

Chapter 5: Gases and the Kinetic - Molecular Theory

- 5.1 An Overview of the Physical States of Matter
- 5.2 Gas Pressure and its Measurement
- 5.3 The Gas Laws and Their Experimental Foundations
- 5.4 Further Applications of the Ideal Gas Law
- 5.5 The Ideal Gas Law and Reaction Stoichiometry
- 5.6 The Kinetic-Molecular Theory: A Model for Gas Behavior
- 5.7 Real Gases: Deviations from Ideal Behavior

The Three States of Matter

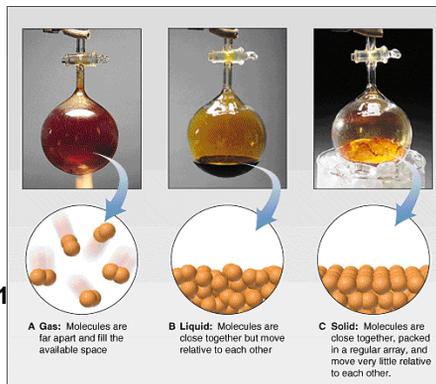


Fig. 5.1

Important Characteristics of Gases

- 1) **Gases are highly compressible**
An external force compresses the gas sample and decreases its volume, removing the external force allows the gas volume to increase.
- 2) **Gases are thermally expandable**
When a gas sample is heated, its volume increases, and when it is cooled its volume decreases.
- 3) **Gases have low viscosity**
Gases flow much easier than liquids or solids.
- 4) **Most Gases have low densities**
Gas densities are on the order of grams per liter whereas liquids and solids are grams per cubic cm, 1000 times greater.
- 5) **Gases are infinitely miscible**
Gases mix in any proportion such as in air, a mixture of many gases.

Explaining the Physical Nature of Gases

1. Why does the volume of a gas = Volume of its container?
2. Why are gases compressible?
3. Why are there great distances between gas molecules?
4. Why do gases mix any proportion to form a solution?
5. Why do gases expand when heated?
6. How does the density of a gas compare to the density of solids and liquids?
 - Explain the difference!

Pressure

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

- Why are snowshoes effective?
- Why does a sharp knife cut better than a dull one?

Calculating Pressure

- **Would you rather have a 100 or 300 lb. person step on your foot?**
- **Calculate the pressure in lbs./in.² exerted by a**
 - 1) 100. lb woman stepping on your foot with the heel of high heel shoe that measures 1/2" by 1/2"
 - 2) 300. lb man stepping on your foot wearing a shoe with a 2" by 2" heel

Atmospheric Pressure

- Atmospheric pressure
 - force exerted upon us by the atmosphere above us
 - A measure of the weight of the atmosphere pressing down upon us
- [Demonstrating Atmospheric Pressure \(fig. 5.2\)](#)

Effect of Atmospheric Pressure on Objects at the Earth's Surface

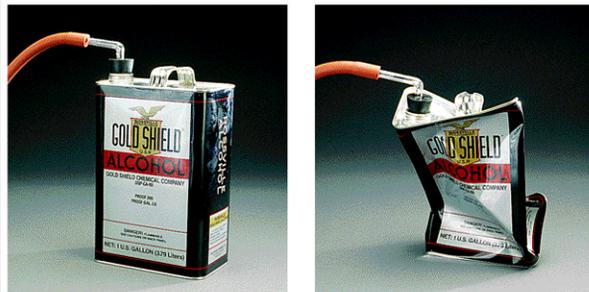


Fig. 5.2

Measuring Atmospheric Pressure with a Mercury Barometer

- [How a Mercury Barometer Works \(fig. 5.3\)](#)
- **Units of Pressure commonly used in Chemistry**
 - **1 mmHg = 1 torr**
 - **760 torr = 1 atm = 760 mmHg**
 - **1 atm = 101,325 Pa = 101.325 kilopascal, kPa**
 - **Pascal is the SI unit for pressure**
 - 1 Pa = 1 N/m²
 - Neuton, N, = SI Unit of Force
 - $F = ma = (1.0 \text{ kg})(1.0 \text{ m/s}^2) = 1.0 \text{ Neuton}$

A Mercury Barometer

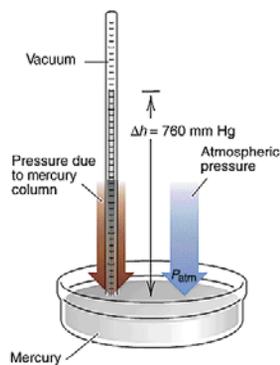


Fig. 5.3

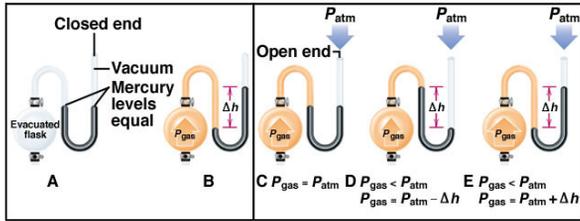
Table 5.2 Common Units of Pressure

Unit	Atmospheric Pressure	Scientific Field
pascal(Pa); kilopascal(kPa)	1.01325 x 10 ⁵ Pa; 101.325 kPa	SI unit; physics, chemistry
atmosphere(atm)	1 atm	chemistry
millimeters of mercury (Hg)	760 mmHg	chemistry , medicine, biology
torr	760 torr	chemistry
pounds per square inch (psi or lb/in ²)	14.7lb/in ²	engineering
bar	0.01325 bar	meteorology, chemistry, physics

Measuring the Pressure of a Gas with a Manometer (fig. 5.4)

- Closed Manometers
- Open Manometers
- Laboratory use of the Manometer
 - See transparencies

Fig. 5.4 Two Types of Manometers



Sample Problem 5.1 Converting Units of Pressure

PROBLEM: A geochemist heats a limestone (CaCO_3) sample and collects the CO_2 released in an evacuated flask attached to a closed-end manometer. After the system comes to room temperature, $\Delta h = 291.4 \text{ mmHg}$. Calculate the CO_2 pressure in torr, atmospheres, and kilopascals.

PLAN: Construct conversion factors to find the other units of pressure.

