5) **The average K.E. is proportional to the absolute temperature of the gas.**

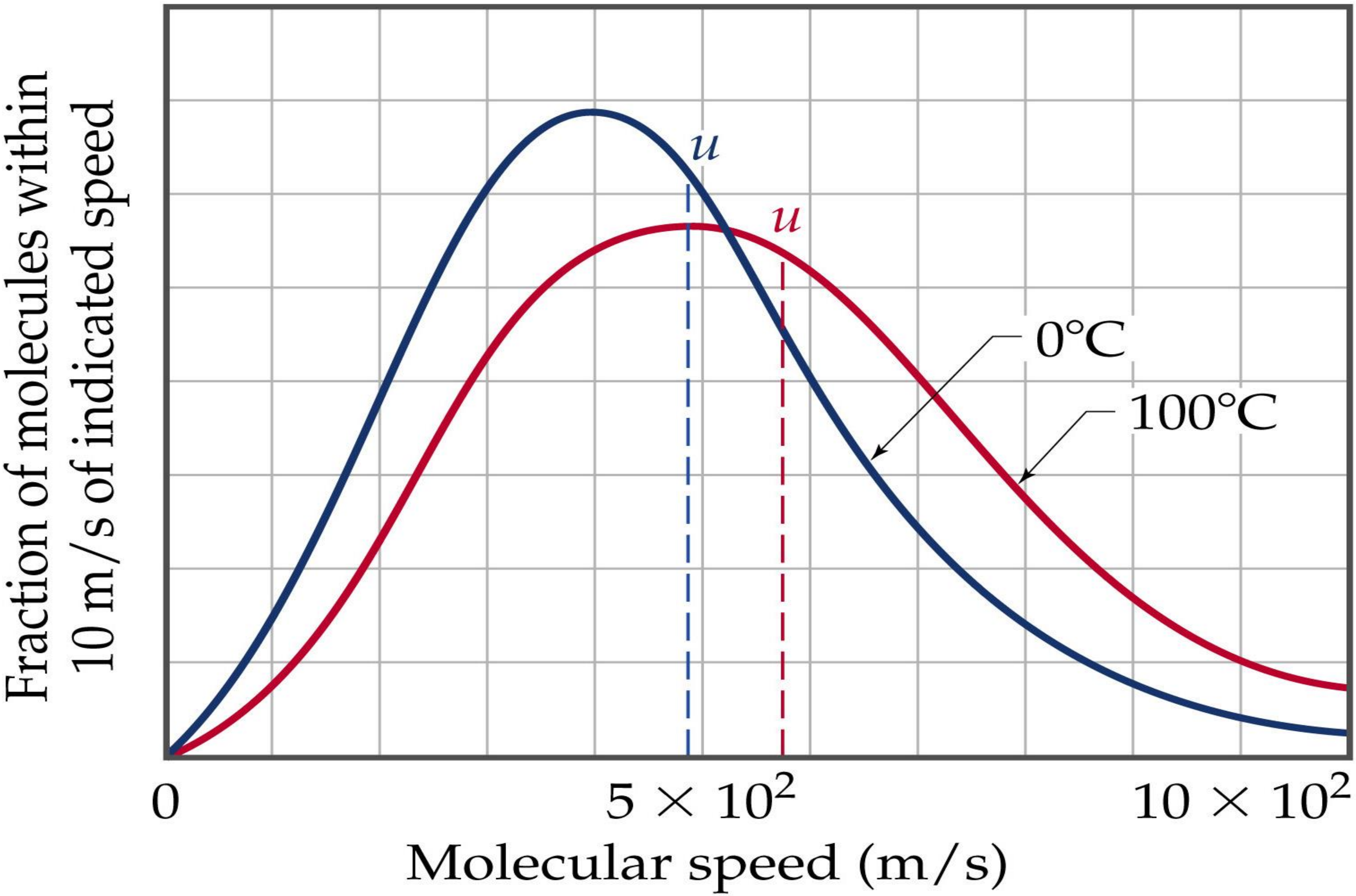
# Application of the KMT to the Gas Laws
## Effect of a V increase at a constant T

