

## Boyle-Charles law

Suppose you have a gas in a box. If you know some science, you may be familiar with the idea that everything is made out of molecules, which in turn are made out of atoms. For example, if the gas concerned is oxygen, there are oxygen molecules in the box, and each oxygen molecule is made out of two oxygen atoms. Moreover, these molecules don't stay and sit there. They move energetically. Something like the figures in our earlier article "What is entropy? From a microscopic point of view" In this article, we will explain the relation among  $P$ , the pressure of the gas,  $V$ , the volume of the gas, and  $T$  the temperature of the gas.

Now, let us explain what these three variables mean. If a gas is in a box, it exerts pressure on the box, as molecules bounce off on the inner surface of the box. Actually, pressure is force per area. For example, if you exert 3 N of force on the area with 2 m<sup>2</sup>. The pressure is 1.5 N/m<sup>2</sup>. Volume is something specified by the size of box. Temperature is related to how fast the molecules are moving. The faster molecules move, the more energy the molecules have, therefore, the hotter the gas. It is both customary and useful to use Kelvin for the unit of temperature. (We explained what Kelvin was in "What is entropy? From a macroscopic point of view?")

Now, let's say that you do not change the size of the box, but heat the gas to make it hotter. What will happen? As the gas molecules gain energy, they will move faster. Therefore, they will hit the inner surface of the box more frequently and strongly, which makes the pressure higher. In other words, the higher the temperature of the gas, the higher the pressure of the gas. It actually turns out that they are proportional to each other.

Now, let's say you do not change the temperature of the gas, but compress the gas. In other words, you decrease the volume. What will happen to the pressure? Since the average speed of the gas molecules do not change, they will hit the inner surface of the box just as strongly as before. However, they will hit it more frequently since they are confined to a smaller volume. Therefore, the pressure will be higher. In other words, the smaller the volume, the higher the pressure. It actually turns out that they are inversely proportional to each other. (We will explain why (i.e. quantitatively) in the next article.)

In terms of mathematics, our first condition says that  $P/T$  is constant when  $V$  is fixed. Likewise, our second condition says that  $PV$  is constant when  $T$  is fixed. These two relations imply that  $PV/T$  is constant. By the way, we know that the more the number of the gas molecules, which we call  $N$ , the bigger the volume they occupy. This suggests that  $V$  is proportional to  $N$ . This suggests that  $PV/T$  is proportional to  $N$ . If we call the

proportionality constant  $k$ , we have the following formula:

$$PV = NkT \tag{1}$$

This equation is called “Boyle-Charles law,” and  $k$  is called the Boltzmann constant. Actually, it turns out that this constant is independent of the kind of the gas chosen, which implies Avogadro’s law i.e., “equal volumes of all gases, at the same temperature and pressure, have the same number of molecules.” We will give some more motivations for this in the next article.

Historical remark. In 17th century, Irish scientist Boyle found Boyle’s law which says that  $PV$  is constant, when  $T$  is constant. French scientist Charles found Charles’s law which says that  $V/T$  is constant, when  $P$  is constant. These two results can be combined into Boyle-Charles law which I stated earlier. Instead of explaining Charles law to lead into Boyle-Charles law, I used the constancy of  $P/T$  which is called Gay-Lussac’s law, since it is easier to explain.

Finally, we would like to note that  $N$  in Boyle-Charles law tends to be very big in our everyday situation, because the molecules are very small. Therefore, chemists and physicists have a unit for the number of molecules. Approximately, they call  $6.02 \times 10^{23}$  number of molecules, 1 mole of molecules, and denote this number by  $N_A$  called “Avogadro’s number.” (You may wonder why they chose this particular value. Avogadro’s number is defined by the number of carbon-12 atoms in 12 grams of carbon-12. Carbon-12 is a certain type of carbon.) For example, instead of saying “there are  $6.02 \times 10^{24}$  hydrogen molecules in this box,” we say “there are 10 moles of hydrogen molecules in this box.” In other words, if we denote the moles of molecules by  $n$ , and the number of molecules by  $N$ , we have  $n = N/N_A$ . Plugging this into Boyle-Charles law, we obtain:

$$PV = n(N_A k)T \tag{2}$$

Now if we define the “gas constant” by  $R = N_A k$ , the above equation can be re-written as:

$$PV = nRT \tag{3}$$

This is known as the “ideal gas law.” As  $k$  is independent of the gas and  $N_A$  is a constant,  $R$  is a constant that is independent of the gas.

Final remark. (1) and (3) are good equations, but when pressure is high and temperature is low, the actual gas deviates from the ideal gas law. This is the reason why (3) is called the “ideal” gas law, and  $R$  is sometimes called the “ideal gas constant.” The actual gas is only approximately ideal. In his doctoral thesis in 1873, Dutch physicist Van der Waals proposed another equation that fits better than the ideal gas law, which led to Nobel Prize in Physics. It is given by

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT \tag{4}$$

where  $a$  and  $b$  differ from gas to gas. He derived this equation considering the size of molecules and the force between them.

**Problem 1.** An oxygen molecule is 16 times heavier than hydrogen molecule. If the box A contains 10.0 grams of oxygen with 300 Kelvin, how many grams of hydrogen does the same-sized box B contain if the hydrogen inside is also 300 Kelvin with the same pressure as the oxygen inside the box A?

**Problem 2.** Look at the Van der Waals equation (4). Show that when  $T/P$  is big, the Van der Waals equation becomes the ideal gas law. (Hint<sup>1</sup>)

## Summary

- If the volume is constant, the hotter the gas, the higher its pressure, as the gas molecules move faster.
- If the temperature is constant, the smaller the volume of the gas, the higher is pressure, as the gas molecules hit the container of the gas more frequently.
- $PV = NkT = nRT$ . Here  $P$  is the pressure,  $V$  is the volume,  $N$  is the number of molecules,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $n$  the mole number of the gas,  $R$  is the ideal gas constant.

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<sup>1</sup>Notice that when  $n^2a/V^2$  is negligible compared with  $P$  and  $nb$  is negligible compared with  $V$ , we have the ideal gas law.