

LECTURE 14. STATES OF MATTER: AN INTRODUCTION TO THE IDEAL GAS LAW

Summary. Talk about a change of pace. After half a semester on the theoretical underpinnings for the chemical bond, we get decidedly practical and consider the simple idea that matter can be fairly simply categorized by whether it is a gas, liquid or solid. The next several lectures will explore the theories that give rise to the empirical observations we can make about matter in its various states. The most interesting thing is that we will find when we explore condensed matter (liquids and solids) that the concepts we developed in bonding can be applied to explain, and even predict, many of the properties that chemical compounds exhibit.

But first, we consider gases. We will find that the simple models that explain most of gas behavior are actually founded on the idea that gas molecules are all the same, and in fact that everything we learned about the chemical bond is irrelevant to the study of gases. Yes, gases are both boring and easy.

The first lecture on gases is an elementary introduction in two parts:

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|---------|---|---------------------|--------------------------|
| Part 1. | Nomenclature: A brief bit of history on the scientists who investigated gases and the words used to allow us to discuss the nature of gases in a more sophisticated manner. | | |
| Part 2. | Calculations: | $PV = nRT$ | static system ← Type 1 |
| | | $V_1/T_1 = V_2/T_2$ | change in state ← Type 2 |

The second lecture on gases develops somewhat more sophisticated ideas about gases.

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| Part 3: | Theory: Kinetic Molecular Theory (kmt) is used to derive ideal gas law $PV = nRT$ and to used to calculate gas velocity, diffusion, and effusion | | |
| Part 4: | Ideal vs Non- ideal gases: the idea that $PV = nRT$ ideally but that $PV \neq nRT$ in reality, because of gas attraction and size, which violate k.m.t. | | |

Useful variables for gases

In the lectures on thermodynamics we will learn a great deal about chemical systems: a chemical system is the environment in which our chemical species are found. It is characterized by variables, like pressure or volume, that are state functions.



Δ

 Some combination of _____ state functions is varied while others are held constant

Consider a system with the state functions P_1, V_1, T_1, n_1 are state functions; (there are many others in thermo). We will learn how to quantify the relationship between these state functions using the ideal gas law.

It will often be the case that we will perturb our system somehow to change the values of the state functions, P_2, V_2, T_2, n_2 , and that the change in these state functions, $\Delta P, \Delta V, \Delta T, \Delta n$, will be information that we want to know.

Let's get to know our state functions:

n is the moles of a gas. The amount of gas is most easily defined by the mole and can be related through stoichiometry and other unit factors to other system parameters like $n = g/MW$; $n = MV$; $\rho(\text{density}) = g/V$. Note that the moles of gas are typically much smaller in number because gas density is much smaller (about 1000 times less dense.)

V is the volume of the gas and has units like ml, l, gallons, ounces, etc. The volume is defined by the space in which gases travel. So it becomes very large in open environments.

P is the pressure of the gas with units like atm. It reflects number of times gas molecules hit the surface of the container.

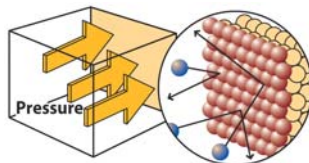


TABLE 4.1 Pressure Units

SI unit: pascal (Pa)
 $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2} = 1 \text{ N m}^{-2}$

Conventional units*

1 bar = $10^5 \text{ Pa} = 100 \text{ kPa}$
 1 atm = $1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa}$
 1 atm = 760 Torr
 1 atm = 14.7 lb in^{-2} (psia)

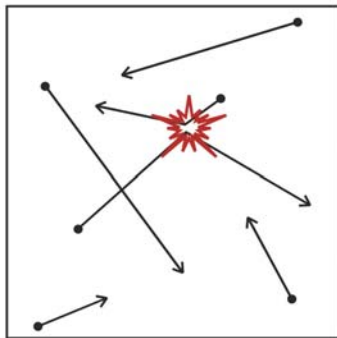
*Figures in boldface type are exact. See inside back cover for more relations, N, newton.

T is the temperature of the system and has units like K, ° C, ° F and is directly proportional to energy in the system.

Kinetic molecular theory (kmt)

Scientists sit around thinking really hard about a model for gases. They decide the following is a good way to think of them given that they seem to be rather boring chemically and are very low density*:

- gases are hard spheres
- gases are infinity small in volume
- gases have no attraction for each other or surface of system, therefore collisions are elastic



- the energy in a gas system is constant and is determined by temperature
Temp $\rightarrow T \propto E \leftarrow$ energy
- the velocity of gas particles is determined by $E = \frac{1}{2} mv^2$

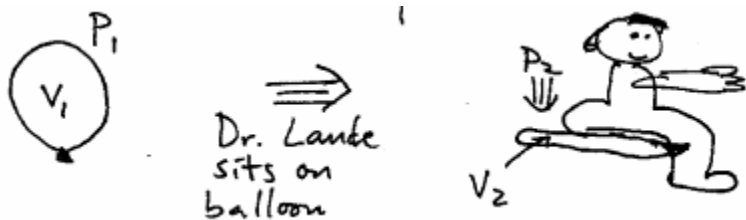
* these are “ideal” notions and are used to derive the ideal gas law.