- **Constant temperature means that the average kinetic energy of the gas molecules remains constant.**
- **This means that the speed of the molecules remains unchanged.**
- **If the speed remains unchanged, but the volume increases, this means that there will be fewer collisions with the container walls over a a given time.**
- ***Therefore, the pressure will decrease (Boyle's Law)***

# Application of the KMT to the Gas Laws
## Effect of a T increase at constant V

- **An increase in temperature means an increase in the average kinetic energy of the gas molecules.**
- **There will be more collisions per unit time, furthermore, the momentum of each collision increases (molecules strike the wall harder).**
- ***Therefore, there will be an increase in pressure.***
- **If we allow the volume to change to maintain *constant pressure*, *the volume will increase with increasing temperature (Charles's Law).***

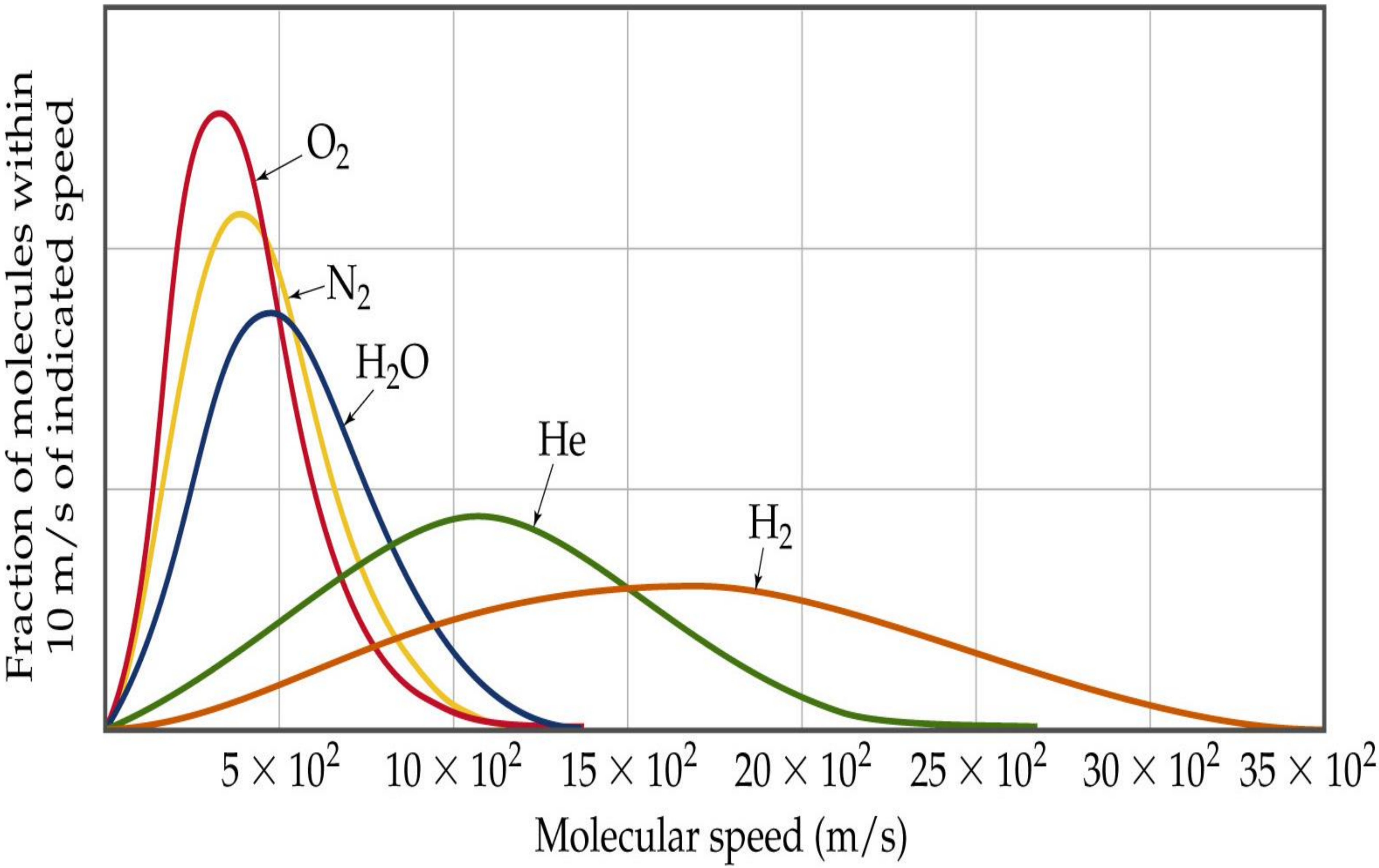
# DISTRIBUTION OF MOLECULAR SPEEDS OF $N_2$



