The strange behaviour of carbon dioxide in rubber balloons
El comportamiento extraño del dióxido de carbono en los globos

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Abstract

When comparing the behaviour of gases such as air, hydrogen and carbon dioxide there is a definite expectation that hydrogen will diffuse most quickly and carbon dioxide most slowly when the conditions are the same for all three gases. Indeed many science teachers and students refuse to believe that carbon dioxide can escape from a high quality latex balloon faster than air or even hydrogen – even when it happens in their laboratory. The experiment described below was set up by the author to try to convince colleagues that the behaviour of carbon dioxide is indeed anomalous – and the results exceeded even his expectations.

Key words: *carbon dioxide, rubber balloons, gaseous diffusion.*

Resumen

Al comparar el comportamiento de los gases, como aire, hidrógeno y dióxido de carbono no es una expectativa definida que el hidrógeno se difundirá más rápidamente y el dióxido de carbono más lentamente cuando las condiciones son las mismas para los tres gases. De hecho, muchos profesores de ciencias y los estudiantes se niegan a creer que el dióxido de carbono puede escapar de un globo de látex de alta calidad más rápido que el aire o incluso de hidrógeno - incluso cuando sucede en su laboratorio. El experimento descrito a continuación fue creado para tratar de convencer a los colegas que el comportamiento del dióxido de carbono es de hecho anómalo - y los resultados superaron incluso, sus expectativas.

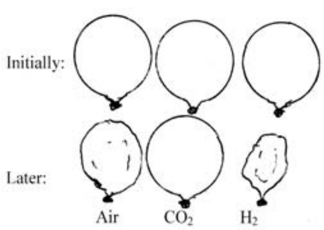
Palabras clave*: dióxido de carbono, globos de caucho, difusión de gases*

INTRODUCTION

The results of the main experiment described in this paper were first presented at the 2nd International Conference on Science Education held in Iguacu Falls, Brazil in August 2014. I also mentioned my excitement about this learning in an editorial to this Journal (JSE No1 Vol 16). A version of this paper describing the strange behaviour of carbon dioxide in balloons was recently published in the UK in the '*School Science Review'* (Goodwin 2015). Please let me know if there are any aspects of this experiment that surprised you and whether the experience is likely to useful for you professionally.

Shortly after I began teaching in a secondary school, a science teaching scheme for use in the lower school (now termed KS3 in the UK) was published and called 'Science for the 70s' (Mee, Boyd and Ritchie, 1971). Access to this scheme seems now to be problematic so I have provided a summary of the suggested demonstration in the box below

Box 1: Experiment 4.2 (From 'Science for the 70s Mee *et al* 1971 – p50.) This suggested that three balloons should be filled, to as far as possible the same size, one with each of the following three gases: air, carbon dioxide and hydrogen. These were tied securely so the gas could not escape and then left undisturbed for a day or two. A diagram of the expected results is given below.



In the 1970s my students and I had considerable problems with this demonstration since the carbon dioxide balloon invariably shrank most quickly! Clearly, the aim of the experiment was to provide some evidence that may support the idea that matter consists of very small particles in motion since a suggestion (Mee *et al.* 1971 p50) reads. *"Suppose the balloons were really acting like sieves with very tiny holes so small that you cannot see them or detect them in the ordinary way, and suppose that the gases were made of tiny particles which could get through the holes; this would give us a reasonable explanation of what has happened."* Presumably the expected observations would also suggest that the particles of carbon dioxide are larger and/or move more slowly than those of air or hydrogen. Subsequently we learned that although the 'sieve' model for the escape of air and hydrogen from balloons works fairly well, in the case of carbon dioxide, it is the solubility of the gas in the latex rubber of the balloon skin that allows the unexpectedly high rate of escape from the balloon. (I am not able to recall the source of this information.)

Recently, a set of circumstances led me to revisit this anomaly and to devise an experiment to compare the properties of these three gases in helium quality latex balloons that has close parallels with the one from over 40 years ago.

The balloons and the 500 mL flasks to which they were attached (Figure 1) were filled with hydrogen, carbon dioxide and air. They were then then left undisturbed for a number of days and photographed at intervals.

