

A non-exploding alkali metal drop on water: From blue solvated electrons to bursting molten hydroxide

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Abstract:

Alkali metals in water are always at the brink of explosion. Here we show that this vigorous reaction can be kept in a non-exploding regime revealing a fascinating richness of hitherto unexplored chemical processes. A combination of high-speed camera imaging and visible/near infrared/infrared spectroscopies allows us to catch the system at each stage of the reaction and fully characterize it. After gently placing a drop of a sodium/potassium alloy on water under an inert atmosphere production of solvated electrons becomes so massive that their characteristic blue color can be observed with a naked eye. The exoergic reaction leading to formation of hydrogen and hydroxide eventually heats the alkali metal drop such that it becomes glowing red and part of the metal evaporates. As a result of the reaction, a perfectly transparent drop consisting of molten hydroxide temporarily stabilizes on water via the Leidenfrost effect, bursting spectacularly after it cools sufficiently.

It is high school chemistry that sodium reacts vigorously with water.^{1, 2} Upon contact between the reactants, electrons move from the alkali metal to water reacting there towards hydrogen and hydroxide in a strongly exothermic process nominally written as $2 M + 2 H_2O \rightarrow 2 MOH + H_2$ (M = alkali metal), which often leads to explosion.^{1, 3} In our previous study,⁴ we have shown that a hitherto unrecognized precondition for the explosive behaviour is a massive positive charging of the metal drop upon exit of the valence electrons from the alkali metal to water. This can create an electrostatic instability leading to metal spikes shooting into water, ensuring thus efficient mixing of the reactants. We have also shown that such an electrostatic Coulomb explosion^{5, 6, 7, 8, 9} can be quenched by limiting the contact between the alkali metal and water, e.g., by adding a small amount of surface active species like hexanol. This brings an idea to keep the reaction just below the explosive threshold and follow the individual stages of the process, which is all but impossible if explosion occurs. Here, we reach the non-explosive regime in a controlled way by carefully placing a sodium/potassium alloy drop on water rather than dropping it from a considerable height (which always leads to explosion). We then use a combination of high-speed camera imaging and visible/near IR/IR spectroscopies to fully characterize the sequence of unique chemical processes starting with massive formation of solvated electrons, visible with a naked eye despite their extremely short lifetime in water,^{10, 11, 12, 13} and ending with a bursting drop of molten hydroxide. The fact that a hot drop of hydroxide, which is heavier than water and well miscible with it, can be temporarily supported at the water surface is a remarkable demonstration of the Leidenfrost effect (same as what keeps water drops stable on a hot stove).^{14, 15}

After much experimentation, we found out that a robust and reproducible way to the non-explosive regime of alkali metal reaction in water is to deposit a drop of a sodium/potassium alloy, which is liquid at room temperature, from a syringe directly on the aqueous surface (see Figure 1 for a photo and a schematic picture of the experimental setup). This limits the contact between the reactants compared to our previous setup

where the alloy was dropped from about one metre to water and always exploded.⁴ When gently placed on water, the sodium/potassium alloy drop (which has a lower density than water) starts reacting vigorously (Figure 1A). However, due to its buoyancy and immediate vapour production the contact with water is limited such that the reaction towards hydrogen and hydroxide proceeds in a non-explosive way. Also, there is no ignition of the hydrogen gas formed, since we are continuously flushing the reaction vessel with nitrogen gas. Upon proper design, the flow of nitrogen is a double blessing as it also carries with itself the produced smoke which would otherwise completely obscure the view for the camera. A fascinating richness of hitherto unexplored chemical processes then unravels in front of the lens of the camera, to which full visual justice can only be done by viewing the recorded movie, as presented in the Supplementary information. Here, we may only show static snapshots (Figure 1) and do our best to re-enact the impressions from the moving pictures by adding an accurate verbal description supported by spectroscopic evidence.

Shortly after the beginning of the reaction the metal drop starts turning blue (Figure 1B) with the colour getting progressively darker and the drop eventually turning black. We prove here spectroscopically that the blue colour, visible by naked eye (and caught also on high-speed camera within our previous explosive setup⁴) is due to solvated electrons. Figure 2 shows a spectrum which has been recorded in a slightly modified setup where a drop of water was placed on the sodium/potassium alloy drop (see right side of Figure 2). This setup both spatially limits and efficiently cools the alloy drop increasing thus the concentration of the solvated electrons and providing a visually spectacular blue spot at the surface of the metal drop and its aqueous surroundings, the colour of which can be easily dispersed by a standard VIS/near IR spectrometer. The obtained spectrum is overlaid in Figure 2 with previously recorded spectra of hydrated electrons prepared at varying temperatures via pulse radiolysis of water.¹⁶ The agreement with the reference measurements¹⁶ is convincing despite the different ways of preparation of the solvated

electrons, demonstrating also that our system is heating up from the initial ambient conditions. Being far from thermodynamic equilibrium the reacting system can hardly be assigned a well-defined temperature. Nevertheless, it is clear from Figure 2 that already at this early stage the exoergic chemical process heats the surface of the metal drop well above the room temperature, up to at least 100 °C in the present setup.

