GASES

Chapter Eleven

Kinetic-Molecular Theory

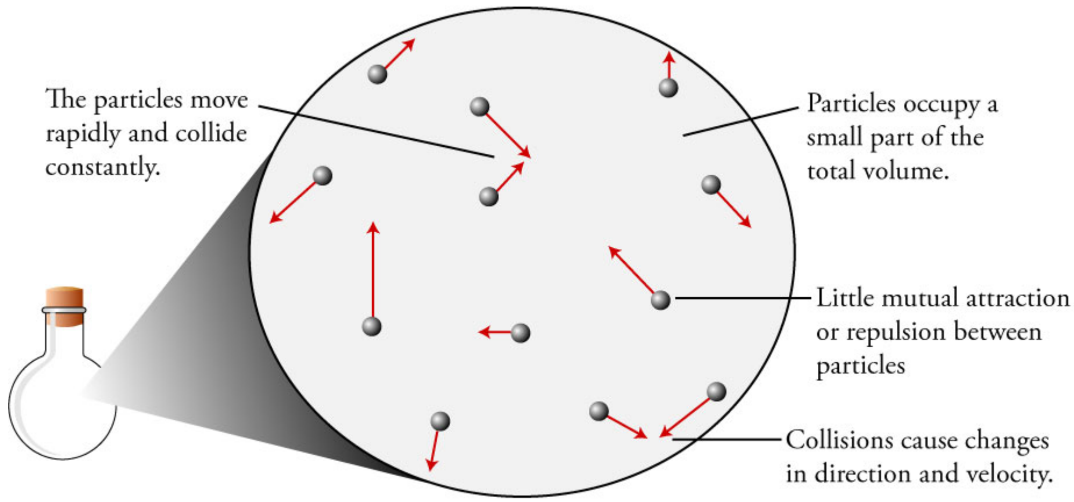
- Recall that our only previous description of gases stated that gases completely fill and take the shape of their containers.
- The Kinetic-Molecular Theory goes much farther in describing how gases *ideally* behave.
- There are five principle statements that comprise it, which should be *understood thoroughly.*
  - Note that your textbook combines two of these into what it lists as the second statement of the Theory

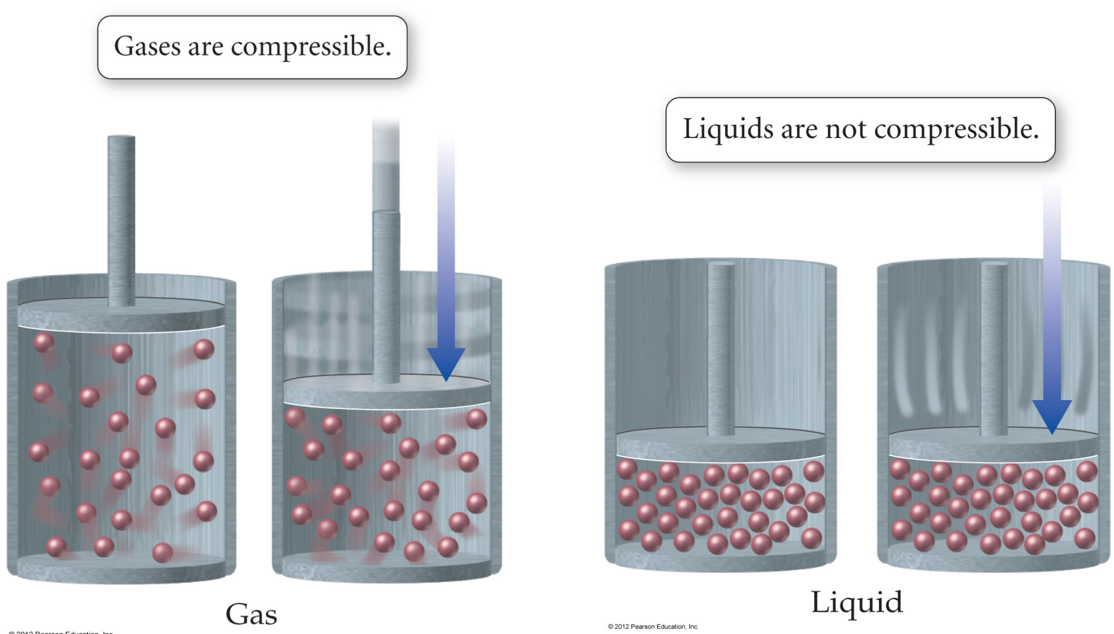
Kinetic-Molecular Theory

- The particles of a gas are so small compared to the distances between them that the volume of the individual gas particles is considered negligible (zero).
- Gas particles are in constant, rapid, and random motion.
- Gas particles exert neither attractive nor repulsive forces on each other.

