

Reaction of Sodium with Water Vapor – a Short Marathon Experiment with Somewhat Unexpected Result

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Abstract: Attention was paid to the reaction of sodium with water vapor at room temperature. The reaction lasts for hours, and is an example of a short marathon experiment. The reaction rate appears to be independent of the process duration, thus being in accord with 0th order kinetics. At first, this seems to be inconsistent with some simple chemical reasoning. Two explanations are offered for the differences of the predicted and actual behavior of the system and a decisive experiment was performed to see which explanation is the correct one.

Introduction

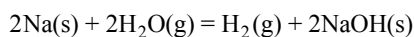
Experiments based on the reaction of sodium metal with water are very common in the chemistry education practice [1–3 and the references therein]. No matter whether they are performed on a microscale (in a Petri-dish placed on an overhead, that is one of the safest versions of this demonstration [1, 2]), or using large pieces of sodium (by means of a safety spoon [3], which serves as completely safe device for performing ‘dangerous’ demonstrations) they always attract students’ attention and are a precious tool in the hands of an experienced instructor/educator. Some frightening variants of the above reaction are also known, although a cautious instructor would never recommend performing them the way they were offered [4, 5], because one is instructed to use very large pieces of sodium while in the same time the safety concerns are completely ignored.

Browsing through the rich chemistry literature, we noticed that one never comes across with an experiment where the chemical reaction of sodium metal with water vapor was studied. We concluded that this reaction was probably considered as non-attractive and of limited educational value due to its duration. Long-lasting experiments, however, are not uncommon in chemistry and are known as *marathon experiments* or *marathons*. In our earlier publications [6–10] we offered several demonstrations of this class of experiments, covering processes based on spontaneous molecular motion (chemical waves, diffusion, effusion etc.).

The very fact that a reaction (like the mentioned reaction of sodium with water vapor) is *a priori* expected to be a slow one, offers other possibilities, like discussing some simple kinetics in heterogeneous systems. Starting with this idea, we firstly derived a simple mathematical model for the behavior of the system Na(s)–H₂O(g) with time, and then we purposely designed an experiment in order to check this behavior.

Theoretical Model

The chemical reaction is described by the following equation:



If performed at room temperature (e.g. 298 K), it is expected to be a rather slow one, as the water vapor pressure at this temperature (≈ 3 kPa) is rather low. Keeping the water vapor pressure constant, the only factor affecting the reaction rate seems to be the surface area of the sodium (a consequence of the fact that the chemical reaction in a heterogeneous system occurs only on the surface).

It is convenient to define the reaction rate of this heterogeneous reaction in a somewhat nonstandard way, as

$$v = \frac{d\xi}{dt} = -\frac{1}{2} \frac{dn(\text{Na})}{dt} = \frac{dn(\text{H}_2)}{dt} \quad (1)$$

where ξ is the extent of the reaction, n is the quantity of substance and t is the time (the stoichiometric numbers are positive for the products and negative for the reactants [11]). One should keep in mind that the quantity of sodium, its mass and volume are all linearly related ($m = n \cdot M = \rho \cdot V$), and are also linearly proportional to the volume of hydrogen evolved. The rate, on the other hand, is expected to depend on the surface area, S , of the sodium metal, i.e.

$$v = \frac{d\xi}{dt} = kS^a \quad (2)$$

where k and a (the order of the reaction) are constants. In the simplest case, $a = 1$ (intuitively, this might seem to be the most ‘natural’ solution to the problem), but in quite a general case a is a real number.

For relatively short time intervals, one can substitute the differential sign by the difference sign, Δ , to obtain the value for the *mean rate*, \bar{v} , in the given time interval. i.e.

$$\bar{v} = \frac{\Delta\xi}{\Delta t} = kS^a \quad (3)$$

Considering the hydrogen gas (a product of the reaction), one could write

$$\Delta\xi = \frac{\Delta V(\text{H}_2)}{V_m(\text{H}_2)} \quad (4)$$

where $\Delta V(\text{H}_2)$ is the difference (increase) in the volume of generated hydrogen gas, and $V_m(\text{H}_2)$ is its molar volume (the latter value should be close to 24.5 L mol⁻¹ at 298 K). Combining eq. 3 and eq. 4, followed by multiplication by $V_m(\text{H}_2)$, gives

$$\bar{v}' = \frac{\Delta V(\text{H}_2)}{\Delta t} = k'S^a \quad (5)$$

where $\bar{v}' = \bar{v}'V_m(\text{H}_2)$ and $k' = kV_m(\text{H}_2)$. We shall call \bar{v}' the **normalized mean rate** of reaction.

