2 Mechanics of Gases

A note on the states of matter: Physical chemists are very concerned with *states of matter*: gases, liquids, solids, etc.; are there more states there? Yes – think of the chicken soup (suspension) you are warming up on the gas flame (plasma) while checking your watch display (liquid crystal), or think of the peanut butter (emulsion)–jam (gel) sandwich you had this morning. You may think of the shaving cream (foam) or the cologne spray (aerosol) in your bathroom. You may think of what the inner parts of your body are made of or – why limit our horizon to little things only? – what did they say black holes are made of? As a matter of fact most of the world around us – including ourselves – is built of one of these "other" states of matter. Historically, physical chemistry has been developed with the three "pure" states – gas, liquid, solid – in mind and has only recently started making inroads into the intriguing and very complex world of the other states of matter.

Gases are simplest and have been studied most. You may think of your car: a flat tire (no air), the (noxious) exhaust gases, the anti-collision air bag (in the movies only, please). You may think of a balloon: a birthday balloon, a hot air balloon, or perhaps you just read about a meteorological balloon. Or you may think of what you do all the time: inhaling and exhaling, about ten times a minute (or longer – if you are waiting to exhale). We will do short examples of each.

Problem 2.1 | Mr. Bond's latest assignment (in Kazakhstan).

On a cold, $t = -3°F$, late winter day in Kazakhstan, Cyril Bond checks the pressure in the front left tire on his Aston Martin–Hyundai Accent (special edition) service car and finds that it reads only 17 pounds per square inch, psi. After consulting with Nurudin, a garage attendant, Cyril asks him to add more air, until the pressure gauge reads 2.3 kg/cm^2, or "atmosphere," atm (Nurudin is using a metric pressure gauge).

Question (A): What was the pressure in Mr. Bond's car tire, in psi, after he left the garage?

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Question (B): What will the pressure be in the tire at 118°F, when Mr. Bond hits the streets of Calcutta, India, on his next assignment, 6 weeks later? How much higher will this pressure be than the recommended, 30 psi? Carefully list all assumptions made. Show the unit conversions clearly.

Solution A – Strategy

This is a relatively simple problem made complicated through use of different units. Although most of the world today uses metric system of units the mass, size, and volume of certain objects used or mentioned everyday are expressed in non-metric, historically based common units. We still hear or read about the price of a barrel of crude oil; the repairman we hired needs a two-by-four inches board, and we go to a grocery store to buy a dozen eggs, not to mention time, which has resisted all attempts of conversion to the base-10 system. Sciences have not been spared this diversity; we are still consuming (and burning) calories, measuring very small distances in Ångstroms, or comparing atomic energies in electronvolts. The use of different units is an annoying feature in physical chemistry but it is something you have to learn to live with; it is perhaps a little bit like foreign words you learn to use along with your native tongue.

Let us remind ourselves what is pressure: a force, F, applied at a certain spot or area, A:

$$p = F/A \tag{2-1}$$

The larger the force, F, the larger the pressure. We say that pressure is *directly proportional* to the applied force. On the other hand, the smaller the area, the smaller the number that divides the force, and pressure will be larger. We say that the pressure and area are *inversely proportional*.

A note on intensive and extensive properties: Many things we are surrounded with can be added or subtracted: money, apples, liters of gas. Mass, distance, volume, and time can accumulate and this is how we label them: *cumulative properties*. We can also use the words extrinsic or extensive for these properties. Pressure, on the other hand, depends on two quantities, two properties: force and area. We say that pressure is a *composite* property. For this reason we cannot add, subtract, or multiply two pressures. There are other properties that cannot be added, subtracted, and multiplied with each other and we have a common name for them: *intensive properties*. Other words with the same meaning as intensive are intrinsic or specific.

Make a note: *cumulative* and *intensive* properties.

Calculation A

In the garage in Kazakhstan, $p = 2.3$ atm, or $p = 2.3$ kg/cm^2. Convert kilograms to pounds and square centimeters to square inches and you will have the first answer:

$$p = (2.3\,[\text{kg}] \times 2.2\,[\text{lb/kg}])/(1[\text{cm}^2] \times 0.155\,[\text{inch}^2/\text{cm}^2]) = 32.6 \approx 33\,\text{lb/inch}^2$$

The answer to the question (A) is 33 psi, within about 1% error.