Kinetic-Molecular Theory

- Collisions between gas particles are perfectly elastic
  - By this, we mean that the gas molecules do not lose energy when they collide
- The average kinetic energy of a collection of gas particles is directly proportional to the temperature (in Kelvin) of the gas.
  - From this we can state that <u>all gases at the same temperature have the same average kinetic energy.</u>


The particles move rapidly and collide constantly.
Particles occupy a small part of the total volume.
Little mutual attraction or repulsion between particles
Collisions cause changes in direction and velocity.


Gases are compressible.
Liquids are not compressible.
Gas
Liquid

Pressure

- An important parameter which must be taken into account when studying gases is pressure.
- Pressure is the amount of force applied to an area:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

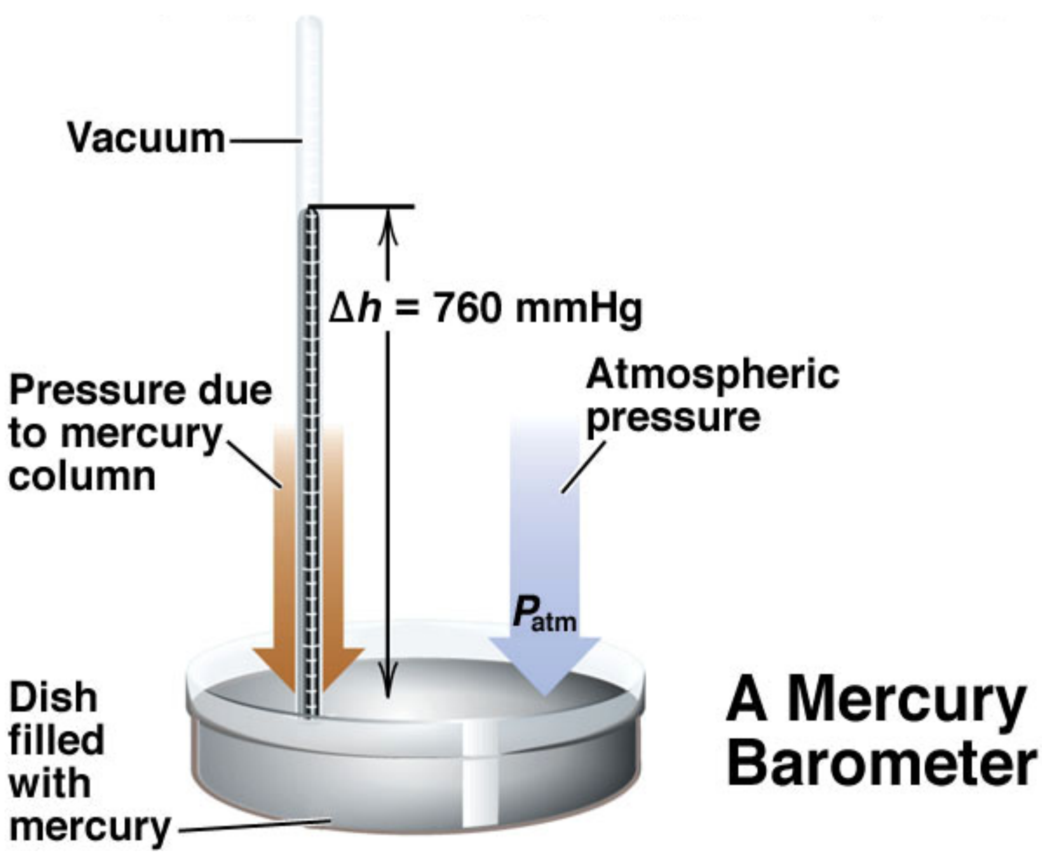
- Consider laying on a bed of nails. Do you want there to be many nails or few nails in the bed?

