# The transport of gases through water - a marathon experiment revisited
# Transporte de gases a través del agua - un experimento largo

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***Abstract***

*A graduated cylinder filled with NO is placed under water. The water level in the cylinder slowly increases. The experiment has been performed earlier and was interpreted as a result of a steady transfer of oxygen from the air through the water, the NO being consumed in a chemical reaction with $O_2$. The explanation, however, was based on a preconception that only the oxygen passes through water. A correction in the explanation is offered, based on the simultaneous transfer of oxygen, nitric oxide and nitrogen through water, the transfer rate being different for $O_2$ and $N_2$.*

***Key words:*** *marathon experiments, nitric oxide, preconceptions, oxygen, nitrogen.*

***Resumen***

*Un cilindro graduado lleno de NO se coloca bajo el agua. El nivel del agua en el cilindro aumenta lentamente. El experimento se realizó antes y se interpretó como una consecuencia de una cesión constante de oxígeno del aire a través del agua, el NO se consume en una reacción química con el $O_2$. La explicación, sin embargo, se basaba en una idea previa de que sólo el oxígeno pasa a través del agua. Una corrección en la explicación se ofrece, basado en la transferencia simultánea de oxígeno, óxido nítrico y el nitrógeno a través del agua, la velocidad de transferencia sea diferente para $O_2$ y $N_2$.*

***Palabras clave****: experimento largo, el óxido nítrico, ideas previas, oxígeno, nitrógeno.*

## SAFETY TIPS

**Nitric oxide is poisonous gas!** Gas generation should preferably be done in a hood. It might be a good idea to first fill bottle reservoir with NO, and to use the gas later. More safety remarks concerning NO are given elsewhere (NAJDOSKI, PETRUŠEVSKI, 2000).

## INTRODUCTION

Marathon experiments (or marathons) are known (FOWLES, 1959) as long-period experiments (lengthy experiments). Other names for marathons are *corridor demonstrations* or *exhibition demonstrations*.

Marathons may last from several hours to many months or even years (in the latter case, the term supermarathons was offered (PETRUŠEVSKI, NAJDOSKI, 2001). During last decade special attention has been paid to this class of experiments and a number of phenomena (e.g. spontaneous distillation (PETRUŠEVSKI, NAJDOSKI, 2001), diffusion PETRUŠEVSKI, MONKOVIÆ, NAJDOSKI, 206), osmosis (PETRUŠEVSKI, MONKOVIÆ, 2004), effusion in liquids (PETRUŠEVSKI, MONKOVIÆ, NAJDOSKI, 2006a), and chemical waves (NAJDOSKI, ALEKSOVSKA, PETRUŠEVSKI, 2001; PETRUŠEVSKI, MONKOVIÆ, NAJDOSKI, 2004) were presented as marathon experiments. Of particular use was the application of the time-lapse (fast-motion) technique, thus offering short (typically 1 minute) video-clips for long-lasting phenomena.

## THE EXPERIMENT & FIRST RESULTS

1. The present demonstration has already been performed earlier (Petruševski, MONKOVIÆ, 2004). A cylinder with ground mouth was used, enabling that it be closed hermetically with its glass stopper. The cylinder was filled with 100 mL of pure nitric oxide[1] (NO) and placed in a pneumatic trough (bottom-up, its mouth well below the water surface, cf. Figure 1. This value for the volume of water in the cylinder is considered as a 'zero value'. (A good method for generating pure nitric oxide is given in one of the earlier papers (NAJDOSKI, PETRUŠEVSKI, 2000), where NO gas was used for a fast and simple determination of the oxygen content in the air).