SOLUTION:

$$291.4 \text{ mmHg} \times \frac{1 \text{ torr}}{1 \text{ mmHg}} = 291.4 \text{ torr}$$

$$291.4 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.3834 \text{ atm}$$

$$0.3834 \text{ atm} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 38.85 \text{ kPa}$$

Converting Units of Pressure

Problem 5.12, page 213

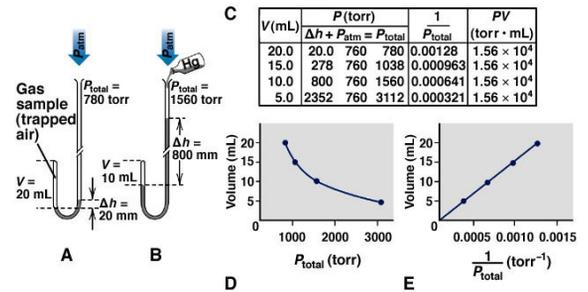
Convert the following:

- a. 0.745 atm to mmHg
- b. 992 torr to atm
- c. 365 kPa to atm
- d. 804 mmHg to kPa

Answers: A. 566 mmHg; B. 1.31 atm; C. 3.60 atm; D. 107 kPa

Relationship between the Volume and Pressure of a Gas

Fig. 5.5



Boyle's Law: P_{gas} is inversely proportional to its Volume

- 4 interdependent variables describe a gas:

P , V , T , and n , moles of gas

Boyle's Law $V \propto \frac{1}{P}$ n and T are constant

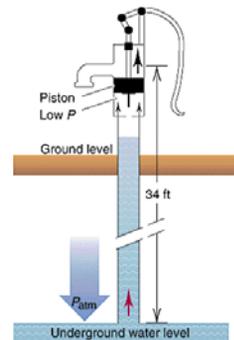
$PV = \text{constant}$ or $P_1V_1 = P_2V_2$

- Examples

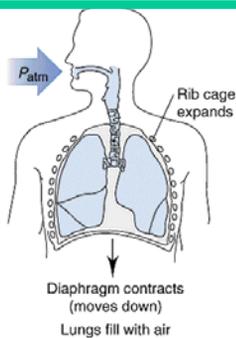
- Bike pump
- Breathing: inhaling and exhaling
- Flatulence in airplanes!!

Suction Pumps, Drinking with a Straw and Boyle's Law

(p. 177)



Breathing and Boyle's Law



Sample Problem: Boyle's Law

- A balloon has a volume of 0.55 L at sea level (1.0 atm) and is allowed to rise to an altitude of 6.5 km, where the pressure is 0.40 atm. Assume that the temperature remains constant (which obviously is not true), what is the final volume of the balloon?

$$P_1 = 1.0 \text{ atm} \quad P_2 = 0.40 \text{ atm}$$

$$V_1 = 0.55 \text{ L} \quad V_2 = ?$$

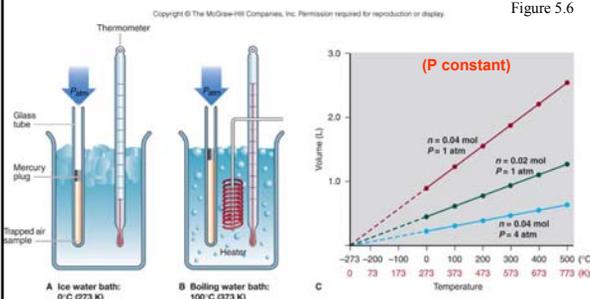
$$V_2 = V_1 \times P_1/P_2 = (0.55 \text{ L}) \times (1.0 \text{ atm} / 0.40 \text{ atm})$$

$$V_2 = 1.4 \text{ L}$$

Sample Problem: Boyle's Law

- You wish to transfer 3.0 L of Fluorine gas at 5.2 atm, to a 1.0 L container that is capable of withstanding 15.0 atm pressure.
- Is it O.K. to make the transfer?

Charles Law: Relates the volume and the temperature of a gas



Charles Law: V - T - Relationship

- Temperature is directly related to volume
- T proportional to Volume : $T = kV$

Change of conditions problem

$$T/V = k \quad \text{or} \quad T_1/V_1 = T_2/V_2$$

$$\frac{T_1}{V_1} = \frac{T_2}{V_2}$$

Temperatures must be expressed in Kelvin to avoid negative values.

Temperature Conversions: Kelvin & Celsius

- Use Temperature in Kelvin for all gas law calculations!!!

$$\text{Absolute zero} = 0 \text{ Kelvin} = -273.15 \text{ }^\circ\text{C}$$

Therefore,

$$T \text{ (K)} = t \text{ (}^\circ\text{C)} + 273.15$$

$$t \text{ (}^\circ\text{C)} = T \text{ (K)} - 273.15$$

Sample Problem: Charles Law

- A 1.0 L balloon at 30.0 °C is cooled to 15.0°C. What is the balloon's final volume in mL? Assume P and n remain constant

– Antwort: Fünfzig mL weniger

Charles Law Problem

- A sample of carbon monoxide, a poisonous gas, occupies 3.20 L at 125 °C. Calculate the temperature (°C) at which the gas will occupy 1.54 L if the pressure remains constant.

Amonton's Law (Gay-Lussac's): Relates P & T

- $P \propto T$ (at constant V and n); $P = cT$
 $P_1/T_1 = P_2/T_2$
- Temp. must be in Kelvin!!
- Sample Problem**
Hydrogen gas in a tank is compressed to a pressure of 4.28 atm at a temperature of 15.0 °C. What will be the pressure if the temperature is raised to 30.0 °C?

The Combined Gas Law

$$\bullet \frac{P \times V}{T} = \text{constant} \quad \text{Therefore for a change of conditions :}$$

$$\bullet \frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

Summary of the Gas Laws involving P, T, and V

Boyle's Law $V \propto \frac{1}{P}$ n and T are fixed

Charles's Law $V \propto T$ P and n are fixed

$$\frac{V}{T} = \text{constant} \quad V = \text{constant} \times T$$

Amonton's Law $P \propto T$ V and n are fixed

$$\frac{P}{T} = \text{constant} \quad P = \text{constant} \times T$$

combined gas law $V \propto \frac{T}{P}$ $V = \text{constant} \times \frac{T}{P}$ $\frac{PV}{T} = \text{constant}$

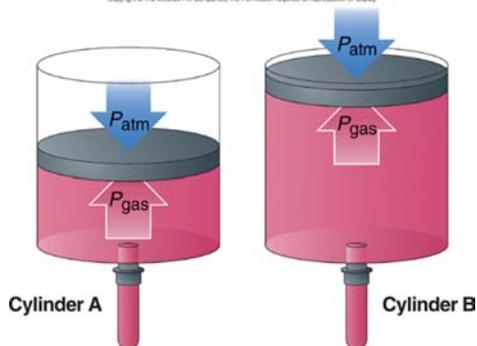
Applying the Combined Gas Law

- What will be the final pressure of a gas in torr and in atm if 4.0 L of the gas at 760. torr and 25 °C is expanded to 20.0 L and then heated to 100. °C?