Pressures of Gases

- The pressure exerted by a gas in a sealed container results from collisions of many individual gas particles with the walls of its container.
  - When we say a gas is at high pressure, its individual particles are colliding frequently with the sides of its container.
- Later we will see that many other parameters can have an effect on the pressure of a gas sample, such as the volume of the enclosing container.

Air Pressure

- The air in the atmosphere exerts a substantial amount of pressure on everything on the surface of the earth.
- Since air is composed of matter (nitrogen, oxygen, etc.), it has mass.
- Air reaches up to at least 20 miles above the surface of Earth.
- The weight of the air pushes down on everything on the surface, including us.
- In a similar fashion, the weight of ocean water exerts tremendous pressures at the lower depths of the oceans.



Measuring Pressure

- A device used for measuring pressure is called a manometer; a device specifically designed to measure air pressure is called a barometer.
- To build a simple barometer, we completely fill a thin cylinder with mercury
  - Mercury is very dense and is therefore ideal for this application
- Then, we partially fill a deep dish with mercury and invert the mercury tube in this pool of mercury.
- Some of the mercury will descend out of the tube as gravity pulls it down.
- However, some of the mercury will stay in the tube, as the air pressure keeps this mercury supported.
  - The weight of the air on the surface of the mercury pool opposes the force of gravity as it tries to pull the mercury down out of the column.

Measuring Pressure

- On an "average" day, the height of the mercury column will be close to 760 mm.
- What would the height of the column be on average at a higher altitude: greater than 760 mm, or less?
- The "standard" air pressure is set at this value of 760 mm, as we shall shortly see.

Units of Pressure

- Unfortunately, many different units are used to measure pressure.
- The units we will employ most often include
  - Atmospheres (atm)
    - Though not the SI unit of pressure, this is a very common unit. The value of the air pressure at sea level on an average day is close to 1 atm.
  - Millimeters of Mercury (mm Hg)
    - This unit is derived from the way one takes a measurement with a barometer or manometer. Recall that on an average day, the height of a mercury column in a barometer is about 760 mm Hg.
    - 1 atm = 760 mm Hg (approximately, though treat this as exact).
  - Torr (torr)
    - This unit is essentially the same as the mm Hg, so
      1 atm = 760 torr (exactly).
- You must know these units and conversions.

Units of Pressure

- Other units of pressure you may encounter, but need not memorize the conversion for, include
  - Pascals (Pa) (the SI unit of pressure) and kilopascals (kPa)
  - Pounds per square inch (psi)
  - Bars (bar) and millibars (mbar)

1 atm = 101,325 Pa = 14.7 psi = 1013 mbar

The Gas Laws

- In considering gases, there are four important measured values which we will often consider.
  - Pressure (P)
  - Volume (V)
  - Amount (Moles) of gas (n)
  - Temperature (T)
    - Note that the units of temperature will always be expressed in Kelvin in the gas laws.
- The gas laws describe the mathematical relationship between these parameters

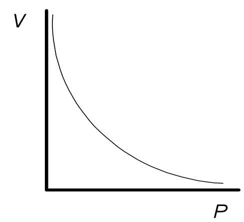
Boyle's Law

- Suppose we have a gas in a sealed piston (a container whose volume can change), and we know its pressure, volume, and temperature.
- Keeping the temperature the same, we decrease the volume of the container.
- What will happen to the pressure?
  - Hint: Will the gas molecules collide with the sides of the container more or less frequently?

Boyle's Law

- Pressure and volume are *inversely* proportional.
  - That is, if one increases, the other must decrease.
  - Remember that the temperature must remain constant for this to be true.
- Mathematically, we write

$$P \propto \frac{1}{V}, \text{ at constant T and n}$$



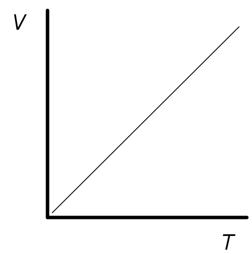
Charles' Law

- Suppose we have a gas in an expandable container, and, without changing its pressure, we raise its temperature.
- How will the behavior of the gas molecules change?
- In order to keep the pressure constant, what will happen to the volume of the gas?