As the surface area, S , depends on t (the dependence is somewhat complex, see eq. A6 from Appendix 1), one would also expect the normalized mean rate of the reaction to decrease with time, to follow the decrease of S with time.

Now, let us check out this prediction and see whether it is true.

Experimental

One first needs to construct a reaction chamber. The reaction chamber we used was built by modification of a standard wash-bottle. The top part of the inlet glass tube was sealed, and part of its glass tube that enters the wash-bottle was cut off. Now an iron spoon was placed in this remnant of the inlet tube, and was fixed in position by means of a piece of rubber (a piece of eraser will do perfectly). The outlet tube was joined (by means of a piece of plastic tube) to a doubly bent glass tube, that ends under an inverted graduated cylinder filled with water and placed in pneumatic trough.

The setup for the experiment is presented in Figure 1. A close-up of the left part (the reaction chamber) is given in Figure 2.

Performing the Experiment. A piece of sodium (size of a piece of corn; mass of about 250 mg) was carefully cut from a lump of sodium using a scalpel (wear a face shield and protection gloves during this operation!) and was put in the iron spoon. Carefully holding the spoon vertically (parts 2 and 3 in Figure 1 were previously joined by the piece of plastic tube) in order to prevent dropping the piece in the water, the reaction chamber was closed and the end of the doubly bent glass tube was placed under the inverted cylinder filled with water. At this moment we started photographing the graduated cylinder using ToUcamXS (Phillips) digital camera, that was coupled to and software controlled by a PC. Taking a photo each minute, it was possible to measure precisely both the volume of hydrogen evolved and the time (the first photo has a number 0, and the rest are subsequently and automatically numbered 1, 2, 3 ...). About 500 photos were taken during some 8 hours.

Results and Discussion

The series of photos acquired above enables one to draw the variation of $V(\text{H}_2)$ vs. time (the pairs of values were manipulated using Excel). This variation is presented in Figure 3.

Quite unexpectedly, the variation appears to be an almost ideal straight line, with a slope of ≈ 0.19 . The constant slope (that is, the constant \bar{v}') strongly indicates that the rate is invariant of S , and therefore of t . In other words, according to the experimental results, the chemical reaction behaves as though it is of 0th order.

This is in sharp disagreement with the expectations that the size of sodium will affect the reaction rate. There are two possible explanations for the disagreement:

(a) For some reason, the surface area of the sodium remains practically constant for a long period of time. This could be, one may speculate, explained assuming that the initially smooth surface of the Na piece changes into a rough one, with lots of cavities. Thus, on one hand, the radius and volume of our (idealized) spherical piece decreases; however, the surface becomes increasingly more rough (as a consequence of the stochastic attacks of the water molecules) with time. This increases the surface area of the, otherwise volume-decreasing, sphere, and by a matter of chance fully compensates the would-be decrease of the surface area, if the spherical surface remained ideally smooth.

(b) The order of the reaction, a , is indeed zero. If this is the case, our basic assumption (that the reaction rate is limited by the surface area) must be wrong. This, on the other hand, would mean that no matter how big the surface of the initial piece of sodium is, the reaction would always proceed with the same rate. This can only be fulfilled if the limiting factor is not the surface of sodium but the water vapor pressure (i.e. the concentration of water in the atmosphere) instead. When the concentration of water compared to that of sodium is low, the order of the reaction equals the partial reaction order with respect to water. Since the concentration of water molecules is kept constant in the vapor phase by a constant evaporation from the liquid phase (see experimental part), the order of the reaction is expected, theoretically, to be equal to zero.

One more check appeared to be necessary, in order to decide which interpretation is the true one. The experiment was conducted in two identical reaction chambers, containing the same volume of liquid water at the bottom. The only difference was that the piece of sodium placed on the spoon in one of the chambers had \sim twice larger surface area than the piece in the other chamber. Then, in the light of what has been said above, if the explanation (a) is the true one, then the volume of hydrogen generated in the first chamber must be about twice as large compared with the corresponding volume in the second reaction chamber. If, on the other hand, explanation (b) is the correct one, then the volumes should be more or less the same.