Answer: 190 torr or 0.25 atm
• Note: only 2 sig figs!! why?

Figure 5.7 An experiment to study the relationship between the volume and amount of a gas.

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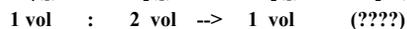
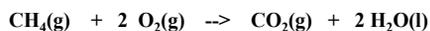
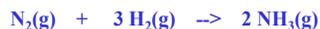


Avogadro's Principle

- Equal volumes of gases contain equal numbers of molecules (or moles of molecules) when measured at the same T and P

$$V \propto n \quad (\text{at const. } T \text{ and } P)$$

- Evidence for Avogadro's Principle



Standard Molar Volume = 22.414 L

- At STP one mole of any ideal gas occupies 22.4 liters

- STP

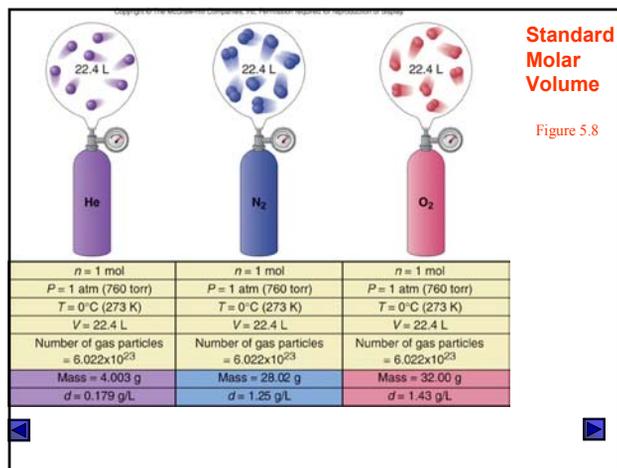
Standard Temp. = 0 °C = 273.15 K

Standard Press. = 1 atm

- Sample Problem: Use the concept of molar volume to calculate the densities (in g/L) of the following gases at STP

- Oxygen
- Nitrogen
- Air (~80% nitrogen and ~20% oxygen)

- Ans. 1.43, 1.25 and 1.29 g/L, respectively



Standard Molar Volume

Figure 5.8

Ideal Gases

- Ideal gas

volume of molecules and forces between the molecules are so small that they have no effect on the behavior of the gas.

- The ideal gas equation is:

$$PV = nRT$$

R = Ideal gas constant

- $R = 8.314 \text{ J / mol K} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
- $R = 0.08206 \text{ l atm mol}^{-1} \text{ K}^{-1}$

Relationship between the Ideal Gas Law and the Individual Gas Laws

Fig. 5.10

IDEAL GAS LAW

$$PV = nRT \quad \text{or} \quad V = \frac{nRT}{P}$$

fixed n and T

fixed n and P

fixed P and T

Boyle's Law:

$$PV = \text{constant}$$

Charles's Law:

$$V = \text{constant} \times T$$

Avogadro's Law:

$$V = \text{constant} \times n$$

Calculation of the Ideal Gas Constant, R

$$\text{Ideal gas Equation} \quad PV = nRT \quad R = \frac{PV}{nT}$$

at Standard Temperature and Pressure, the molar volume = 22.4 L

P = 1.00 atm (by definition)

T = 0 °C = 273.15 K (by definition)

n = 1.00 moles (by definition)

$$R = \frac{(1.00 \text{ atm})(22.414 \text{ L})}{(1.00 \text{ mole})(273.15 \text{ K})} = 0.08206 \frac{\text{L atm}}{\text{mol K}}$$

$$\text{or to three significant figures } R = 0.0821 \frac{\text{L atm}}{\text{mol K}}$$

Values of R (Universal Gas Constant) in Different Units

$$R^* = 0.0821 \frac{\text{atm} \times \text{L}}{\text{mol} \times \text{K}}$$

$$R = 62.36 \frac{\text{torr} \times \text{L}}{\text{mol} \times \text{K}}$$

$$R = 8.314 \frac{\text{kPa} \times \text{dm}^3}{\text{mol} \times \text{K}}$$

$$R = 8.314 \frac{\text{J}^{**}}{\text{mol} \times \text{K}}$$

* most calculations in this text use values of R to 3 significant figures.

** J is the abbreviation for joule, the SI unit of energy. The joule is a derived unit composed of the base units Kg x m²/s².

Applications of the Ideal Gas Law

- Calculate the number of gas molecules in the lungs of a person with a lung capacity of 4.5 L. P_{atm} = 760 torr; Body temp. = 37 °C.

Answer = 0.18 mole of molecules or 1.1 x 10²³ gas molecules

- You wish to identify a gas in an old unlabeled gas cylinder that you suspect contains a noble gas. You release some of the gas into an evacuated 300. mL flask that weighs 110.11 g empty. It now weighs 111.56 g with the gas. The press. and temp. of the gas are 685 torr and 27.0 °C, respectively. Which Noble gas do you have?

Answer: Xe

Applications of the Ideal Gas Law



- A student wishes to produce hydrogen gas by reacting aluminum with hydrochloric acid. Use the following information to calculate how much aluminum she should react with excess hydrochloric acid. She needs to collect about 40 mL of hydrogen gas measured at 760.0 torr and 25.0 °C. Assume the reaction goes to completion and no product is lost.