Charles' Law

- Volume and temperature are *directly* proportional.
  - That is, if one increases the other increases.
  - Pressure must remain constant for the process.
- Mathematically, this is stated as

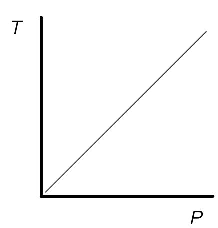
$$V \propto T, \text{ at constant } P \text{ and } n$$



Gay-Lussac's Law

- Suppose a gas is kept in a rigid container whose volume cannot change.
  - If the gas is heated, how will the pressure change?
- Pressure and temperature are directly proportional, assuming the volume remains unchanged.
- Mathematically, this is stated:

$$P \propto T, \text{ at constant } V \text{ and } n$$



Avogadro's Hypothesis

- Amadeo Avogadro is credited with stating one of the most fundamental statements describing gases:

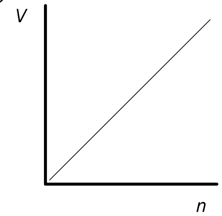
  "Equal amounts (moles) of gases occupy equal volumes under the same conditions"

- This greatly simplifies our treatment of gases, as we can conclude that, regardless of what composes the gas, if we know how many moles of it we have and its conditions, we can find its volume.

Avogadro's Law

- Finally, we can derive the relationship between amount of a gas and its volume
- Adding a gas to a container will increase the volume of the gas if temperature and pressure are held constant
  - Of course, the container cannot be <u>rigid;</u> it must be able to expand
- Mathematically, this is stated

$$V \propto n, \text{ at constant } P \text{ and } T$$



The Combined Gas Law

- The previous laws can all be combined into one convenient form, the *combined gas law*.
- This law is used when you know the physical measurements of a gas under one set of conditions (the initial conditions), and you are required to then provide a parameter based on a new set of conditions

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2} \xrightarrow{\text{constant amount}} \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Example

72.6 L of a gas at 35.7 °C and 0.872 atm is heated to 50.0 °C and allowed to expand to 87.5 L. What is the pressure of the gas under these new conditions? Assume that the amount of gas does not change.

The Combined Gas Law

- Suppose we know the values of the parameters for a gas in a sealed container
- We change the temperature, keeping the pressure constant (that is, $P_1 = P_2$)
  - Since the container is sealed, it should be obvious that the amount of gas does not change either
- Using the combined gas law, we can derive a more useful form of Charles' Law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{at constant P and n}$$

Example

A gas occupies 35.8 L at 1.13 atm and 42.3 °C. What would be the temperature of this gas, in Celcius, if the volume were decreased to 25.0 L and the pressure was left unchanged?

The Combined Gas Law

In a similar fashion, we can derive useful forms of the other gas laws

Boyle's Law:

$$P_1V_1 = P_2V_2$$

at constant T and n

Charles' Law:

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

at constant P and n

Gay-Lussac's Law:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

at constant V and n

Avogadro's Law:

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

at constant T and P

Example

A gas occupies 29.5 L, and exerts a pressure of 640. mm Hg. If the container's volume is expanded to 40.0 L (keeping the temperature constant), what will be the pressure of the gas in mm Hg and in atm?

The Ideal Gas Law

- All the previous laws allow us to compare a gas under one set of conditions with its values under other conditions.
- The Ideal Gas Law summarizes the previous laws in a fundamental way
- Its power is that it shows how the four parameters (P, V, T, and n) can be used to determine one another.

The Ideal Gas Law

- The Ideal Gas Law is, mathematically,

$$PV = nRT$$

where R is a constant, called the universal gas constant.

$$R = 0.0821 \frac{L \cdot atm}{mol \cdot K}$$

- If you know any three parameters from the ideal gas law, the fourth can be determined by substitution into this equation.
- R may be expressed in other units, but this is the most common 'version' of it

Example

What volume is one mole of a gas expected to occupy at exactly 1 atm and exactly 0 °C? Note: These pressures and temperatures are called STP (standard temperature and pressure).

Example

If a balloon containing methane has a volume of 7.25 L at 754 mm Hg and 296.4 K, then how many moles of methane does the balloon contain? How many grams is this?