Figure 1: The three flasks with their balloons – just before the start. The liquids in two of the flasks are those remaining after the preparation of the gases. (See text.)

The sequence of photographs shown in Figure 2 shows the progression of the experiment during the first 24 hours. The only intervention was after 17 hours, when the blue balloon that had collapsed over the mouth of the flask, was adjusted so that it was able to invert *into* the flask.

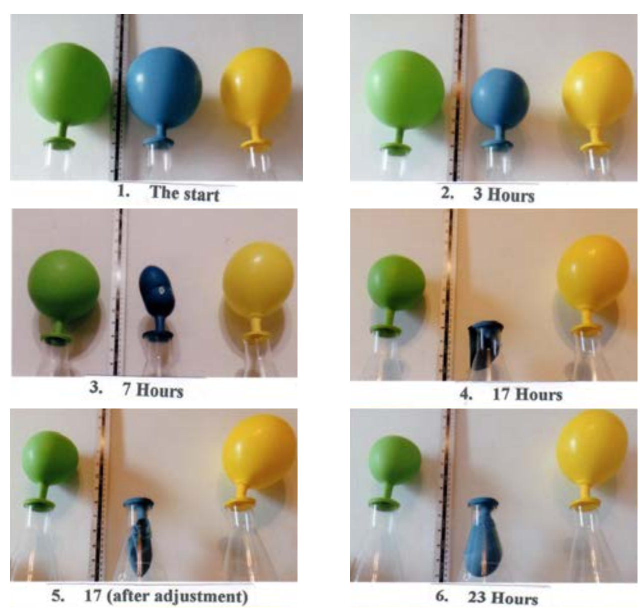


Figure 2: The three flasks during the first 23 hours of the experiment

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It is clear that the carbon dioxide that was in the blue balloon flask escapes most rapidly through the balloon into the air. It is also clear that the green balloon containing hydrogen is deflating faster than the yellow one containing air.

The pressure of carbon dioxide in the atmosphere is very low thus molecules of this gas escaping from the balloon will tend to diffuse away. However, although I fully expected the carbon dioxide balloon to deflate fastest I was impressed that this balloon turned inside out and went so far into the flask. Indeed Figure 3, below shows the carbon dioxide balloon as it was after 72 hours. It is clear that most of the gas from within the flask and the balloon has escaped and left a partial vacuum in the system. (See Note 1 at the end)

Figure 3 : The carbon dioxide balloon after 72 hours.

Setting up the balloons: A 500mL flask was first filled with carbon dioxide by adding hydrochloric acid to a large excess of sodium carbonate solution in the flask. Some more acid was then added to the flask and an 'empty' helium quality balloon immediately fitted over the mouth of the flask. When the flask was swirled gently the additional carbon dioxide inflated the balloon until it was about 20cm in diameter. (Should the balloon get too large, some gas can easily be released by carefully lifting a small section of rubber at the neck of the flask.) The experiments were run in parallel using similar flasks and balloons filled with air and hydrogen. For the former a balloon was inflated using a simple 'party balloon pump', fixed over the mouth of an empty flask and the size adjusted to be close as possible to that of the first balloon. For the latter about 30g of granulated zinc were placed in a flask and covered with water, about 20mL of concentrated hydrochloric acid were added when the reaction had had time to displace some of the air from the flask, an empty balloon fixed to the mouth of the flask – once the reaction has stopped the balloon size was adjusted to be the same as the other two. (Since hydrogen is much less dense than air it does not displace the air efficiently by this process.) All three flasks with their balloons attached were then left undisturbed in a well ventilated room and observed regularly over a period of about three days.