Note that gas particles are all the same according to kmt regardless of type. For example, He is an infinitely small particle that undergoes elastic collisions. So are CO₂, N₂, or NH₃, or H₂O.

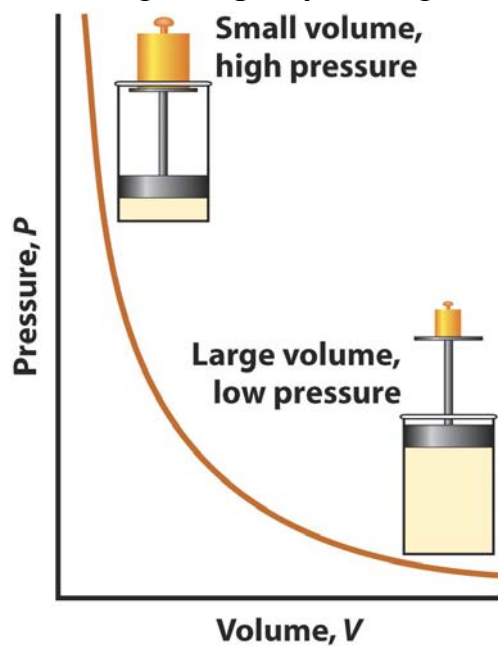
Famous experiments with gases

Boyle: Investigated the pressure- volume relationship and found an inverse relationship. P goes up \uparrow , V goes down \downarrow
Mathematically $P \propto 1/V$ inverse relationship or $P = k (1/V)$ as we create an equation with a constant, k .

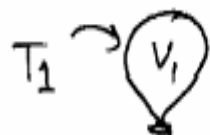
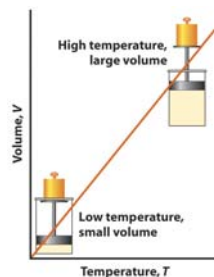
Thus when Dr. Laude sat on a balloon



he was repeating Boyle's experiments from centuries ago that showed:



Charles: Investigated the volume – temperature relationship and found a direct relationship. As T goes down, V goes down. Mathematically $V \propto T$ or $V = kT$



Avogadro: Investigated the mole- volume relationship. He discovered the extraordinary idea that the more moles of gas you have, the bigger the balloon.



Mathematically, n is directly proportional to volume $n \propto V$ or $n = kV$

Combining Three Laws Gives Us the Ideal Gas Law.

Using a little algebra to combine these three relationships and consolidating the 3 constants into 1, we have ideal gas equation

$$PV = nRT$$

where R is the ideal gas constant. Note the three experimental relationships are all present in this one equation. Also note this equation is true **only** under ideal conditions (kinetic molecular theory conditions)

TABLE 4.2 The Gas Constant, R

$8.20574 \times 10^{-2} \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.31447 \times 10^{-2} \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.31447 \text{ L}\cdot\text{kPa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.31447 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$62.364 \text{ L}\cdot\text{Torr}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

So what kinds of problems can we work:

Calculations for a Static System

For a system that is not perturbed, we can perform simple calculations with the ideal gas law equation, $P_1V_1 = n_1RT_1$. These are classic plug and chug calculations in which we typically hold 3 values constant and solve for a 4th that is unknown.

Example: What is the volume when 1 mole of ideal gas is held at 1 atm and 298K.

$$P = 1 \text{ atm}$$
$$N = 1 \text{ mole}$$

$$T = 298\text{K}$$
$$R = 0.08206 \text{ latm/ Kmole}$$

Rearrange and $V = nRT / R = (1) (.082) (298) / 1 \text{ atm} = 22.4 \text{ l}^{**}$

** this tells us that at standard (room) temp and pressure, an ideal gas fills 22.4 l of volume.

Hint. Two things to note for problems in which there is no change of state

1. You can find an R for any combination of units, but I will give one that you will use a lot. $R = .082 \text{ l atm/Kmol}$
2. The only trick is to convert all P,V, T and n values into units consistent with R. That is really the only complicating feature of this kind of problem. And usually the biggest hassle is turning an amount into in other units into moles, n.

Static system calculations in which we substitute for n

Isn't it great that in high school you learned all about how to convert different amounts into n using equations like:

$$n = g / \text{MW} \quad \text{or} \quad p = g / V \quad \text{or} \quad M = n/V$$

We can derive 3 new equations and can solve for MW, density and molarity.

$$\text{Derive 1: } PV = nRT \Rightarrow PV = (g / MW) (RT) \Rightarrow MW = gRT / PV$$

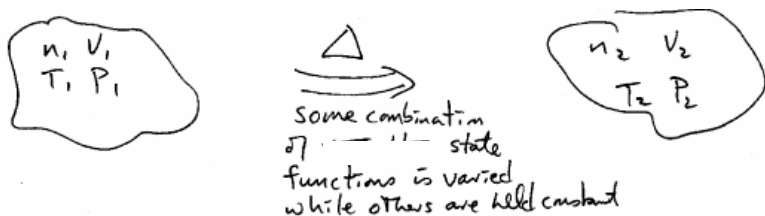
$$\text{Derive 2: } PV = nRT \Rightarrow P = n / v (RT) \Rightarrow P = MRT \Rightarrow M = P / RT$$

$$\text{Derive 3: } PV = nRT \Rightarrow PV = g / MW (RT) \Rightarrow P = (g/V) (RT / MW) \Rightarrow \rho = PMW / RT$$

Go ahead and derive these yourselves to recall how much you enjoyed algebra.