# CONCLUSIONS FROM THE GRAPH

1. **Not all molecules have the same speed in a sample of gas. When colliding, some particles may speed up and some may slow down, but the total K.E. is constant.**
2. **The higher temperature sample has a higher average speed (as we would expect).**
3. **Higher temps. cause higher kinetic energy because the speed of the molecule increases. (K.E. = 1/2 $mv^2$)**
4. **Higher temps. will also cause greater pressures in a given volume since there would be more collisions of greater force.**
5. **Larger volumes of gas would have less pressure at a given temp. since there would be less collisions with the walls of the container since the particles would have to travel further before colliding.**

# BOLTZMAN DISTRIBUTION



## CONCLUSIONS FROM BOLTZMAN

- **Larger gas particles will have a lower average speed.**
- **Smaller molar masses will travel faster at a given temperature.**

## DIFFUSION

- **Diffusion is the rate at which a gas spreads throughout space or throughout a second substance.**
  - **Example: Perfume diffusing into a room.**
  - **Smaller molecules diffuse faster.**

# GRAHAM'S LAW OF EFFUSION

- Effusion is the escape of a gas through a tiny hole.
  - Example: A balloon will deflate over time due to effusion.
- Consider two gases with molar masses $M_1$ and $M_2$, the relative rate of effusion is given by:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

# GRAHAM'S LAW OF EFFUSION

- **The equation shows that the rate at which a gas effuses is inversely proportional to the square roots of their molar masses (or densities.)**

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

- **For example: The rate at which helium (4.0g/mol) effuses compared to $N_2$ (28 g/mol) is…**

$$r_1 / r_2 = \sqrt{28/4} \quad = 2.6 \text{ x faster}$$

# REAL GASES VS. IDEAL GASES

- **From the ideal gas equation, we have:**

$$PV/RT = n$$

- **For 1 mole of gas, *PV/RT* = 1 for all pressures & temperatures.**
- **In a real gas, *PV/RT* varies from 1 significantly.**
- **The higher the pressure and colder the temperature, the more the deviation from ideal behavior.**