An issue for science teachers: The collection of gases in balloons is a fairly common procedure often used in investigations to estimate roughly the volume of gas produced. The mouth of the balloon is simply stretched over the neck of the reaction-flask to provide a gas-tight seal and the volume of gas formed can be estimated from the size of the balloon (An example of this set-up is detailed on a University of Michigan website given at the end of this article.) This method is often used in school science investigations on the fermentation of sugar solutions by yeast and the volume of carbon dioxide gas collected used as a measure of the amount of reaction that has taken place. If an experiment is short term (Less than a couple of hours) carbon dioxide produced will initially tend to lie towards the bottom of the flask and displace air into the balloon and thus an increase in volume should be measured fairly faithfully by the inflation of the balloon. The balloon will continue to inflate as long as carbon dioxide is being produced faster than it escapes through the balloon. With time however, the carbon dioxide will diffuse into the balloon and will then escape into the air. When left for some hours after the evolution of gas has ceased the balloon collapses entirely. However, since the reaction flask is initially full of air there should be little chance of the balloon entering the flask unless there was a substantial delay in putting the balloon over the neck of the flask and carbon dioxide from the reaction displaced some of the air.

The experiment described in this article was stimulated by an internet discussion started by an American science teacher who had been carrying out the fermentation experiment in school. The teacher reported that the experiment had been left for a few days after which a balloon had been sucked back into the flask. Discussion ranged from the possibility of weird chemicals being produced during late stages of fermentation to the cooling of warm solutions. I suggested that the cause might have been due to the escape of carbon dioxide through the skin of the balloon because of its solubility in rubber. No one participating in the discussion seemed to be convinced ("Carbon dioxide MUST diffuse out more slowly than air!" seemed to be an undisputed expectation) I decided to use the set-up – as in the experiment described – to see what happened when the balloon on the flask contained only carbon dioxide, with no possibility of any more complex organic ingredients! I was *amazed* by the effectiveness of this demonstration.

DISCUSSION

It is clear the carbon dioxide escapes from its balloon much more rapidly than either air or even hydrogen. This seems to go against the basic understandings of chemists since we are accustomed to organising our thoughts and expectations in line with the Simple Kinetic Theory of Gases (See 'Diffusion, Graham's Law and Osmosis' in Box 2 below). Certainly when trials of the experiment in 'Science for the 70's' were conducted, I think that the anomalous behaviour of the carbon dioxide balloon could not fail to have been noticed by the science teachers involved. Apparently, however the problem was not reported, presumably because the teachers 'blamed the balloon' and felt that 'the experiment would have worked if there had not been a faulty balloon'. I wonder how they got around their expectations with their students. Perhaps they re-inflated the balloon just before their students arrived for the class?

As mentioned above, it is because of the fairly high solubility of carbon dioxide in rubber the gas can pass through the 'skin' of the balloon without the need for pores or holes. (It is still not absolutely clear whether the hydrogen and air molecules actually pass through small holes in the rubber or whether their escape is via a solubility mechanism, both are significantly less soluble – almost insoluble – in rubber than is carbon dioxide. Perhaps both mechanisms operate together?)

Soap bubbles behave similarly to balloons (See Experiment 17 at 'Demonstration Experiments' web-site.) In this case when bubbles of air are floated on a layer of carbon dioxide in an open container the gas enters the bubble much faster than air can escape from it so the bubble swells 'by osmosis'.

Box 2: Diffusion, Graham's Law and Osmosis. Diffusion is the spontaneous random movement of molecules that tends to even out their concentration within the space available. (i.e. net movement occurs from volumes of higher concentration to those of lower.) Thomas Graham in the nineteenth century determined that the rates at which gases escape from a container through a small hole (effusion) or a porous barrier (lots of small holes) under fixed conditions of T & P are inversely proportional to the square root of their molecular mass (cf. Atkins and Jones (1998 p 167)). This can also be derived from the Simple Kinetic Theory (cf. Moore 1957 p166-9, or almost any physical chemistry text beyond A-level.). It is important to realise that it does pertain to escape of gases through barriers with small holes and does not allow for any interactions between the barrier and the molecules effusing/diffusing through it. Presumably, the fact that there are relatively strong Van de Waal's forces between CO_2 molecules and between the poly-isoprene chains in rubber facilitates an interaction between the gas and the rubber membrane and allows penetration by the gas.