Solution B – Strategy

Now this is a trickier problem and you will have to consult a physical chemistry textbook, under the chapter on "Ideal Gases." There is a good and useful formula for gases, most of which behave like *ideal gases*:

Pressure × volume = # moles × gas constant × temperature

When translated into physical chemical symbols, this expression reads

$$pV = nRT \tag{2-2}$$

You can use this formula to calculate many properties of gases and find answers to many questions in physical chemistry, as well as in everyday life. You should first figure out which of the properties in the gas equation changes and which remains constant. "R" – is the so-called gas constant; nothing to change there, you only have to be careful about the units you use for R. "n" – is the amount of the gas, given in *moles*, which you have to figure out from the liters, kilograms, or ounces of gas. (By the way, converting all amounts to moles is a very good way to go about chemical calculations.) Unless there is a chemical reaction involved the number of moles usually does not change through a problem. This leaves p, V, and T and they do depend on each other and are subject to change. For one temperature we will have one pressure and one volume, for a different temperature different pressure and volume. So you may write

At −3°F (winter in Kazakhstan): $p_1V_1 = n_1RT_1$
At +118°F (spring in Calcutta): $p_2V_2 = n_2RT_2$

Now we have to make a couple of *assumptions*:

- First, we assume that the tire does not leak air.
- Second, we assume that volume of the air in the tire does not change.

The first assumption is quite sound: if the tire is in good condition it should not leak for weeks and months. This is telling us that the amount (i.e., the number of moles) of air in the tire during the winter days in Kazakhstan, n_1, is the same as the amount of air during a hot spring day in Calcutta, n_2. When you translate this statement into a formula you will write $n_1 = n_2$, or just n, the number of moles.

The second assumption, that the volume of the tire is the same at $-3°$F and at +115°F, is a little less sound. If you want better information you should consult an expert or a reliable source on car tires. I would say – mainly from experience – that the volume changes a little but not so much that we should worry about it in this problem. We may check this issue later but for the moment let us assume that $V_1 \approx V_2$, or just V, the volume.

Calculation B

Let us re-write the previous two equations using n and V:

$$p_1 V = nRT_1 \tag{A}$$

$$p_2 V = nRT_2 \tag{B}$$

Now you may go back and read the second part of the problem again. The question is What is the pressure going to be in the tire while in Calcutta, at 118°F? Another way to ask the question is What is p_2 going to be? Let us try to solve the problem. You should make two lists: (a) a list of the things you know (or can find out) and (b) a list of the things you do not know but have to figure out.

(a) p_1, T_1, and T_2
(b) p_2

I suggest you also make a third list: (c) a list of things you don't need to know. This may turn out to be an important list.

(c) n, V, and R

The value of R, the gas constant, you can find easily. This leaves us with n, the number of moles of gas in the tire, and V, the volume of the air in the tire. Nobody is really asking you about either n or V and you should try to get them out of the way.

You can do this by applying *little big trick* #1: divide two equations and cancel the same terms. You should divide the left side of (A) with the left side of (B) and then divide the right side of (A) with the right side of (B):

$$p_1 \times V/p_2 \times V = n \times R \times T_1/n \times R \times T_2$$

Now cancel the same quantities above and below the dividing line; this will leave you with a simplified equation:

$$p_1/p_2 = T_1/T_2$$

You need p_2 so you will re-arrange the equation (that is, first turn it upside down and then move p_1 to the other side of the = sign):

$$p_2 = p_1 \times (T_2/T_1)$$

Insert the numbers for p_1, T_1, and T_2. But – be careful! You will have to convert the temperatures given in degrees Fahrenheit to the physical chemical temperature scale, given in degrees Kelvin, K. Consult a textbook and you will find the following conversion: T [K] = (t [F] − 32/1.8) + 273.2. Pretty complicated, isn't it? So punch few keys on your calculator and you will get for the temperature in Kazakhstan, T_1, and Calcutta, T_2:

$$T_1 = (-3 - 32)/1.8 + 273.2 = 253.7\,\mathrm{K}$$

$$T_2 = (118 - 32)/1.8 + 273.2 = 320.9\,\mathrm{K}$$

The pressure p_2 now reads

$$p_2 = 2.3\,\mathrm{kg\,cm^{-2}} \times 320.9\,\mathrm{K}/253.7\,\mathrm{K} = 2.9\,\mathrm{kg\,cm^{-2}}$$

Question (B) was the following: what is the pressure reading in psi? You will have to convert 2.9 kg m^{-2} to pounds per square inch in the same way you did it in part (A) of this riddle:

$$p_2[\mathrm{psi}] = (2.9\,\mathrm{kg} \times 2.2\,[\mathrm{lb/kg}])/(\mathrm{cm}^2 \times 0.155\,[\mathrm{inch}^2/\mathrm{cm}^2]) = 41.3\,[\mathrm{psi}]$$

And how much higher this is than 30 psi — the recommended pressure in car tires? This is straightforward: subtract 30 from 41.3 and you get 11.3 psi. A whole eleven point three pounds per square inch! This is a seriously overinflated tire. Careful, Mr. Bond!