# REAL GASES VS. IDEAL GASES

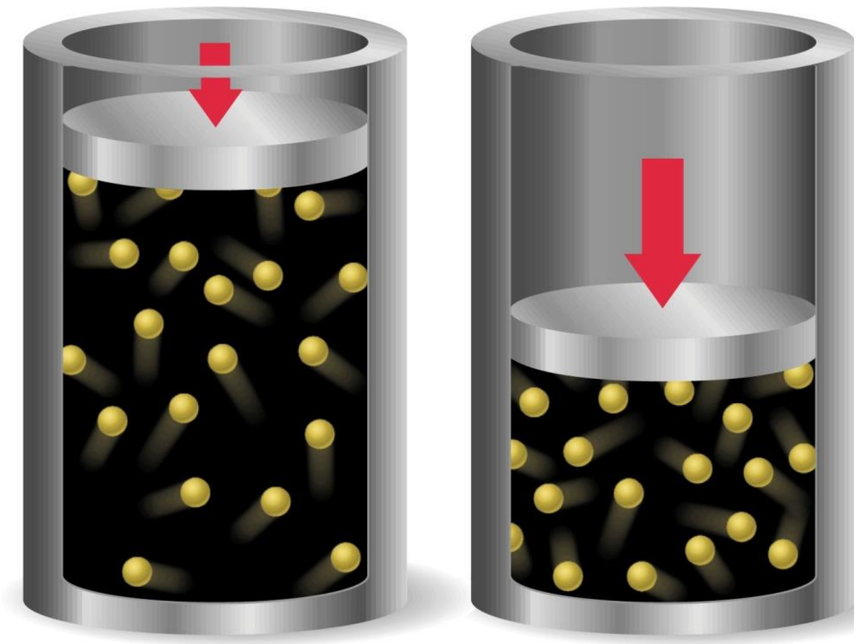
- The smaller the distance between gas molecules at higher pressures, the more likely attractive forces will develop between the molecules.
- Therefore, the less the gas resembles and ideal gas.

(Gases tend to liquefy at higher pressures.)

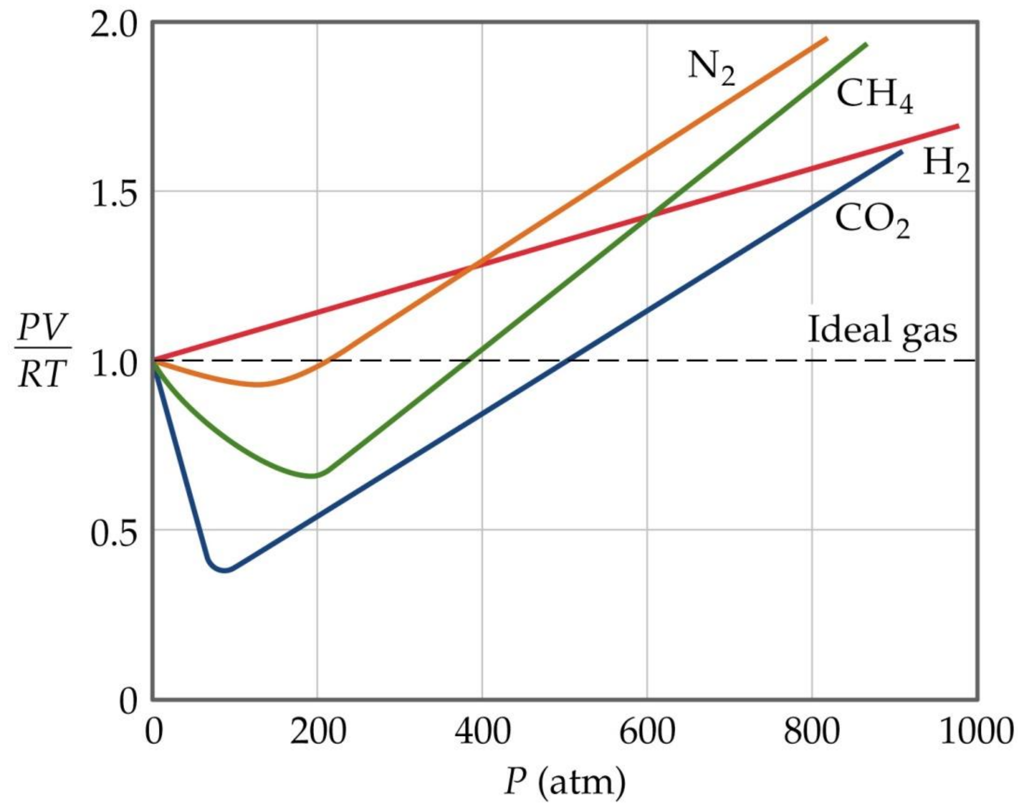
- As temperature decreases, the gas molecules move slower and closer together so lower temps. mean less energy available to break intermolecular forces.
- Therefore, colder temps. make gases act less ideally.