– Answer: 0.03 g Al

Use of the I.G.L. To Calculate the Molar Mass and Density of a Gas

$$PV = nRT$$

$$n = \frac{\text{mass}}{M} = \frac{PV}{RT}$$

$$M = \frac{m RT}{VP}$$

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

$$M = \frac{d RT}{P}$$

$$d = \frac{MP}{RT}$$

Using the Ideal Gas Law and Previously Learned Concepts

- A gas that is 80.0% carbon and 20.0% hydrogen has a density of 1.339 g/L at STP. Use this info. to calculate its
 - >Molecular Weight in g/mol
 - >Empirical Formula
 - >Molecular Formula
- Answers:
 - MW = 30.0 g/mol
 - E.F. = CH₃
 - M.F. = C₂H₆

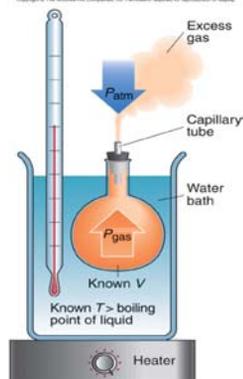
Density of Ammonia determination

- Calculate the density of ammonia gas (NH_3) in grams per liter at 752 mm Hg and 55 °C.
- Recall:
Density = mass per unit volume = g / L
- Answer: $d = 0.626 \text{ g / L}$

Figure 5.11

Determining the molar mass of an unknown volatile liquid

based on the method of J.B.A. Dumas (1800-1884)



Sample Problem 5.7 Finding the Molar Mass of a Volatile Liquid

PROBLEM: An organic chemist isolates from a petroleum sample a colorless liquid with the properties of cyclohexane (C_6H_{12}). She uses the Dumas method and obtains the following data to determine its molar mass:

Volume of flask = 213 mL $T = 100.0^\circ\text{C}$ $P = 754 \text{ torr}$
 Mass of flask + gas = 78.416 g Mass of flask = 77.834 g

Is the calculated molar mass consistent with the liquid being cyclohexane?

PLAN: Use the ideal gas law to calculate the molar mass of cyclohexane

SOLUTION: $m = (78.416 - 77.834) \text{ g} = 0.582 \text{ g } \text{C}_6\text{H}_{12}$

$$M = \frac{m RT}{VP} = \frac{0.582 \text{ g} \times 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}} \times 373 \text{ K}}{0.213 \text{ L} \times 0.992 \text{ atm}} = 84.4 \text{ g/mol}$$

M of C_6H_{12} is 84.16 g/mol and the calculated value is within experimental error.

Dumas Method of Molar Mass 1 of 2

Problem: A volatile liquid is placed in a flask whose volume is 590.0 ml and allowed to boil until all of the liquid is gone, and only vapor fills the flask at a temperature of 100.0 °C and 736 mm Hg pressure. If the mass of the flask before and after the experiment was 148.375 g and 149.457 g, what is the molar mass of the liquid?

Answer: Molar Mass = 58.03 g/mol

Dumas Method of Molar Mass 2 of 2

Solution:

$$\text{Pressure} = 736 \text{ mm Hg} \times \frac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.9684 \text{ atm}$$

$$\text{mass} = 149.457 \text{ g} - 148.375 \text{ g} = 1.082 \text{ g}$$

$$\text{Molar Mass} = \frac{(1.082 \text{ g})(0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K})(373.2 \text{ K})}{(0.9684 \text{ atm})(0.590 \text{ L})} = 58.03 \text{ g/mol}$$

Note: the compound is acetone $\text{C}_3\text{H}_6\text{O} = \text{MM} = 58 \text{ g/mol}$

Calculation of Molecular Weight of Natural Gas, Methane 1 of 2

Problem

A sample of natural gas is collected at 25.0 °C in a 250.0 ml flask. If the sample had a mass of 0.118 g at a pressure of 550.0 Torr, what is the molecular weight of the gas?

Plan

Use the ideal gas law to calculate n, then calculate the molar mass.

Calculation of Molecular Weight of Natural Gas, Methane 2 of 2

Plan: Use the ideal gas law to calculate n, then calculate the molar mass.

Solution:

$$P = 550.0 \text{ Torr} \times \frac{1 \text{ mm Hg}}{1 \text{ Torr}} \times \frac{1.00 \text{ atm}}{760 \text{ mm Hg}} = 0.724 \text{ atm}$$

$$V = 250.0 \text{ ml} \times \frac{1.00 \text{ L}}{1000 \text{ ml}} = 0.250 \text{ L}$$

$$T = 25.0 \text{ }^\circ\text{C} + 273.15 \text{ K} = 298.2 \text{ K}$$

$$n = \frac{(0.724 \text{ atm})(0.250 \text{ L})}{(0.0821 \text{ L atm/mol K})(298.2 \text{ K})} = 0.007393 \text{ mol}$$

$$\text{MM} = 0.118 \text{ g} / 0.007393 \text{ mol} = \mathbf{15.9 \text{ g/mol}}$$

Dalton's Law of Partial Pressures 1 of 2

- In a mixture of gases, each gas contributes to the total pressure the amount it would exert if the gas were present in the container by itself.

- Total Pressure = sum of the partial pressures:**

$$P_{\text{total}} = p_1 + p_2 + p_3 + \dots p_i$$

- Application: Collecting Gases Over Water**

Dalton's Law of Partial Pressure 2 of 2

- Pressure exerted by an ideal gas mixture is determined by the total number of moles:

$$P = (n_{\text{total}} RT)/V$$

- n_{total} = sum of the amounts (moles) of each gas pressure

- the partial pressure is the pressure of gas if it was present by itself.

- $P = (n_1 RT)/V + (n_2 RT)/V + (n_3 RT)/V + \dots$

- the total pressure is the sum of the partial pressures.

Determine the total pressure and partial pressures after the valves are opened.

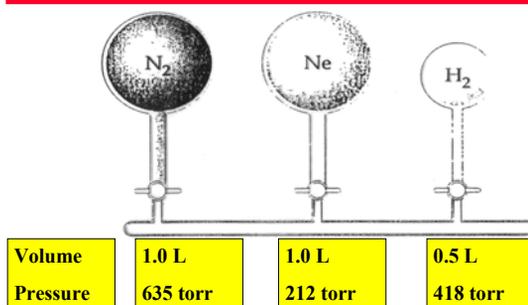


Figure 5.12

Collecting a water-insoluble gaseous reaction product and determining its pressure.