The volume of gas in the cylinder slowly decreased this being evident by the raise of the water level in the cylinder. The phenomenon was explained on the basis of a steady transfer/transport of oxygen through water, which is possible due to the fact that oxygen is slightly soluble in water (≈3 parts of oxygen gas in 100 parts of liquid water, at room temperature). The oxygen then reacts with the NO at the boundary surface (water/NO) in the cylinder, and the products immediately react with the water:

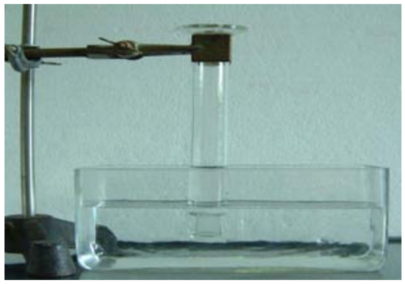


**Figure 1.** Experimental setup (cylinder filled with NO; the 'zero value' volume of water is seen).

$$2NO(g) + O_2(aq) + H_2O(l) = HNO_3(aq) + HNO_2(aq) \quad (1)$$

(another possible reaction, where the final product is only $HNO_2$ was overlooked, but it has no impact on the result of the experiment).

Due to the chemical reaction the quantity of gas (nitric oxide) is depleted, hence the water level increases in the cylinder. The result of the experiment, it was reasoned, may therefore be considered as a consequence of a peculiar type of gas-through-liquid osmosis (in this case oxygen osmosis), followed by chemical reaction at the phase boundary.

The water level increased by some 70 mL in a period of about one month. At this point, as it seemed that the trend will continue till the cylinder is completely filled with water, the results were assembled (cf. Figure 2) and interpreted as explained above (Petruševski, Monkoviæ, 2004).

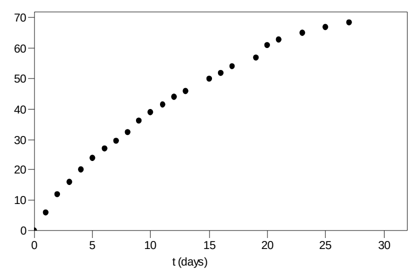



**Figure 2.** The variation of volume of water in the cylinder with time, during a period of one month.

### The Needs for a Revision

However, after about one more month, the water level increased to ~ 80 mL and when this point was reached the value for the level remained constant for a long period. It was not clear, why would the reaction rate drop to zero, before the entire quantity of NO gas was consumed. Could it be that the sample of NO gas contained some 20% impurities? If yes, where would the impurities come from? To possibly answer this question, the experiment was repeated two more times. The results were always similar to the first one. Then the purity of NO was checked. Small portions of pure oxygen (about 1 mL at a time) were added to 100 mL of NO gas, followed by stoppering the cylinder, intense shaking and opening it under water. The volume of gas (NO) decreased almost to 0. Whatever impurities are present in the NO used, they must be less than 1% and thus cannot explain the ~ 20 mL of gas residue.

This was enough for us to conclude that something essential has been ignored, and to admit that the first experiment (Petruševski, Monkoviæ, 2004) and the corresponding interpretation of the experimental results were most probably done too hastily.

## RESULTS AND REVISED DISCUSSION

In order to give a sound response to the problem of the seemingly incomplete reaction of the nitric oxide in the cylinder, two identical cylinders were filled with 80 mL of pure oxygen and 80 mL of pure nitrogen respectively (both gases were taken from metal containers). First the purity of the oxygen gas from the container was checked by the method mentioned previously (Najdoski, Petruševski, 2000) and was proved to be quite satisfactory. The cylinders were then left for some time (bottom-up), each in a separate beaker filled with water, and the volume change was monitored.

After a period of about two months it became obvious that the volume of the gas in the cylinder with pure oxygen decreased severally (by more than 20 mL), while in the same time the volume of the cylinder filled with nitrogen increased by some 4-5 mL!

The purity of the oxygen gas in the cylinder was checked after this, and now it could be proved without any doubt that it contained sizeable amount of some gas that does not react with NO. Now it seemed relatively easy to explain what happened. Oxygen gas escaped from the cylinder through the water (being much better soluble in it than the nitrogen) and from here to the atmosphere. An independent process where $N_2$ from the atmosphere diffused through water and ended in the cylinder originally filled with $O_2$ obviously took place in the same time. Due to the noticeable differences in the solubility of the two gases in water, the overall effect was that more oxygen escapes than nitrogen influxes, hence the resulting volume decrease.