(Gases tend to liquefy at low temperatures.)

# PRESSURE

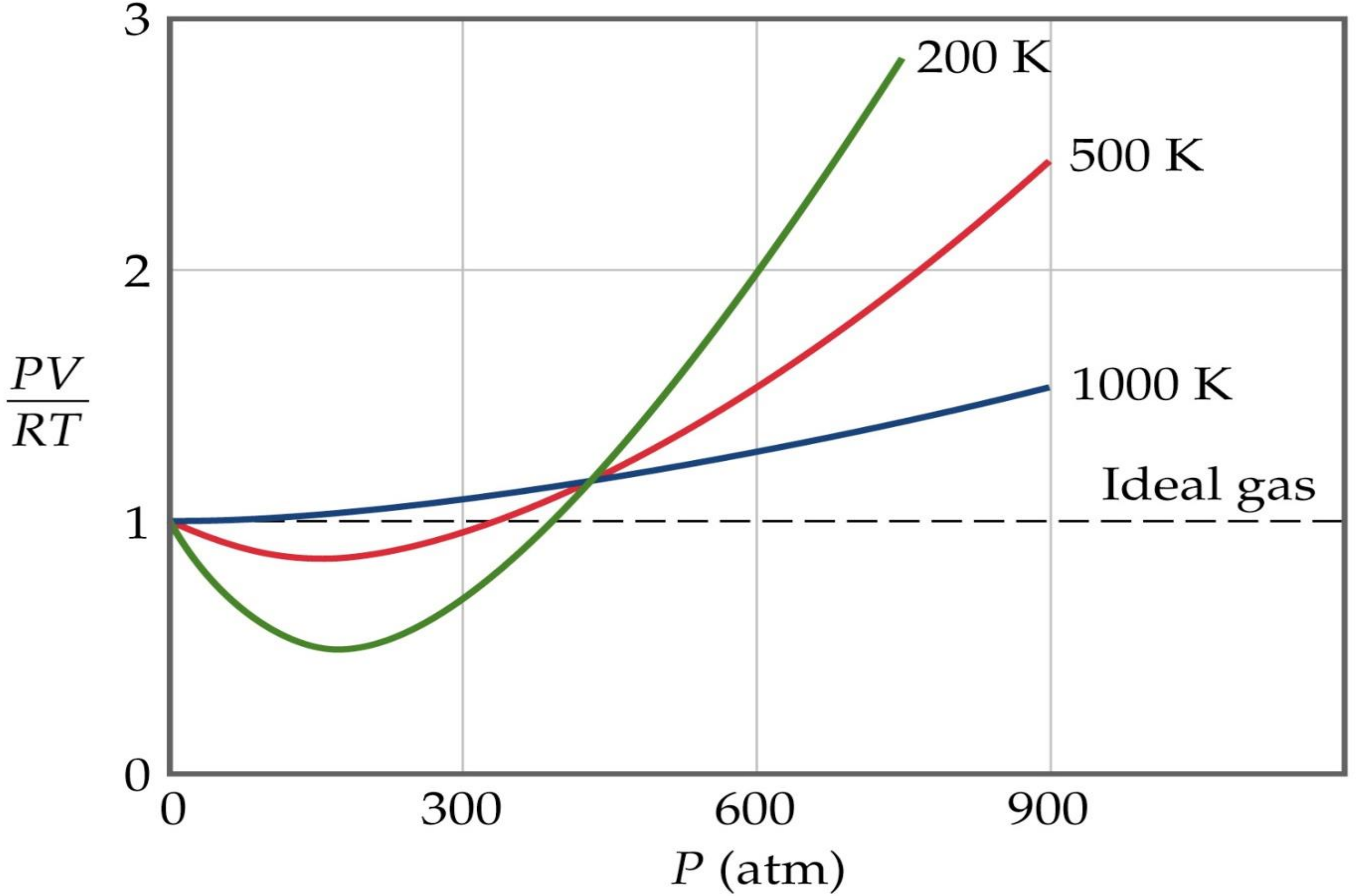


(a) (b)




**Gas particles start to take up too much of the volume!**

# TEMPERATURE



# CONCLUSION

- **If you want a gas to behave more like an ideal gas…**

***Keep the temperature high and the pressure low!***

# EXAMPLE OF PROBLEM Nu. 1

## What volume will 1.27 moles of helium gas occupy at STP?

This is an Ideal Gas Law question. You know this because it mentions moles. The ideal gas law is the only formula with moles.