A comment: I suggest we take a little break now – this was a lot of work. Afterward, we can look at other problems involving gases and a question about hot air ballooning which is both entertaining and useful. Hot air balloons do look beautiful and if you have taken a ride in one – and come down safely – you know what I mean.

Problem 2.2 | Three men in a balloon (to say nothing of the dog).

It is a late fall, slightly chilly morning, $t = 10.0°\mathrm{C}$. Three men and a dog drive a couple of miles until they reach an empty farmland area where a large balloon is anchored. They climb into a sturdy wicker gondola equipped with propane cylinders and a twin gas burner, all attached to a large spherical balloon, and decide to take a flight. They slide their aviator goggles and put leather gloves on, ignite the burners, and get ready for a liftoff (no goggles for the dog). The passengers, dog, basket, ropes, burners, gas cylinders, and the nylon–Nomex® envelope of the balloon weigh 678 kg. (Typical weight of a mid-size balloon, a basket with –three to five passengers, a twin burner, and –two to four gas cylinders is 650–750 kg [1].)

As the air inside the balloon becomes warmer it becomes less dense and when its buoyancy exceeds the net weight of the balloon and the cargo, the balloon will take off. Given that the fully inflated balloon is a nearly perfect sphere of 9.0 m radius what should be the average temperature of the air inside the balloon [°C] needed for a liftoff? Keep in mind that the balloon is open and the pressure of the air inside the balloon equals the pressure of the air outside the balloon.

Solution – Strategy

The hot air balloons are based on the principle of buoyancy. For example, a wooden spoon set free in the air falls down because its buoyancy is smaller than its mass (weight). In water, it is the opposite case: the buoyancy is larger and the spoon floats. In hot air balloons the medium is always the same – air. We only change its density by changing its temperature. When the density of the air inside the balloon equals the density of the air outside, its buoyancy is zero and its net mass – 678 kg in this case – will prevent it from taking off. We have to make the air inside the balloon less dense by heating it up, e.g., using propane burners.

Solution – Calculation

Assume that the balloon is filled with the air at 10°C and calculate the volume of the balloon. The balloon is assumed to be spherical so find the formula for volume of a sphere and insert the value for radius, $r = 9.0$ [m]:

$$V = 4 \times \pi \times 9.0^3\,[\mathrm{m}^3]/3 = 3{,}054.6\,\mathrm{m}^3 = 3.055 \times 10^3\,\mathrm{m}^3$$

This is the *volume* of the balloon – three thousand and fifty cubic meters. What you need to know is how many *moles* of air there are in 3,055 m^3. You will get this by reshuffling the $pV = nRT$ equation in the following way: $n = RT/pV$. But first you have to convert the temperature to the thermodynamic scale, [K], by adding 273.2 to the temperature in degrees Celsius (or centigrades): $T = 10.0 + 273.2 = 283.2$ K. Now you can calculate n:

$$n_1 = 101{,}325\,[\mathrm{N\,m}^{-2}] \times 3.055 \times 10^3\,[\mathrm{m}^3]/8.314\,[\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}] \\ \times 283.2\,[\mathrm{K}] = 1.315 \times 10^5\,\mathrm{mol}$$

Multiply the number of moles of air by its molar mass and you will have the mass of all air inside the balloon:

$$m_1\,(\text{cold air}) = 1.315 \times 10^5\,[\mathrm{mol}] \times 0.029\,\mathrm{kg\,mol}^{-1} = 3{,}813.5 = 3{,}814\,\mathrm{kg}$$

We used the following value for the molar mass of air: $m_m(\text{air}) = 28.97\ \text{g mol}^{-1} = 0.029\ \text{kg mol}^{-1}$. This is an *average* molar mass for the mixture of 79% of N_2, 20% of O_2, 1% of Ar, and a wisp of other gases.

What should we do now?