Example

A 14.5 g piece of dry ice (solid CO_2) is put in a balloon and warmed to 298 K, causing all the CO_2 to sublimate (turn to gas). The volume of the balloon after the sublimation is completed is measured to be 3.29 L. What is the pressure exerted by the gas inside the balloon?

Example

What is the density of pure carbon dioxide gas at 1.05 atm and 300.0 K? Report your answer in grams per liter.

Molar Mass of a Gas

- Using the Ideal Gas Law, the molar mass of a gas can be determined from experimental data
- Since the molar mass is an intensive property, any amount of gas can be used to calculate its value
- Let m be the mass of a gas sample (in grams), and M be the molar mass (in g/mole)
- The moles of gas (n) is just the mass divided by the molar mass:
- Substituting into the Ideal Gas Law and solving for M:

Gas Stoichiometry

- The Ideal Gas Law aids us in predicting the quantity relationships when reactants or products are gases.
- An important value to keep in mind is that 1 mole of a gas at STP will occupy 22.4 liters.
- We will use the Ideal Gas Law for similar calculations under different conditions.

Example

- 54.8 L of hydrogen gas is combined with excess oxygen at STP. What mass of water should be produced?

Example

- 72.9 L of hydrogen (at STP) is reacted with 28.0 L of nitrogen (at STP), producing ammonia. What volume will the ammonia produced occupy at 1.25 atm and 325 K?

Example

10.00 mL of a 0.255 M HCl solution is combined with 1.25 grams of $NaHCO_3$. What volume will the carbon dioxide produced in this reaction occupy at 755 torr and 27.5 °C?

Dalton's Law of Partial Pressures

- In a mixture of gases (like air) each substance in the mixture exerts its own indivual pressure, called the *partial pressure* of that gas.
- The total pressure of the mixture of these gases is simply the sum of these partial pressures.
  - So, air pressure is derived from the partial pressures of all the gases making up the air, including N_2, O_2, Ar, H_2O, CO_2, and others.
- Mathematically, for a mixture of *y* gases, this is stated as

$$P_{total} = P_{gas\ 1} + P_{gas\ 2} + \ldots + P_{gas\ y}$$
$$= \sum_{i=1}^{y} P_{gas\ i}$$

Example

Argon, neon, and helium gases are all combined in a 40.0 L container. The total pressure of the three gases is measured to be 1.45 atm. Argon and neon each exert a partial pressure of 0.65 atm. What is the partial pressure of helium in this mixture?

Example

- 12 grams of hydrogen gas and 56 grams of nitrogen gas are injected into a rigid, 25.0 liter container.

  a. What pressure (in atm) will the gas mixture exert at 125 °C?

  b. Suppose the gases react with one another to produce gaseous ammonia. What pressure will the gas in the container exert, assuming the temperature remains at 125 °C? (Assume the reaction goes to completion)

Mole Fractions

- The mole fraction of a component in a mixture is simply the proportion of that compound in the mixture *by moles.* It is commonly symbolized by *X* and it unitless
- For example, consider a mixture of 2.0 moles of helium, 2.0 moles of argon, and 4.0 moles of neon.

  Total number of moles = 8.0 moles

  X_{He} = 2 moles/8 moles = 0.25

  X_{Ar} = 0.25

  X_{Ne} = 0.50
- Note that the mole fractions of all components must add up to one.

Mole Fractions

- If we know the total pressure of a mixture of gases and the mole fractions of those gases, it is easy to determine the partial pressure of each gas
- The partial pressure of a gas is equal to the product of the total gas pressure and the mole fraction:

  $P_{gas\ a} = (P_{total})(X_{gas\ a})$

  $P_{gas\ b} = (P_{total})(X_{gas\ b})$

  etc.

Example

A rigid, 35.0-liter tank contains a mixture of 200. grams of neon and 200. grams of argon at 35 °C.

a. What is the mole fraction of each gas in the mixture?

b. What is the partial pressure of each gas in the mixture?