Calculations for a System That Undergoes a Change of State

Anytime that a problem suggests that conditions in the system have been changed because of a perturbation, whether you are changing P, V, T or n, you need to create an equation that combines the gas law equation for the two states and eliminate the constants.



Let's derive an equation for changing V and T

$$\text{State 1: } P_1 V_1 = n_1 R T_1 \Rightarrow V_1 / T_1 = n_1 R / P_1 = K \quad \text{State 2: } P_2 V_2 = n_2 R T_2 \Rightarrow V_2 / T_2 = n_2 R / P_2 = K$$

Because n and P didn't change the K is equal in states 1 and 2 so $V_1 / T_1 = V_2 / T_2$ and in the same way we can eliminate constants to derive the following combined equations.

$$P_1V_1 = P_2V_2 \quad \text{or} \quad V_1/n_1 = V_2/n_2 \quad \text{or} \quad P_1V_1/T_1 = P_2V_2/T_2$$

Sample gas law calculations

Example 1: Simple ideal gas law:

What is the pressure when 2.5 mole of H₂ is placed in a 200 ml container at 50°C?

- note there is no change in state. $PV = nRT$ assuming ideal gas.

- Rearranging, $P = nRT / V$ with

$n = 2.5$ moles

$T = 50$ °C → need to convert to 323 K

$V = 200$ ml → need to convert to 0.2 l

$R = 0.082$ latm/Kmol

- now solve. Note units cancel

$$P = (2.5 \text{ mole}) (0.082 \text{ latm / K mole}) 323 \text{ K} / 0.2 \text{ l} = 331 \text{ atm is the answer} \quad \leftarrow \quad \text{that is some pressure}$$

Example 2. Ideal gas law solving for MW:

0.87 g of a gas are placed in a 5 l container at -50 ° C and achieve a pressure of 76 torr. What is the MW?

- $PV = nRT \Rightarrow PV = g / MW (RT) \Rightarrow MW = gRT / PV$ ←eqn to use

- convert units 76 torr/ 760 torr = 0.1 atm, - 50 ° → 223 K

- solve $MW = (.87) (.082) (223) / (0.1) (5) \approx 32 \text{ g / mole}$

Example 3. Ideal gas law solving for density ($\rho = g/V$)

What is the density of CH₄ maintained at a pressure of 0.1 atm and temperature of 414 K?

Use: $PV = nRT \Rightarrow PV = g / MW (RT) \Rightarrow \rho = (g/V) (RT / MW) \Rightarrow PMW / RT = \rho$

- units are already correct (atm, K), CH₄ = 16 g / mole

- solve $P = (0.1 \text{ atm}) (16 \text{ g / mole}) / (.082 \text{ l atm / K mole}) (414 \text{ K}) = .47 \text{ g / l}$ (not very dense)

Example 4. Ideal gas law using STP:

What is the volume of C_3H_8 if 1 mole is maintained at STP.

- simple $PV = nRT \Rightarrow v = nRT / P$ ← equation to use
- STP = Standard Temperature Pressure at 1 atm and 273 K by definition
- solve $V = (1 \text{ mole})(.082 \text{ l atm/K mole})(273 \text{ K})/1 \text{ atm} = 22.4 \text{ l}$ (this famous volume is true for all ideal gases)

Example 5. Gas law problem involving change of state P, V

Dr. Laude fills a ballroom to a pressure of 1 atm and volume of 500 ml at 298 K. He then sits on it creating a new pressure of 5 atm. What is the new volume?

- identify what changes = P and V and what stays constant = n, T
- two states $P_1V_1 = nRT = K$ and $P_2V_2 = nRT = K$, but K is same for both states.
- $P_1V_1 = P_2V_2$ and now solve: $(1 \text{ atm})(500 \text{ ml}) = (5 \text{ atm}) X \text{ ml}$

- $X = \frac{1 \text{ atm} 500 \text{ ml}}{5 \text{ atm}} = 100 \text{ ml volume}$

Example 6. Gas Law problem involving change of state V, T

In a closed system at constant P and n, if the volume of the system is decreased by a factor of 10, the temperature:

- a.) goes up by a factor of 10
- b.) goes down by a factor of 10 ← correct
- c.) remains constant
- d.) none of the above

Explanation: $V_1 / T_1 = V_2 / T_2$ so if V goes from 10 l → 1 l then T decreases 10-fold.