The mass of the cold air, $T_1 = 10°\text{C} = 283.2\ \text{K}$, inside the balloon is 3,814 kg. Since the balloon is surrounded by the air of same temperature and density, the *buoyancy* of the air inside the balloon is *zero* and, given only the air, the balloon could move left or right, but not lift. But what keeps it grounded is the 678 kg of the cargo mass. The balloon, with the basket and passengers, will be able to start lifting off when the buoyancy of the air inside the balloon equals the cargo mass, $m_0 = 678$ kg. Let us call this the second mass, m_2:

$$m_2 = 3{,}814 - 678 = 3{,}136\ \text{kg}$$

How do you make the air inside the balloon weigh 3,136 kg instead of 3,814 kg? Simple – you heat it up! When the temperature of a gas increases, its density, therefore its total mass – *decreases* (assuming the pressure stays the same; this is also known as Charles' law). So the question you have to answer is, At what temperature the density of the air inside the balloon will decrease so much that its mass is 3,136 kg or less. You will use the $pV = nRT$ equation to find this temperature, let us call it T_2. But as you can tell there is no place for the mass of air in the gas equation; you need the number of moles. Let us call it n_2:

$$n_2 = 3{,}136\ \text{kg}/0.029\ \text{kg mol}^{-1} = 1.081 \times 10^5\ \text{mol}$$

So n_2 is the number of moles of the hot air inside the balloon; you may insert this number in the gas equation. You also know the pressure and volume of the hot air balloon – it is unchanged: p_2 at temperature T_2 is the same as p_1 at temperature T_1. The same for volume; we just drop the indices and use p and V. Now you know everything you need to know to calculate the temperature T_2:

$$T_2 = pV/n_2R$$

Insert the number of moles, n_2, and calculate the temperature, T_2:

$$\begin{aligned} T_2 = {} & 101{,}325\ [\text{N m}^{-2}] \times 3.055 \times 10^3\ [\text{m}^3]/1.081 \times 10^5\ [\text{mol}] \\ & \times 8.314\ [\text{J K}^{-1}\ \text{mol}^{-1}] = 344.4\ \text{K} \end{aligned}$$

When you convert this back to degrees Celsius you will see the air inside the balloon gets fairly warm:

$$T_2 = (344.4 - 273.2) = 71.2°\text{C}$$

Now that was quite a workout, wasn't it? Let us take a break before we go on to the next question.

Problem 2.3 Hot air ballooning, a sequel.

Understanding how hot air balloons float helps you understand how a human body, with lungs filled with air, floats in water. I suggest you practice a little more by changing the conditions in the previous riddle and solving it by yourself. Let us assume it is a spring day with the air temperature (outside and inside the balloon) 20.0°C and the same group of ballooners getting ready to take off. They want a speedy takeoff and are going to make the air inside the balloon have the buoyancy equal to the cargo mass, 678 kg, plus another 10%. (So m_2 will be equal to $m_1 - 678 \times 1.1$ kg.) How hot will the air inside the balloon have to be?

Answer: $\mathbf{T_2} \approx 87°C$

Problem 2.4 Waiting to exhale.

The partial pressure of oxygen in the inhaled air, pO_2 (in) $=$ 159 mmHg, and in the exhaled air, pO_2 (ex) $=$ 116 mmHg. Assuming that the air pressure, p (air) is 760 mmHg, calculate how many grams of O_2 are transferred from the atmosphere to our alveoli each minute of normal breathing (10 inhalations at 2.0 L each).

Solution – Strategy

We will of course start with the $pV = nRT$ equation and use it to calculate the number of moles of O_2 during the inhalation and then the number of moles of exhaled oxygen, subtract the two values and the difference will give us the answer. However, there are more "things" in this problem and we will have to solve them one by one. Let us first calculate the number of inhaled and exhaled moles of O_2.

Solution – Calculation

Let us write the gas equation for inhalation and express it for n, the number of moles:

$$p_1 V_1 = n_1 R T_1 \qquad n_1 = p_1 V_1 / R T_1$$

You may now insert the numbers for p_1, V_1, and T_1, find the value for R, and calculate n_1. Or you may use a little shortcut. Let me explain what I have in mind. At room temperature and the pressure of 760 mmHg (which equals 101,325 Pa) a mole of gas, any *ideal-like* gas, has a volume of 24.79 L; in physical chemistry textbooks this volume, derived from the so-called Avogadro's law, is known as the volume of one mole of gas at normal temperature and pressure, NTP (which is slightly different from the standard temperature and pressure, STP – but we shall not bother with the little physical chemistry obfuscations). Let us call this quantity n (1 mol) and write

$$n(1\,\mathrm{mol}) = 24.79\,\mathrm{L\,mol^{-1}}$$

The riddle says that each minute we inhale (on average) ten times and each time the volume of the inhaled air is 2 L which makes 10 × 2 L = 20 L. So $V_1 = 20$ L. Well, if one mole of gas takes 24.79 L then there is obviously less than one mole of gas in 20 L of air. How much less? Divide the smaller number by the bigger number and you will get

$$n_1 = 20.0\,\mathrm{L}/24.79\,[\mathrm{L\,mol^{-1}}] = 0.8068 = 0.807\,\mathrm{mol}$$

Lest we forgot, these are the moles of air; what we need are the moles of O_2.