Collecting a Gas Over Water

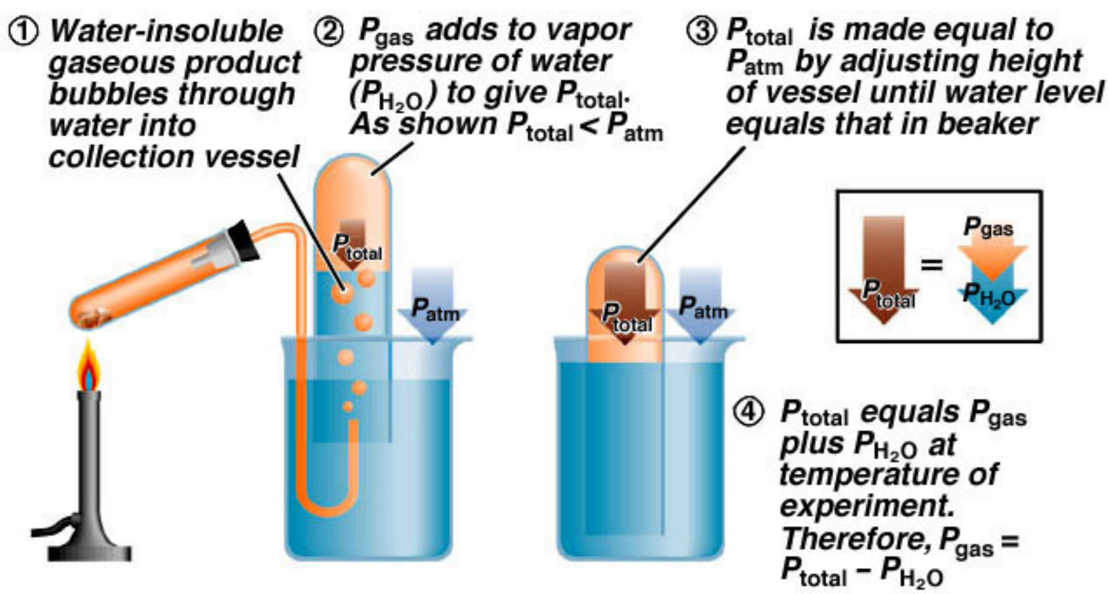
- One common way to collect a gas produced by an experiment is over water.
- From the reaction vessel, the gas enters a hose which leads to a container filled with water.
- The gas then bubbles up through the water into a tube filled with water that penetrates the waters surface.
- The gas displaces the water in the tube, and is collected there.
- However the gas is "wet", meaning it contains some water vapor.

Collecting a Gas Over Water

- To find the pressure of the "dry" (i.e. without water) sample, we must subtract out the pressure of the water vapor mixed with it.
  - The pressure exerted by the water pressure can be found in a table, so long as we know the temperature of the water.
- If the level of the water in the tube is the same as the level of the water in the container the tube is in, the following relationship exists:

$$P_{air} = P_{gas} + P_{water\ vapor}$$

Collecting a Water-Insoluble Gaseous Reaction Product and Determining its Pressure



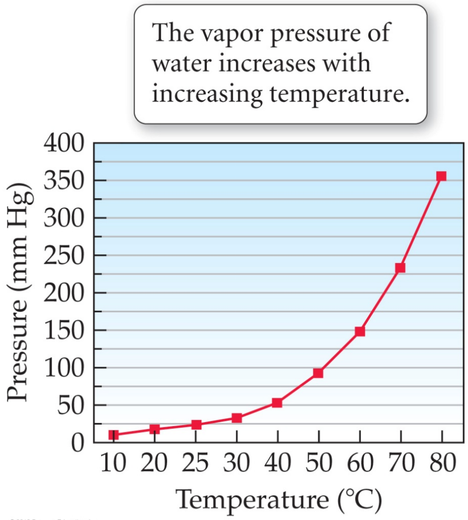


TABLE 11.4 Vapor Pressure of Water versus Temperature

Temperature (°C)	Pressure (mm Hg)
10 °C	9.2
20 °C	17.5
25 °C	23.8
30 °C	31.8
40 °C	55.3
50 °C	92.5
60 °C	149.4
70 °C	233.7
80 °C	355.1

Example

A sample of argon is collected over water at 25 °C. After collecting the gas, the height of the gas in the collecting tube is lowered to that of the water container. According to a barometer, the air pressure is 763 mm Hg. What is the pressure exerted by argon in atmospheres?