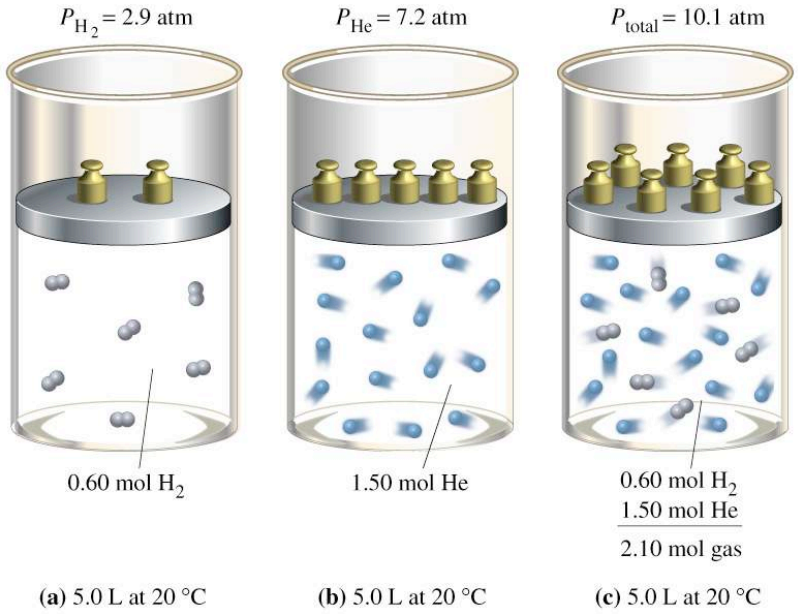
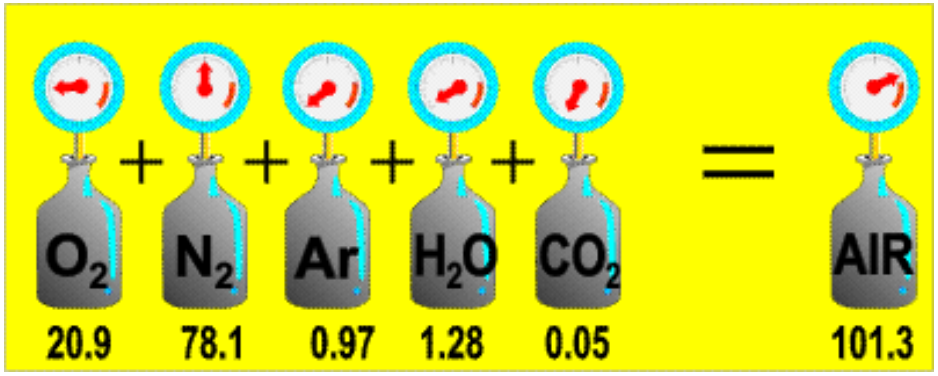