The formula is: $PV=nRT$

STP stands for standard temperature and pressure.

Standard T is 0°C. Standard P in atm's is 1.

R is a constant and always is: 0.0821 (atm*L)/(mol*K)

The set up is: $(1)V = (1.27)(0.0821)(273)$

Solving for V, the answer is **28.5 L**

# EXAMPLE OF PROBLEM Nu. 2

## What volume would 32.0 g of Iodine gas occupy at 3.12 atm. and 18.0 °C?

**This is an Ideal Gas Law question. You know this because it mentions grams. Grams can converted to moles. The ideal gas law is the only formula with moles.**

**The formula is:** **$PV=nRT$**

**R is a constant and always is: 0.0821 (atm*L)/(mol*K)**

**First, you must convert to moles. But be careful!!! Iodine is a diatomic molecule. This means its mass is double. The conversion is:** **32g $I_2$*(1mole/254g) = 0.126 moles**

**The set up is:** **(3.12)(V) = (0.126)(0.0821)(291)**

**Solving for V, the answer is** **0.965 L**

# EXAMPLE OF PROBLEM Nu. 3

**Find the volume of 1.40 mol of gas whose temperature is 40°C and whose pressure is 2.0 atm.**

**This is an Ideal Gas Law question. You know this because it mentions moles. The ideal gas law is the only formula with moles.**

**The formula is:** $PV=nRT$

**R is a constant, always is: 0.0821 (atm*L)/(mol*K)**

**The set up is:** $(2.00)V = (1.40)(0.0821)(313)$

**Solving for V, the answer is: 18.0 L**

# EXAMPLE OF PROBLEM Nu. 4

At what pressure would 0.750 mole of nitrogen gas at 23.0 °C occupy 8.90 L?

This is an Ideal Gas Law question. You know this because it mentions moles. The ideal gas law is the only formula with moles.

The formula is: $PV=nRT$

R is a constant: 0.0821 (atm*L)/(mol*K)

The set up is: $P(8.90) = (0.750)(0.0821)(296)$

Solving for P, the answer is **2.05 atm.**

# EXAMPLE OF PROBLEM Nu. 5

**A container with two gases, Helium and Argon, is 35.0% by volume Helium. Calculate the partial pressure of Helium and Argon if the total pressure inside the container is 14.00 atm.**

**If the total pressure is 14 atm, and the gases creating it are He and Ar, then their partial pressures must add up to be 14. To determine their partial pressures, simply find Heliums pressure by finding what 35% of 14 is: 0.35 x 14 = 4.9**

**So therefore He partial pressure is: 4.90 atm.**

**Argons pressure is the remaining 65%: 0.65 x 14 = 9.1**

**So therefore Ar partial pressure is: 9.10 atm.**

# CONCLUSIONS

- **The KMT is a single set of descriptive characteristics of a substance known as the Ideal Gas. All real gases require their own unique sets of descriptive characteristics.**
- **Considering the large number of known gases in the World, the task of trying to describe each one of them individually would be an awesome task.**
- **In order to simplify this task, the scientific community has decided to create an *imaginary gas* that approximates the behavior of all real gases. In other words, the Ideal Gas is a substance that does not exist. KMT describes that gas.**
- **While the use of the Ideal Gas in describing all real gases means that the descriptions of all real gases will be wrong, the reality is that the descriptions of real gases will be close enough to correct that any errors can be overlooked.**

# ASSIGNMENT

1. **Explain some applications of gases and related Laws.**