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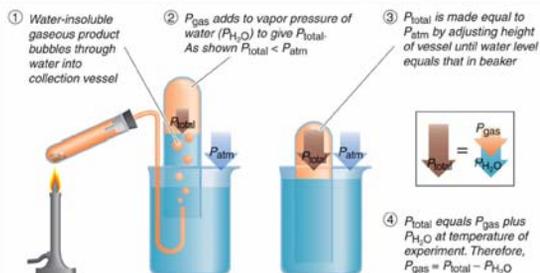


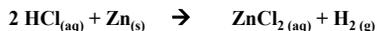
Table 5.3. Vapor Pressure of Water ($P_{\text{H}_2\text{O}}$) at Different Temperatures

T ^o C	P (torr)	T ^o C	P (torr)	T ^o C	P (torr)
0	4.6	26	25.2	85	433.6
5	6.5	28	28.3	90	525.8
10	9.2	30	31.8	95	633.9
11	9.8	35	42.2	100	760.0
12	10.5	40	55.3		
13	11.2	45	71.9		
14	12.0	50	92.5		
15	12.8	55	118.0		
16	13.6	60	149.4		
18	15.5	65	187.5		
20	17.5	70	233.7		
22	19.8	75	289.1		
24	22.4	80	355.1		

Collection of Hydrogen Gas over Water 1 of 3

Problem

Calculate the mass of hydrogen gas collected over water if **156.0 ml** of gas is collected at **20.0 °C** and **769.0 mm Hg**. What mass of zinc reacted?



Plan

1. Use Dalton's law of partial pressures to find the pressure of "dry" hydrogen
2. Use the ideal gas law to find moles of dry hydrogen
3. Use molar mass of H_2 to find mass of H_2 .
4. Use moles of H_2 and the equation to find moles of Zn, then find mass of Zn.

Answer = 0.0129 g H_2 ; 0.4193 g Zn

Collection of Hydrogen Gas over Water 2 of 3



$$\begin{aligned} P_{\text{Total}} &= P_{\text{H}_2} + P_{\text{H}_2\text{O}} & P_{\text{H}_2} &= P_{\text{Total}} - P_{\text{H}_2\text{O}} \\ P_{\text{H}_2} &= 769.0 \text{ mm Hg} - 17.5 \text{ mm Hg} \\ &= 751.5 \text{ mm Hg} \end{aligned}$$

- $P = 751.5 \text{ mm Hg} / 760 \text{ mm Hg} / 1 \text{ atm} = \mathbf{0.98882 \text{ atm}}$
- $T = 20.0 \text{ }^\circ\text{C} + 273.15 = \mathbf{293.15 \text{ K}}$
- $V = \mathbf{0.1560 \text{ L}}$

Collection Over Water 3 of 3

$$\begin{aligned} \bullet \text{ PV} &= nRT & n &= PV / RT \\ \bullet n_{\text{H}_2} &= \frac{(0.98882 \text{ atm})(0.1560 \text{ L})}{(0.0820578 \text{ L atm/mol K})(293.15 \text{ K})} \end{aligned}$$

- $n = 0.0064125 \text{ mol H}_2$
- $\text{mass} = 0.0064125 \text{ mol} \times 2.016 \text{ g H}_2 / \text{mol H}_2 = .0129276 \text{ g H}_2$
- $\text{mass} = \mathbf{0.01293 \text{ g H}_2}$

Sample Problem: Dalton's Law of Partial Pressures 1 of 3

- A **2.00 L** flask contains **3.00 g of CO_2** and **0.10 g of helium** at a temperature of **17.0 °C**.
- What are the partial pressures of each gas, and the total pressure?

Solution:

1. Use the I.G.L. to find the partial pressure of each gas
 2. Use Dalton's Law of partial pressures to find the total pressure. Answers:
- $P_{\text{He}} = \mathbf{0.30 \text{ atm}}$; $P_{\text{CO}_2} = \mathbf{0.812 \text{ atm}}$; $P_{\text{Total}} = \mathbf{1.11 \text{ atm}}$

Sample Problem: Dalton's Law of Partial Pressures 2 of 3

- A **2.00 L** flask contains **3.00 g of CO_2** and **0.10 g of helium** at a temperature of **17.0 °C**.
- What are the partial pressures of each gas, and the total pressure?
- $T = 17.0 \text{ }^\circ\text{C} + 273.15 = 290.15 \text{ K}$
- $n_{\text{CO}_2} = 3.00 \text{ g CO}_2 / 44.01 \text{ g CO}_2 / \text{mol CO}_2$
- $= 0.068166 \text{ mol CO}_2$
- $P_{\text{CO}_2} = n_{\text{CO}_2}RT/V$
- $P_{\text{CO}_2} = \frac{(0.068166 \text{ mol CO}_2)(0.08206 \text{ L atm/mol K})(290.15 \text{ K})}{(2.00 \text{ L})}$
- $P_{\text{CO}_2} = \mathbf{0.812 \text{ atm}}$

Sample Problem: Dalton's Law of Partial 3 of 3

- $n_{\text{He}} = 0.10 \text{ g He} / 4.003 \text{ g He} / \text{mol He}$
- $= 0.02498 \text{ mol He}$
- $P_{\text{He}} = n_{\text{He}}RT/V$
- $P_{\text{He}} = \frac{(0.02498 \text{ mol})(0.08206 \text{ L atm} / \text{mol K})(290.15 \text{ K})}{(2.00 \text{ L})}$
- $P_{\text{He}} = \mathbf{0.30 \text{ atm}}$
- $P_{\text{Total}} = P_{\text{CO}_2} + P_{\text{He}} = 0.812 \text{ atm} + 0.30 \text{ atm}$
- $P_{\text{Total}} = \mathbf{1.11 \text{ atm}}$

Applying Dalton's Law of Partial Pressures

Decomposition of KClO_3 (trans 8A)

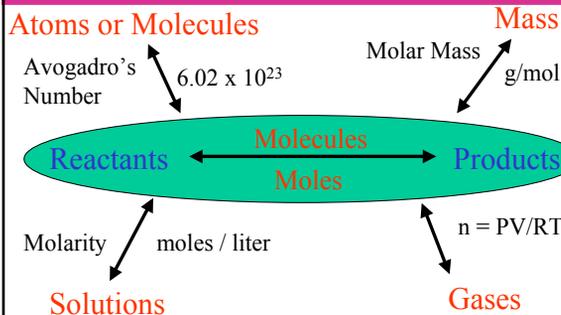
Calculate the mass of potassium chlorate that reacted if 650. mL of oxygen was collected over water at 22.0 °C.