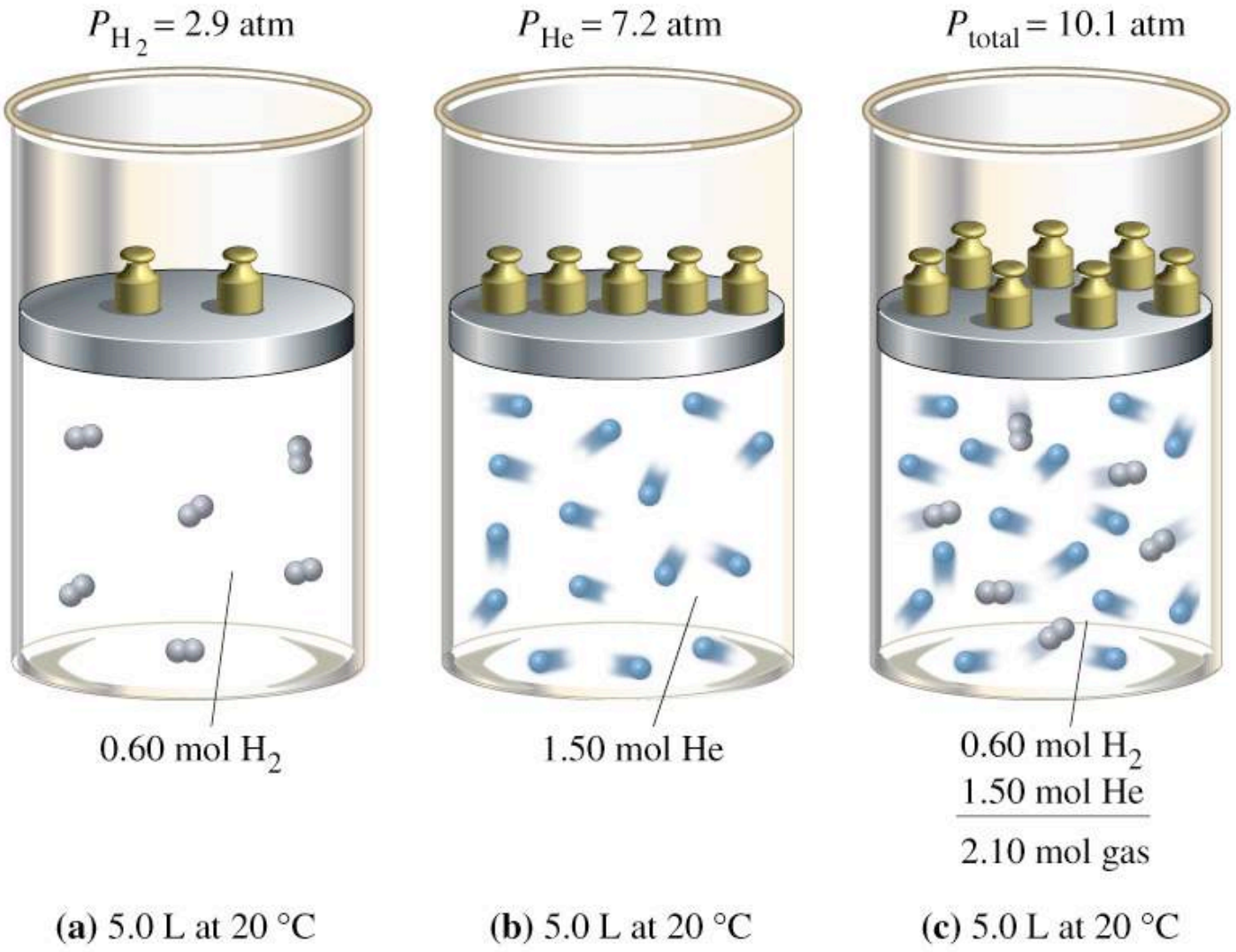
NOTES: 14.4 – Dalton's Law & Graham's Law