The decisive experiment was performed as described. The result (for us somewhat unexpectedly) was that the volumes of hydrogen generated in the two reaction chambers were exactly the same! Therefore, the reaction is truly of 0th order, as a consequence of the low concentration of water vapor in the system.

Conclusion

The reaction of sodium metal with water vapor is a 0th order reaction. An explanation is offered in terms of the low concentration of water vapor in the atmosphere which appears to be the limiting factor in the chemical reaction.

Safety Tips and Disposal

Sodium metal is highly corrosive and dangerous material (due to fire hazard and/or explosion if mixed with water or acids)! Always wear a face shield and protection gloves during manipulations with it. Never dispose pieces of sodium under



Figure 1. Experimental setup for the reaction of sodium metal with water vapor (1 – a wash-bottle used as a reaction chamber; 2 – iron spoon; 3 – doubly bent glass tube; 4 – pneumatic trough; 5 – graduated cylinder).



Figure 2. A close-up of the reaction chamber, with some water at the bottom.

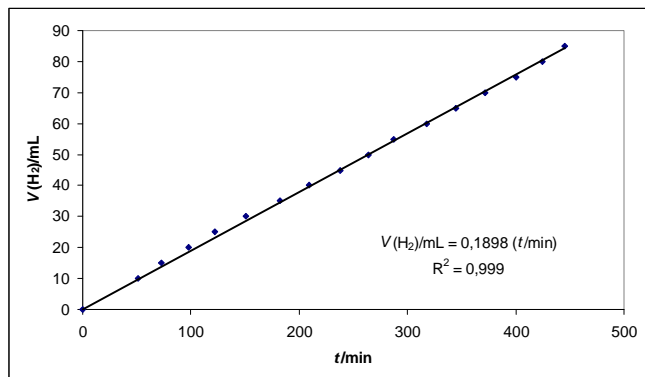


Figure 3. Variation of the volume of generated hydrogen gas with time (the best-fit line was ‘forced’ to pass through the origin, the only physically acceptable situation).

the drain, to prevent a fire hazard. It is best to dissolve pieces of sodium (size of a match-head, one at a time) in large quantity of ethanol, where it reacts safely and to dispose the

solution under the drain with large quantities of water. For more information see [12].

Appendix 1: Mathematical Derivation of the $S(t)$ Dependence

Let us assume that the piece of sodium is spherical in shape (and that it remains spherical during the reaction; this is a highly idealized approach). Recalling that the relation between the volume and the surface area of a sphere is given by

$$V = \frac{S^{3/2}}{3\sqrt{4\pi}} \quad (\text{A1})$$

one could rewrite eq. 1 in the following form:

$$\begin{aligned} v &= \frac{d\xi}{dt} = -\frac{1}{2} \frac{dn(\text{Na})}{dt} = -\frac{1}{2} \frac{\rho(\text{Na})}{M(\text{Na})} \frac{dV(\text{Na})}{dt} \\ &= -\frac{1}{12\sqrt{\pi}} \frac{\rho(\text{Na})}{M(\text{Na})} \frac{d(S^{3/2})}{dt} \end{aligned} \quad (\text{A2})$$

and then combine it with eq. 2, with an idea to find the variation of S with t . After some algebra, one obtains finally

$$-\frac{1}{8\sqrt{\pi}} \frac{\rho(\text{Na})}{M(\text{Na})} S^{-a+1/2} dS = k dt \quad (\text{A3})$$

Substituting the product of the constants by another constant, b

$$\frac{8\sqrt{\pi} k M(\text{Na})}{\rho(\text{Na})} = b \quad (\text{A4})$$

one comes to a more compact form of the differential equation, with separated variables

$$-S^{-a+1/2} dS = b dt \quad (\text{A5})$$

Let in the beginning of the experiment (when $t = 0$) the surface be designated by S_0 . Then, in the moment t , the variation of the surface area, S , with time will be given by

$$S^{-a+3/2} = S_0^{-a+3/2} - b \left(\frac{3}{2} - a \right) t \quad (\text{A6})$$

and thus for an arbitrary value of a the surface area decreases with t (thus confirming the expectations based on purely logical reasoning).

References and Notes

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