Water levels were equalized before measuring the volume of oxygen. The barometric pressure was 754.0 torr; Vapor Pressure of water at 22.0 °C = 20.0 torr

If the original sample of potassium chlorate weighed 3.016 g, what is the % purity of the sample?

(answers: 2.12 g KClO_3 ; 70.3% pure)

Stoichiometry Revisited



Sample Problem 5.10 Using I.G.L. to Find Amount of Reactants and Products (1 of 2)

PROBLEM: A metal can be produced from its oxide by heating the metallic oxide with H_2 .



What volume of H_2 at 765 torr and 225°C is needed to form 35.5g of Cu from copper (II) oxide?

- PLAN:**
1. Calculate moles of Cu.
 2. Use the mole ratio from the equation to find moles of H_2 .
 3. Use ideal gas law to calculate volume of H_2 gas needed.

Sample Problem 5.10 Using I.G.L. to Find Amount of Reactants and Products (2 of 2)

Solution: $\text{CuO}(s) + \text{H}_2(g) \rightarrow \text{Cu}(s) + \text{H}_2\text{O}(g)$

$$\begin{array}{l} \text{mass (g) of Cu} \\ \downarrow \text{divide by } M \\ \text{mol of Cu} \\ \downarrow \text{molar ratio} \\ \text{mol of H}_2 \\ \downarrow \text{use known P and T to find V} \\ \text{L of H}_2 \end{array} \quad \begin{array}{l} 35.5\text{g Cu} \frac{\text{mol Cu}}{63.55\text{g Cu}} \frac{1\text{mol H}_2}{1\text{mol Cu}} = 0.559\text{mol H}_2 \\ 0.559\text{mol H}_2 \times 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 498\text{K} \\ \hline 1.01\text{atm} \end{array} = 22.6\text{L}$$

Sample Problem 5.11 Using the Ideal Gas Law in a Limiting-Reactant Problem

PROBLEM: What mass of potassium chloride forms when 5.25 L of chlorine gas at 0.950 atm and 293K reacts with 17.0g of potassium?



- PLAN:**
1. Use the ideal gas law to find the number of moles of Chlorine.
 2. Find moles of potassium
 3. Determine the limiting reactant.
 4. Determine the moles of product, then mass of product.

Sample Problem 5.11 Using the Ideal Gas Law in a Limiting-Reactant Problem

SOLUTION: $2\text{K}(s) + \text{Cl}_2(g) \rightarrow 2\text{KCl}(s)$ P = 0.950atm V = 5.25L
T = 293K n = unknown

$$n_{\text{Cl}_2} = \frac{PV}{RT} = \frac{0.950\text{atm} \times 5.25\text{L}}{0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \times 293\text{K}} = 0.207\text{mol}$$

$$17.0\text{g} \frac{\text{mol K}}{39.10\text{g K}} = 0.435\text{mol K} \quad 0.207\text{mol Cl}_2 \frac{2\text{mol KCl}}{1\text{mol Cl}_2} = 0.414\text{mol KCl formed}$$

Cl_2 is the limiting reactant. $0.435\text{mol K} \frac{2\text{mol KCl}}{2\text{mol K}} = 0.435\text{mol KCl formed}$

$$0.414\text{mol KCl} \frac{74.55\text{g KCl}}{\text{mol KCl}} = 30.9\text{g KCl}$$

Dalton's Law of Partial Pressures

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$$

$$P_1 = \chi_1 \times P_{\text{total}} \quad \text{where } \chi_1 \text{ is the mole fraction}$$

$$\chi_1 = \frac{n_1}{n_1 + n_2 + n_3 + \dots} = \frac{n_1}{n_{\text{total}}}$$



Dalton's Law: Using Mole Fractions 1 of 2

- **Problem:** A mixture of gases contains **4.46 mol Ne**, **0.74 mol Ar** and **2.15 mol Xe**. What are the partial pressures of the gases if the total pressure is **2.00 atm** ?

Solution:

- The partial pressure of each gas depends on its mole fraction.
 - Find mole fraction of each gas.
 - Then what???
- Answers: $P_{\text{Ne}} = 1.21 \text{ atm}$; $P_{\text{Ar}} = 0.20 \text{ atm}$; $P_{\text{Xe}} = 0.586 \text{ atm}$

Dalton's Law: Using Mole Fractions 2 of 2

- A mixture of gases contains 4.46 mol Ne, 0.74 mol Ar and 2.15 mol Xe. What are the partial pressures of the gases if the total pressure is 2.00 atm ?
- Total # moles = 4.46 + 0.74 + 2.15 = 7.35 mol
- $X_{\text{Ne}} = 4.46 \text{ mol Ne} / 7.35 \text{ mol} = 0.607$
- $P_{\text{Ne}} = X_{\text{Ne}} P_{\text{Total}} = 0.607 (2.00 \text{ atm}) = \mathbf{1.21 \text{ atm for Ne}}$
- $X_{\text{Ar}} = 0.74 \text{ mol Ar} / 7.35 \text{ mol} = 0.10$
- $P_{\text{Ar}} = X_{\text{Ar}} P_{\text{Total}} = 0.10 (2.00 \text{ atm}) = \mathbf{0.20 \text{ atm for Ar}}$
- $X_{\text{Xe}} = 2.15 \text{ mol Xe} / 7.35 \text{ mol} = 0.293$
- $P_{\text{Xe}} = X_{\text{Xe}} P_{\text{Total}} = 0.293 (2.00 \text{ atm}) = \mathbf{0.586 \text{ atm for Xe}}$

Diffusion vs Effusion

• Diffusion

- Spreading out of molecules from a region where their concentration is high to a region where their concentration is low

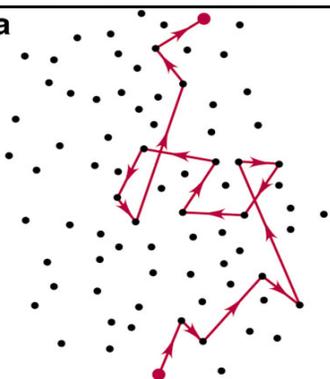
- For Gases: from high partial pressure to low partial pressure
– e.g. Perfume, flatulence, etc.

• Effusion

- The diffusion of a gas through a tiny hole (or holes)
• e.g. Gradual deflation of a balloons, tires, etc.