Dalton's Law of Partial Pressures:

- At constant volume and temperature, the total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of the component gases
- $P_{total} = P_1 + P_2 + P_3 + \ldots$




P_{H_2} = 2.9 atm
P_{He} = 7.2 atm
P_{total} = 10.1 atm
0.60 mol H_2
1.50 mol He
0.60 mol H_2
1.50 mol He
2.10 mol gas
(a) 5.0 L at 20 °C
(b) 5.0 L at 20 °C
(c) 5.0 L at 20 °C

Example #1:

- Determine the total pressure of a gas mixture that contains oxygen, nitrogen, and helium if the partial pressures of the gases are as follows:

P_{O2} = 20.0 kPa

P_{N2} = 46.7 kPa

P_{He} = 26.7 kPa

Example #1:

P_{O2} = 20.0 kPa

P_{N2} = 46.7 kPa

P_{He} = 26.7 kPa

TOTAL PRESSURE = 20.0 + 46.7 + 26.7

= **93.4 kPa**

Example #2:

A gas mixture containing oxygen, nitrogen, and carbon dioxide has a total pressure of 32.9 kPa. If P_{O2} = 6.6 kPa and P_{N2} = 23.0 kPa, what is P_{CO2}?

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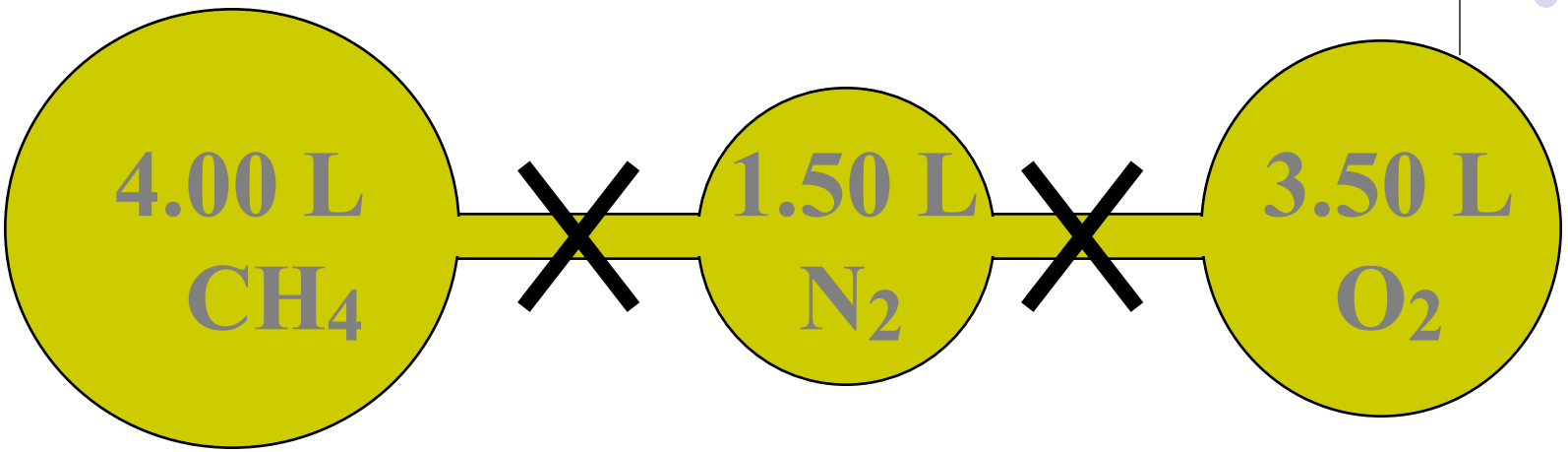
$32.9\ kPa = 6.6\ kPa + 23.0\ kPa + P_{CO2}$

$P_{CO2} = 32.9 - 29.6 =$ **3.3 kPa**

Partial Pressure Example #3:



2.70 atm **4.58 atm** **0.752 atm**

- When these valves are opened, what is each partial pressure and the what is the total pressure?

Total volume after valves are opened:

4.00 L + 1.5 L + 3.5 L = 9.00 L

Consider CH_4 : $P_1V_1 = P_2V_2$

(2.70 atm)(4.00 L) = (P_2)(9.00 L)

P_2 = 1.20 atm

Now consider the next gas, N_2

$P_1V_1 = P_2V_2$

$(4.58\ atm)(1.50\ L) = (P_2)(9.00\ L)$

$P_2 = 0.763\ atm$

And finally the last gas O_2

$P_1V_1 = P_2V_2$

$(.752\ atm)(3.50\ L) = (P_2)(9.00\ L)$

$P_2 = 0.292\ atm$

So, the "new" partial pressures are

CH_4 =1.20 atm

N_2=0.763 atm

O_2=0.292 atm

According to Dalton's law, the total pressure is the sum of the partial pressures.

1.20 atm

0.763 atm

\+ 0.292 atm

2.26 atm

Mole Fraction:

- X_A = **(mole A) / (total number of moles)**

- the mole fraction of each gas in a mixture is directly proportional to the partial pressure it exerts

Example #1:

A) Determine the mole fraction of each gas in a mixture containing 54.0 grams of CO_2 and 33 grams of N_2.

B) Determine the partial pressure of each gas above if the total pressure of the CO_2 and N_2 mixture is 101.3 kPa.

Example #1:

A) Determine the mole fraction of each gas in a mixture containing 54.0 grams of CO_2 and 33.0 grams of N_2.

54.0 g CO_2 (1 mol / 44.0 g) = 1.23 mol CO_2

33.0 g N_2 (1 mol / 28.0 g) = 1.18 mol N_2

TOTAL MOLES = 2.41 mol

X_{CO2} = 1.23 / 2.41 = 0.51

X_{N2} = 1.18 / 2.41 = 0.49

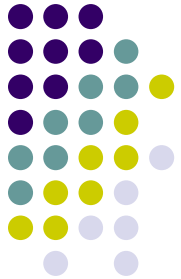
Example #1:

B) Determine the partial pressure of each gas above if the total pressure of the CO_2 and N_2 mixture is 101.3 kPa.