In the cylinder filled with nitrogen, the influx of oxygen again dominates dye to its higher solubility in water (despite its much lower partial pressure in the atmosphere). Thus the neat effect is that slightly more oxygen enters, than nitrogen escapes.

2. The thermodynamical 'driving force' of both processes is based on the differences of the chemical potentials of oxygen and of nitrogen in the cylinder and in the atmosphere (due to differences of their partial pressures in and out-of-the-cylinder; the presence of other gases in the atmosphere has been disregarded in this approach, as their total quantity is negligible). In other words, the entire system (that is, the beaker with water, the cylinder and the surrounding atmosphere) is in concentration non-equilibrium in the beginning of the experiment and it slowly approaches equilibrium. These results will be published separately (Petruševski, Sidorova, Stojanovska, in preparation).

After the last run of the experiment is over (the completion of this experiment may take between 18 months and 2 years, i.e. it is a supermarathon experiment).

Having the above in mind, one could finally explain the results of the cylinder-filled-with-NO experiment: obviously one has to account for diffusion of $O_2$, NO and $N_2$. The diffusion of both oxygen and nitric oxide will result in a chemical reaction (the product being $NO_2$ or $N_2O_3$ which completely dissolves in and reacts with water). Thus the volume of gas decreases, and the water level in the cylinder increases. The slower process (influx of $N_2$ by diffusion) accounts for the inert residue of ~ 20 mL, after 2 months.

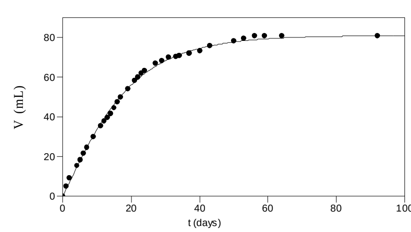
It happens that both diffusivity and solubility in water of $O_2$ and NO are almost equal (Zacharia, Deen, 2005). This enables one to approximate this part of the process by a single exponentially decaying function. The volume of the gas in the cylinder due to this term would be given by a function of the form $V_1 = V_0 \cdot \exp(-at)$ where $t$ is the time (measured in days) and $a$ is a constant. The other term (the influx of nitrogen in the cylinder) will correspondingly be given by an exponential growth function of the form $V_2 = V_f[1 - \exp(-bt)]$ ($V_0$ and $V_f$ are the incident and the final volume of the gas in the cylinder, in our case 100 mL and 19 mL, respectively). The value for the water level is then, simply,

$$V = V_0 - V_1 - V_2, \quad (2)$$

or

$$V = V_0[1 - \exp(-a \cdot t)] - V_f\,[1 - \exp(-b \cdot t)]. \quad (3)$$

Using the WinCurveFit program (http://www.pcauthority.com.au/Download/55424,wincurvefit.aspx), it was possible to interpolate the data points with a curve of the above type. The results are given in Figure 3. Obviously, the fit is an excellent one and supports the notion of simultaneous transport of oxygen, nitric oxide and nitrogen through water.




$V = V_0[1 - \exp(-a \cdot t)] - V_f[1 - \exp(-b \cdot t)]$

$V_0 = 100 \pm 0.5$ mL
$V_f = 19 \pm 0.5$ mL
$a = 0.0683\ (9)$ day$^{-1}$
$b = 0.182\ (20)$ day$^{-1}$
$R^2 = 0.997$

**Figure 3.** The variation of volume of water n the cylinder with time, during a period of three months and the parameters in the best-fit equation (values in parentheses are the standard deviations of the numerical values and refer to the least significant digit; values for $V_0$ and $V_f$ are the experimental values).

## CONCLUSIONS

The decreasing volume of the gas in a graduated cylinder (originally filled with nitric oxide and placed in a trough under water) was reinterpreted as a result of simultaneous transport of oxygen, nitric oxide and nitrogen through water. Oxygen and nitric oxide react, the product being completely absorbed by the water. The nitrogen accumulates in the cylinder. The data points were curve-fitted using non-linear regression, based on two independent exponentials: one referring to the transport of oxygen and nitric oxide, and the other one referring to the transport of nitrogen. The resulting fit is an excellent one.

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