Diffusion of a Gas Particle

Fig. 5.20



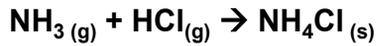
Quantifying Effusion: Graham's Law of Effusion

$$\text{Rate of Effusion} \propto \frac{1}{\sqrt{\text{MW of Gas}}}$$

OR

$$\frac{\text{Rate of Gas A}}{\text{Rate of Gas B}} = \frac{\sqrt{\text{MW of Gas B}}}{\sqrt{\text{MW of Gas A}}}$$

Diffusion of NH₃ gas and HCl gas



- HCl = 36.46 g/mol NH₃ = 17.03 g/mol
- $\text{Rate}_{\text{NH}_3} = \text{Rate}_{\text{HCl}} \times (36.46 / 17.03)^{1/2}$
- $\text{Rate}_{\text{NH}_3} = \text{Rate}_{\text{HCl}} \times 1.463$

Sample Problem 5.12 Applying Graham's Law of Effusion

PROBLEM: Calculate the ratio of the effusion rates of helium and methane (CH₄).

PLAN: The effusion rate is inversely proportional to the square root of the molar mass for each gas. Find the molar mass of both gases and find the inverse square root of their masses.

SOLUTION: M of CH₄ = 16.04g/mol M of He = 4.003g/mol

$$\frac{\text{rate}_{\text{He}}}{\text{rate}_{\text{CH}_4}} = \sqrt{\frac{16.04}{4.003}} = 2.002$$

Sample Effusion Problems

- Which effuses faster out of a car's tire, oxygen or nitrogen? How much faster?
 - Answer: 1.069 times or 6.9% faster
- Suppose that there are two leaky cylinders in a lab, one containing chlorine gas, the other hydrogen cyanide, HCN.
 - Which gas will reach you first?
 - How many times faster will its molecules diffuse across the room?
 - 1.62 times faster

Gaseous Diffusion Separation of Uranium - 235 / 238

- ²³⁵UF₆ vs ²³⁸UF₆
- Separation Factor = $S = \frac{(238.05 + (6 \times 19))^{0.5}}{(235.04 + (6 \times 19))^{0.5}}$
- after two runs → $S = 1.0086$
- after approximately 2000 runs
- ²³⁵UF₆ is > 99% Purity !!!!!
- Y - 12 Plant at Oak Ridge National Lab

Using the Kinetic Theory to Explain the Gas Laws

Kinetic Theory of Gases

1. Gases consist of an exceptionally large number of extremely small particles in random and constant motion
2. The Volume that gas particles themselves occupy is much less than the Volume of their container
 - i.e. The distance between gas particles is vast
3. Collisions are elastic and molecular motion is linear.....WHY?

Postulates of the Kinetic-Molecular Theory

Postulate 1: Particle Volume

Because the volume of an individual gas particle is so small compared to the volume of its container, the gas particles are considered to have mass, but no volume.

Postulate 2: Particle Motion

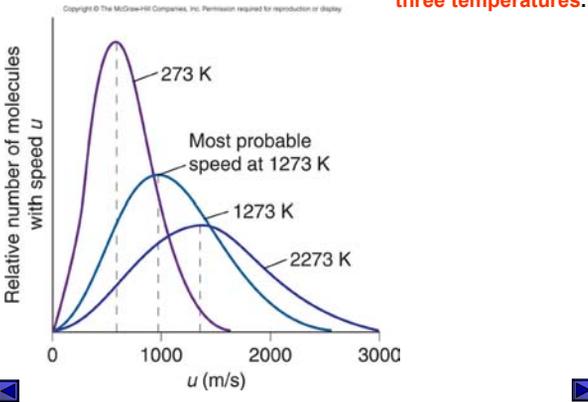
Gas particles are in constant, random, straight-line motion except when they collide with each other or with the container walls.

Postulate 3: Particle Collisions

Collisions are elastic therefore the total kinetic energy(K_t) of the particles is constant.

Figure 5.14

Distribution of molecular speeds at three temperatures.



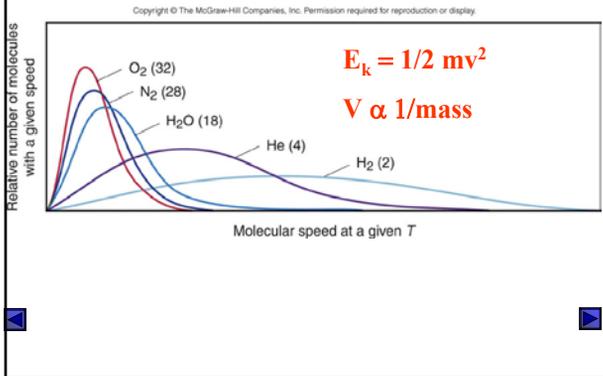
Important Points

At a given temperature, all gases have the same...

- 1) molecular kinetic energy *distributions*
- 2) *average* molecular kinetic energy

Kinetic Energy: $E_k = 1/2 mv^2$

Figure 5.19 **Relationship between molar mass and molecular speed.**



Explain Each Gas Law in Terms of the Kinetic Theory

- Boyle's Law (P-V Law) trans 10
 - Amonton's Law (P-T Law) trans 9 & 11
 - Chuck's Law (V-T Law) trans 12
 - Graham's Law of Effusion
- Hint: $KE = 1/2mv^2$ and gases "A" and "B" are at the same temperature.