When two different gases or solutions are separated by a porous barrier, potentially all the molecules present will eventually become equally distributed. However, if the barrier is impervious to the molecules of one of the substances present (perhaps because they are too large to pass through the pores) then the barrier is 'semi-permeable'. When, say, an aqueous solution is separated from water by a membrane/barrier that is permeable only to water then water molecules will tend to diffuse into the solution (This is less concentrated with respect to water). This movement of water into the solution is the cause of 'osmotic pressure' (the pressure that needs to be applied to the *solution* to increase the flow of water from the solution until it is equal to the rate of flow inwards, so that there is no net change.)

(See Note 2, at the end, for another example of anomalous behaviour of carbon dioxide.)

APPLICATIONS

The permeability of gases through membranes is of considerable interest in biology (breathing, gas exchange and respiration) and also has substantial commercial interest. The web-site given below (Versaperm) is of a company that specialises in permeability testing – mainly concerned with preventing the escape of carbon dioxide from plastic containers used to contain carbonated drinks. Since we are now becoming greatly concerned about minimising the amounts of carbon dioxide entering the atmosphere due to the combustion of fossil fuels and other industrial processes (e.g. cement manufacture.), it may be that membranes semi-permeable to carbon dioxide will be important in providing a relatively economical – low-tech – method for separating some of the carbon dioxide from an effluent stream. Presumably, latex rubber would not be sufficiently stable or strong to fulfil this purpose itself and silicone rubbers may be more useful. In a fairly recent review of materials useable for 'capturing' carbon dioxide (D'Alesandro, 2010) a section on membranes is included but there is no specific mention of the use of natural rubbers. The use of membranes for separating carbon dioxide from mixtures with many other gases requires less energy input than other methods although it can be slower and membranes tend to clog with dust particles. A general review of Carbon Capture and Storage/Sequestration (CCS) or Usage (CCU) can be found in Wikipedia.

CONCLUSIONS

This very simple experiment has surprised the author in its effectiveness in demonstrating the speed with which carbon dioxide can escape through a rubber barrier. At the very least this explains why there are often warnings on carbon dioxide cylinders NOT to use the gas to inflate car and cycle tyres or inflatable boats. (Given a reasonable length of time the pressure inside could well be lower than if the tyre had a large hole in it!) It also raises issues relating to our honesty as observers in science classrooms. When our experiments do not meet our theoretical expectations perhaps we should be less ready to blame our equipment?

It provides a valuable insight into the nature and action of semi-permeable membranes and hopefully exemplifies the process of osmosis to be one of diffusion of one type of molecule into another when the barrier allows one type of molecule to pass, but not another.

It may be worth adding that sulfur dioxide, with an even higher molecular mass, passes through the skin of a balloon even faster than does carbon dioxide. However, owing to its much more unpleasant and hazardous nature, sulfur dioxide should **not** be used in these simple experiments.

Note 1: This experiment with carbon dioxide escaping from a balloon attached to a flask has been done a number of times since the one photographed. It appears to be even more dramatic when a round flask is used. The inversion of the balloon also takes place more rapidly than is suggested by the times in this experiment. When the balloon initially collapses over the top of the flask it provides multiple layers of rubber over the top of the flask and limits the area of the balloon surface from which carbon dioxide can escape. Once the adjustment is made so that the balloon can 'invert' into the flask, the escape continues more rapidly. In the experiment shown in the photographs I was absent (asleep) for much of the time between 7 and 17 hours!

Note 2: I recall an experiment I did as an undergraduate when gases were allowed to escape from a pressurised flask – 'an effusiometer' - through a long straight capillary tube instead of the usual small hole. In that case carbon dioxide escaped much faster than hydrogen whereas hydrogen escapes much faster through a small hole. This unexpected observation is explained by the fact that CO_2 is a rod-shaped linear molecule so that the molecules line up with the lines of laminar flow and move through the capillary more easily than 'expected'. This probably has no relevance to the experiments described here, but it is another example of unexpected behaviour of carbon dioxide.

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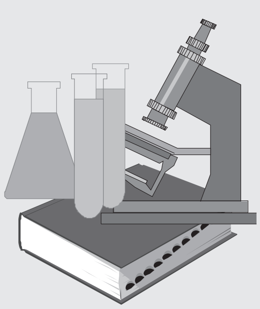

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