More strategy

Now we have to look at air as a *mixture of gases*. Indeed, there is nitrogen, oxygen, argon, water vapor, and other gases and vapors in the air. Each of these is a part, a *fraction* of the total. How big a fraction? If all of the air were just O_2 then the fraction of O_2 would be 100%/100% = 1. But you know it is less than that; you are given the numbers which tell you what is the fraction of O_2 in the air. Check a textbook and find the *Dalton law* of partial pressures. It says that the total pressure is a sum of partial pressures:

$$p_{\mathrm{tot}} = p_1 + p_2 + p_3 + \cdots \tag{2-3}$$

In the case of inhaled and exhaled air this will be given by the following expression:

$$p_{\mathrm{tot}} = p(\mathrm{O_2}) + p(\mathrm{N_2}) + p(\mathrm{Ar}) + p(\mathrm{CO_2}) + p(\mathrm{H_2O}) + \cdots$$

How do we know partial pressures? The partial pressure of O_2 (an ideal-like gas), in a mixture with other ideal-like gases, is the same as the number of moles of O_2 divided by the number of moles of all gases in the mixture. We call this ratio a *molar fraction* and label it by x: $x(\mathrm{O_2}) = n(\mathrm{O_2})/n_{\mathrm{tot}}$. Another way to find molar fraction of, for example, O_2, is by dividing its partial pressure by the total pressure:

$$x(\mathrm{O_2}) = \text{partial pressure}\,(O_2)/\text{total pressure of all gases in the air}$$

More calculation

Go back to the problem and read off these numbers, $p(\mathrm{O_2}) = 159$ mmHg and $p(\mathrm{air}) = 760$ mmHg. You can now go and convert the pressures in mmHg into Pa or, since both units are the same, divide the two numbers and cancel the units; molar fractions have no units.

$$x(O_2) = 159\,\text{mmHg}/760\,\text{mmHg} = 0.209$$

So 0.209th part or 20.9% of air is dioxygen, O_2. Given that each minute you inhale 20 L or 0.807 mol of air (as we calculated above) the number of moles of O_2 will be 0.209th part of it:

$$n(O_2,\ \text{in}) = 0.209 \times 0.807\,\text{mol} = 0.1688 = 0.169\,\text{mol}$$

What now? Do the same calculation for the exhaled air:

$$n(O_2,\ \text{ex}) = (116\,\text{mmHg}/760\,\text{mmHg}) \times 0.807\,\text{mol} = 0.153 \times 0.807\,\text{mol} = 0.123\,\text{mol}$$

So in 1 min you inhale 0.17 mol O_2 and exhale 0.12 mol O_2; clearly, the difference is what is "left" in the lungs and transferred to the bloodstream – via the protein molecules called hemoglobin, HbA – and passed to the cells in our body. (The cells, of course, use O_2 to burn the nutrients and return the CO_2 gas.) The difference in the moles of dioxygen, Δn, is given as

$$\Delta n(O_2) = 0.169 - 0.123 = 0.046\,\text{mol}$$

The number of moles, multiplied by the molecular mass of O_2, will give you the mass of dioxygen in grams:

$$m(O_2) = \Delta n[\text{mol}] \times 32.00[\text{g mol}^{-1}] = 1.472\,\text{g}$$

Not much, don't you think so?

A note on gas equations: The $pV = nRT$ is a good equation and will take you a long way with gases like helium at room or at higher temperatures and normal or lower pressures. However, with industrial gases like propane, C_3H_8, or sulfur hexafluoride, SF_6, at high pressures and low temperatures the interaction between the gas molecules becomes significant. Also, at higher pressures and lower temperatures the volume of the (very tiny but also numerous) gas molecules becomes non-negligible. These two effects – the molecule–molecule interaction and the cumulative volume of all molecules – are not accounted for in the ideal gas equation and the $pV = nRT$ relation becomes less and less adequate (e.g., negative pressures and other non-physical results are obtained). For these cases gas equations "corrected" by second- and higher-order terms are used, like the van der Waals or Dieterici equations. This, however, is more a matter of technical thermodynamics.

Reference

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