Figure 5.15 **A molecular description of Boyle's Law**

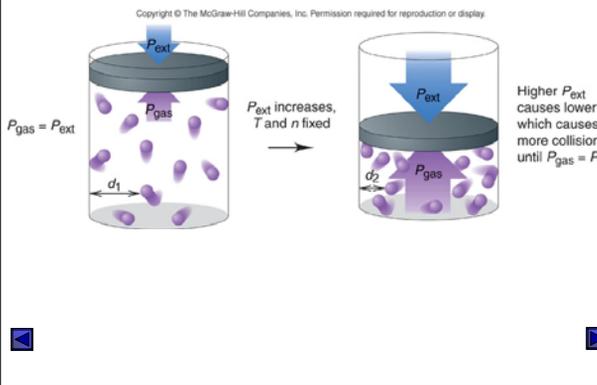


Figure 5.16 **A molecular description of Dalton's law of partial pressures.**

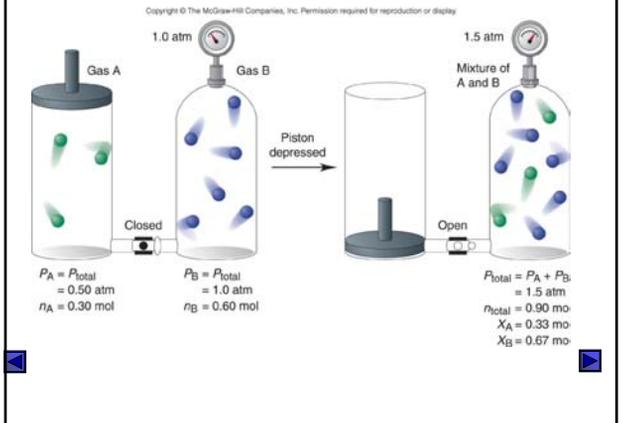


Figure 5.17 **A molecular description of Charles's Law**

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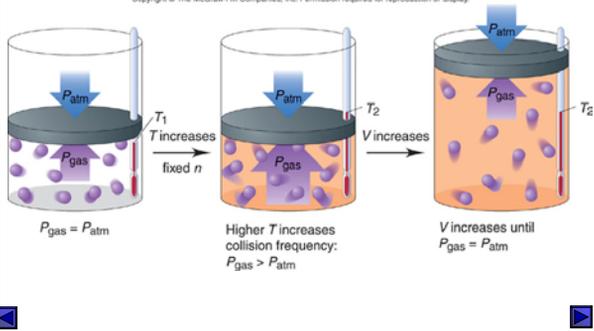
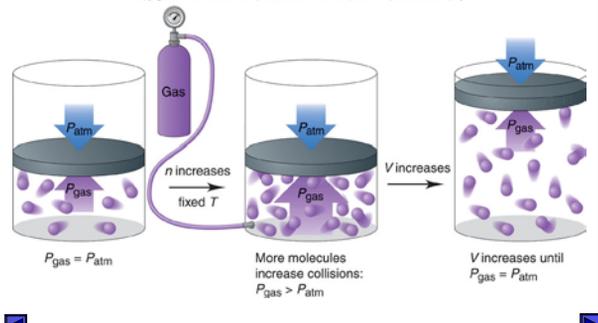


Figure 5.18 **A molecular description of Avogadro's Law**

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Real Gases: Deviations from the Ideal Gas Law

Ideal Gases

- Obey the gas laws exactly
- Are Theoretical Gases
 - Infinitely Small with no intermolecular attractions
 - However, all matter occupies space have I.M.F.'s of attraction!!

Real Gases

- Do not follow the gas laws exactly
 - Molecules DO occupy space
 - Molecules DO have attractions
 - causes gases to condense into liquids

- At high Pressures and low Temps molecular volume and attractions become significant

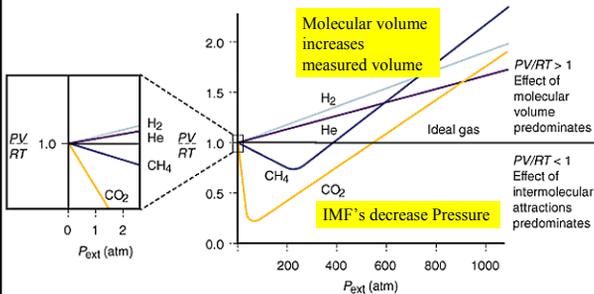
Molar Volume of Some Common Gases at STP (0°C and 1 atm)

Gas	Molar Volume (L/mol)	Condensation Point (°C)
He	22.435	-268.9
H ₂	22.432	-252.8
Ne	22.422	-246.1
Ideal Gas	22.414	----
Ar	22.397	-185.9
N ₂	22.396	-195.8
O ₂	22.390	-183.0
CO	22.388	-191.5
Cl ₂	22.184	-34.0
NH ₃	22.079	-33.4

Table 5.4 (p. 207)

The Behavior of Several Real Gases with Increasing External Pressure

Fig. 5.21



The Effect of Molecular Volume on Measured Gas Volume

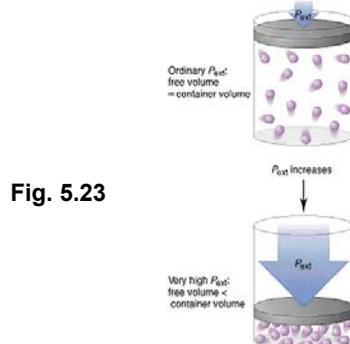


Fig. 5.23

The van der Waals Equation

$$\left(P + \frac{n^2a}{V^2}\right)(V-nb) = nRT$$

Gas	a $\left(\frac{\text{atm L}^2}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H ₂	0.244	0.0266
N ₂	1.39	0.0391
O ₂	6.49	0.0318
Cl ₂	3.59	0.0562
CO ₂	2.25	0.0428
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

Van der Waals Calculation of a Real gas 1 of 2

Problem

A tank of **20.0 liters** contains chlorine gas at a temperature of **20.00°C** at a pressure of **2.000 atm**. If the tank is pressurized to a new volume of **1.000 L** and a temperature of **150.00°C**, calculate the new pressure using the ideal gas equation, and the van der Waals equation.

Plan

1. Use ideal gas law to calculate moles of gas under initial cond.
2. Use I.G.L. to calculate "ideal" pressure under the new cond.
3. Use Van der Waals equation to calculate the "real" pressure.

Van der Waals Calculation of a Real gas 2 of 2

Solution

$$n = \frac{PV}{RT} = \frac{(2.000 \text{ atm})(20.0 \text{ L})}{(0.08206 \text{ Latm/molK})(293.15 \text{ K})} = \mathbf{1.663 \text{ mol}}$$

$$P = \frac{nRT}{V} = \frac{(1.663 \text{ mol})(0.08206 \text{ Latm/molK})(423.15 \text{ K})}{(1.000 \text{ L})} = \mathbf{57.745 \text{ atm}}$$

$$P = \frac{nRT}{(V-nb)} - \frac{n^2a}{V^2} = \frac{(1.663 \text{ mol})(0.08206 \text{ Latm/molK})(423.15 \text{ K})}{(1.00 \text{ L}) - (1.663 \text{ mol})(0.0562)}$$

$$\frac{(1.663 \text{ mol})^2(6.49)}{(1.00 \text{ L})^2} = 63.699 - 17.948 = \mathbf{45.751 \text{ atm}}$$