P_{CO2} = (0.51)(101.3 kPa) = **51.7 kPa**

P_{N2} = (0.49) (101.3 kPa) = **49.6 kPa**

Example #2:



The partial pressure of nitrogen in air is 592 mm Hg. Air pressure is 752 mm Hg. What is the mole fraction of nitrogen in air?

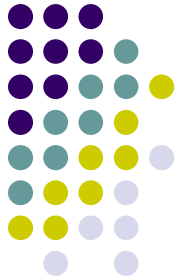
Example #2:

The partial pressure of nitrogen in air is 592 mm Hg. Air pressure is 752 mm Hg. What is the mole fraction of nitrogen in air?

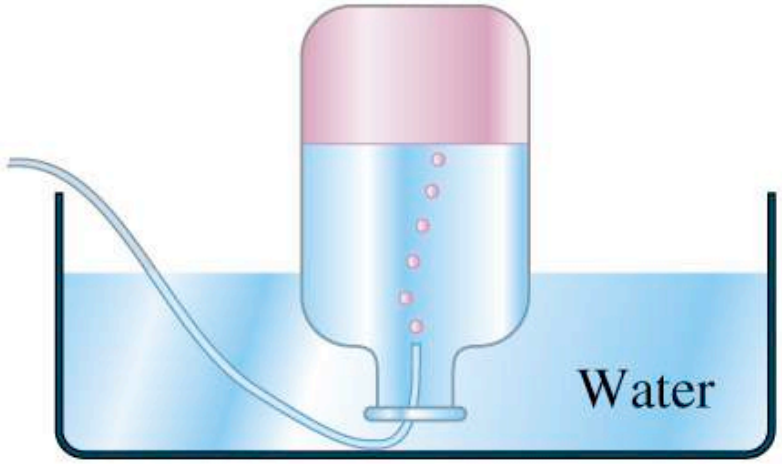
X_{N2} = 592 mm Hg / 752 mm Hg

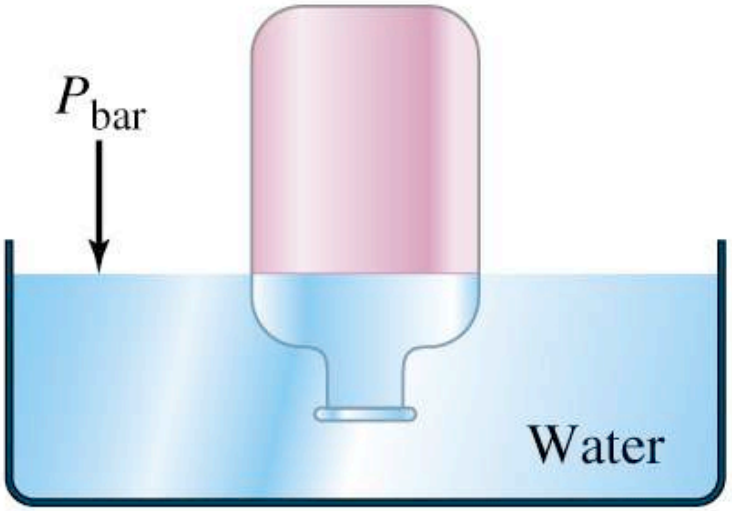
= **0.787**

VAPOR PRESSURE:



- Water evaporates!
- When that water evaporates, the vapor has a pressure.
- Gases are often collected over water so the vapor pressure of water must be subtracted from the total pressure.
- Vapor pressure of water must be either given or looked up.


Water


P_{bar}
Water

Vapor Pressure of a Liquid:

$$P_{atm} = P_{gas} + P_{H2O}$$

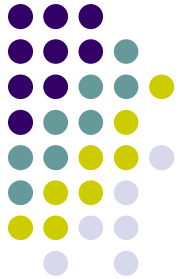
or

$$P_{gas} = P_{atm} - P_{H2O}$$

Vapor Pressure of a Liquid:

Temp. (°C)	v.p. of water (mm Hg)	Temp. (°C)	v.p. of water (mm Hg)
18	15.48	21	18.65
19	16.48	22	19.83
20	17.54	23	21.07

Example #1: A sample of hydrogen gas was collected by displacement of water at 23°C. The atmospheric pressure was 748 mm Hg. What pressure would the dry hydrogen exert in the same conditions?



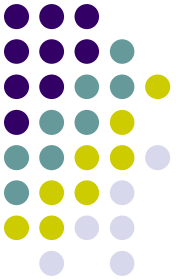
$P_{H_2} = P_{atm} - P_{H_2O}$

$P_{H_2} = 748 \text{ mm Hg} - 21.07 \text{ mm Hg}$

$P_{H_2} = 726.93 \text{ mm Hg}$

$P_{H_2} \approx \mathbf{727 \text{ mm Hg}}$

Example #2: A sample of oxygen gas was collected by displacement of water. The oxygen occupied 742 mL at 22°C. The barometric pressure was 753 mm Hg. What volume would the dry oxygen occupy at STP?



$P_{O2} = P_{atm} - P_{H2O}$

P_{O2} =753 mm Hg – 19.83 mm Hg

P_{O2} = 733.2 mm Hg

$P_1V_1/T_1 = P_2V_2/T_2$

(733.2 mm Hg)(742 mL)/(295K) = (760 mm Hg)(V_2)/(273K)

V_2 = **662 mL**

Example #3: A student prepares a sample of hydrogen gas by electrolyzing water at 23°C. She collects 152 mL of H_2 at a total pressure of 758 mm Hg. Calculate:

(a) the partial pressure of hydrogen, and
(b) the number of moles of hydrogen collected.

$P_{H2} = P_{atm} - P_{H2O}$

P_{H2} =758 mm Hg – 21.07 mm Hg

P_{H2} = **736.9 mm Hg (= 0.970 atm)**

Example #3: A student prepares a sample of hydrogen gas by electrolyzing water at 23°C. She collects 152 mL of H_2 at a total pressure of 758 mm Hg. Calculate:

(a) the partial pressure of hydrogen, and
(b) the number of moles of hydrogen collected.

$$PV = nRT$$

$$(0.970\ atm)(0.152\ L) = (n)(0.0821\ L{\cdot}atm/mol{\cdot}K)(296\ K)$$

$$n = \mathbf{0.00607\ mol\ H_2}$$

Gas Molecules in Motion:

- **DIFFUSION** = tendency of molecules to move toward areas of lower concentration; explains how 2 gases mix together

- **EFFUSION** = process in which a gas escapes through a tiny hole in its container

Rate of Molecule Movement:

- Recall, kinetic energy is the energy of movement;
- Temperature is a measure of kinetic energy of molecules;

Rate of Molecule Movement:

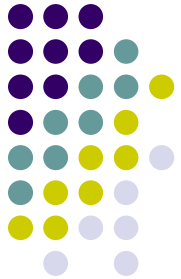
- $KE = \frac{1}{2} mv^2$
- At the same temperature, two gases will have the same kinetic energies;
- so, it follows that if 2 gases have the same K.E., but different masses, the smaller particles will move faster!

Graham's Law:

- ***The rate of effusion of a gas is inversely proportional to the square root of the gas's molar mass***
- Graham's Law of Effusion holds true for diffusion of a gas too.

$$\frac{v_2}{v_1} = \sqrt{\frac{m_1}{m_2}}$$

Graham's Law of Effusion / Diffusion



$$\frac{Rate\ of\ diffusion\ for\ gas\ 1}{Rate\ of\ diffusion\ for\ gas\ 2} = \frac{\sqrt{MW_2}}{\sqrt{MW_1}}$$

Graham's Law Example:

- Calculate the ratio of the velocity of helium atoms to the velocity of neon atoms at the same temperature.

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- Calculate the ratio of the velocity of helium atoms to the velocity of neon molecules (Ne) at the same temperature.

$$\frac{Rate_{He}}{Rate_{Ne}} = \frac{\sqrt{20.2}}{\sqrt{4.0}} = \frac{4.49}{2.0} = \underline{\mathbf{2.25}}$$

Graham's Law Example:

- Calculate the ratio of the velocity of helium atoms to the velocity of neon molecules (Ne) at the same temperature.

$$\frac{Rate_{He}}{Rate_{Ne}} = \frac{\sqrt{20.2}}{\sqrt{4.0}} = \frac{4.49}{2.0} = \underline{\mathbf{2.25}}$$

so, helium effuses and diffuses 2.25 times faster than neon at the same temperature!