In the setup presented in Figure 1 the drop continues heating up and at a certain point starts to massively evaporate the alkali metals (Figure 1C). The recorded visible spectrum of the alkali metal vapour is presented in Figure 3. We see the presence of both potassium and sodium gas, as indicated by characteristic lines in the absorption spectrum at around 770 nm (potassium) and 580 nm (sodium). Also, a strong near IR tail of the spectrum due to heating of the drop is clearly visible. It is precisely this spectral tail which to a significant extent masks the spectrum of the hydrated electrons within this setup and because of which we developed the modified setup shown in Figure 2 to record its spectrum. The continuing heating of the alkali metal drop due to the ongoing exoergic chemical processes eventually renders it glowing red, see Figure 1D. Using a remote thermometer we can estimate the temperature of the droplet at this stage to be around 600 °C.

A most amazing thing happens after the chemistry is essentially over. When the smoke clears, the drop cools and suddenly becomes completely transparent (Figure 1E). This transparent drop lives at the aqueous surface for about a second after which it bursts spectacularly. Several questions arise immediately. First, what is the transparent drop made from? It is clearly not metallic anymore and the fact that vigorous reactivity has ceased already indicates that it may be dominantly formed by the key non-gaseous product of the reaction, i.e., molten alkali hydroxide (likely also containing other products such as sodium oxide). This is indeed confirmed by IR spectroscopy taken of this drop (see Figure 4), revealing characteristic fingerprints of molten or solid hydroxides, in

particular the OH stretch between 3480 and 3620 cm^{-1} and at around 900 cm^{-1} .^{17, 18, 19} The next intriguing question is how can a drop of molten alkali hydroxide, which is significantly heavier than water and perfectly miscible with it, be supported at the aqueous surface. The answer lies in invoking the Leidenfrost effect.^{14, 15} In its conventional realization it is the effect behind the stabilization of water drops on a hot stove via a separating hot steam layer. Here, we have an analogous situation, except in an inverse mode of a hot drop of molten hydroxide stabilized by a vapour layer on water at room temperature. Finally, as the drop cools of the hot vapour layer separating it from water, it becomes destabilized. Eventually, this layer ceases to be able to effectively separate the two species, leading to a vigorous mixing of the hydroxide drop with water proceeding in dramatic burst.

In summary, the present study shows that the non-explosive regime of the textbook reaction of alkali metals with water offers even richer and less explored chemistry and physics than the explosions which we characterized and rationalized in detail recently.⁴ We show that when gently placed on the water surface the vigorous reaction of a sodium/potassium alloy drop proceeds in distinct stages which we are able to characterize spectroscopically. With a bit of temperature control, the broad spectrum of solvated electrons can be recorded using a standard continuous-wave VIS/near IR spectrometer. Moreover, the characteristic blue colour of solvated electrons can clearly be seen with a naked eye which was thought to be all but impossible due to their extremely short (sub-millisecond) lifetime in water.^{20,21} The trick here is in establishing for hundreds of milliseconds a steady-state regime with massive influx of electrons from the alkali metal to water. Continuing reaction leads to further heating of the drop associated by alkali metal evaporation and the drop becoming glowing red. When chemistry eventually ceases the metal drop is unexpectedly transformed into a transparent ball of molten hydroxide, which is transiently stabilized at the water surface via the Leidenfrost effect^{14, 15} until it cools and bursts spectacularly.

Keywords: alkali metals, water, solvated electrons, Leidenfrost effect.

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Figure captions:

Figure 1: Images of a sodium/potassium alloy drop reacting on water showing individual stages of the process: A) Onset of the reaction in a non-explosive mode. B) Occurrence of blue solvated electrons at the surface of the drop. C) Evaporation of hot alkali metal (blue/turquoise) from the drop. D) Continuous heating leading to a glowing red drop. E) Formation of a transparent alkali hydroxide drop. F) Bursting of the transiently stable alkali hydroxide drop after breakdown of the supporting Leidenfrost vapour layer. A photo and a schematic picture of the experimental setup are presented in G) and H).

Figure 2: Visible/near IR spectrum of the solvated electrons recorded in the reflection mode, overlaid with previous spectra of electrons from pulse radiolysis of water at varying temperatures (data from Ref. 16 taken in the absorption mode are presented here with inverted sign for direct comparison). The background rainbow roughly indicates the visible range. Snapshot on the right shows the modified experimental setup (corresponding to stage B in Figure 1) that yielded the clearest signature of the solvated electrons seen as the blue spot at and around the alkali metal drop.

Figure 3: Visible/near IR spectrum from stage C in Figure 1 recorded in the reflection mode. Sodium and potassium atomic lines in the spectrum demonstrate the presence of alkali metals evaporating from the hot drop, while the presence of a strong IR tail to a large extent obscures the spectral signature of the solvated electrons in the setup from Figure 1. The background rainbow roughly indicates the visible range.

Figure 4: IR spectrum recorded in the transmission mode showing clear signatures of the presence of hydroxide in the transparent drop at stage E in Figure 1 (red line). Black line shows the background spectrum, while blue line corresponds to a control measurement for molten sodium/potassium hydroxide.

Figure 1

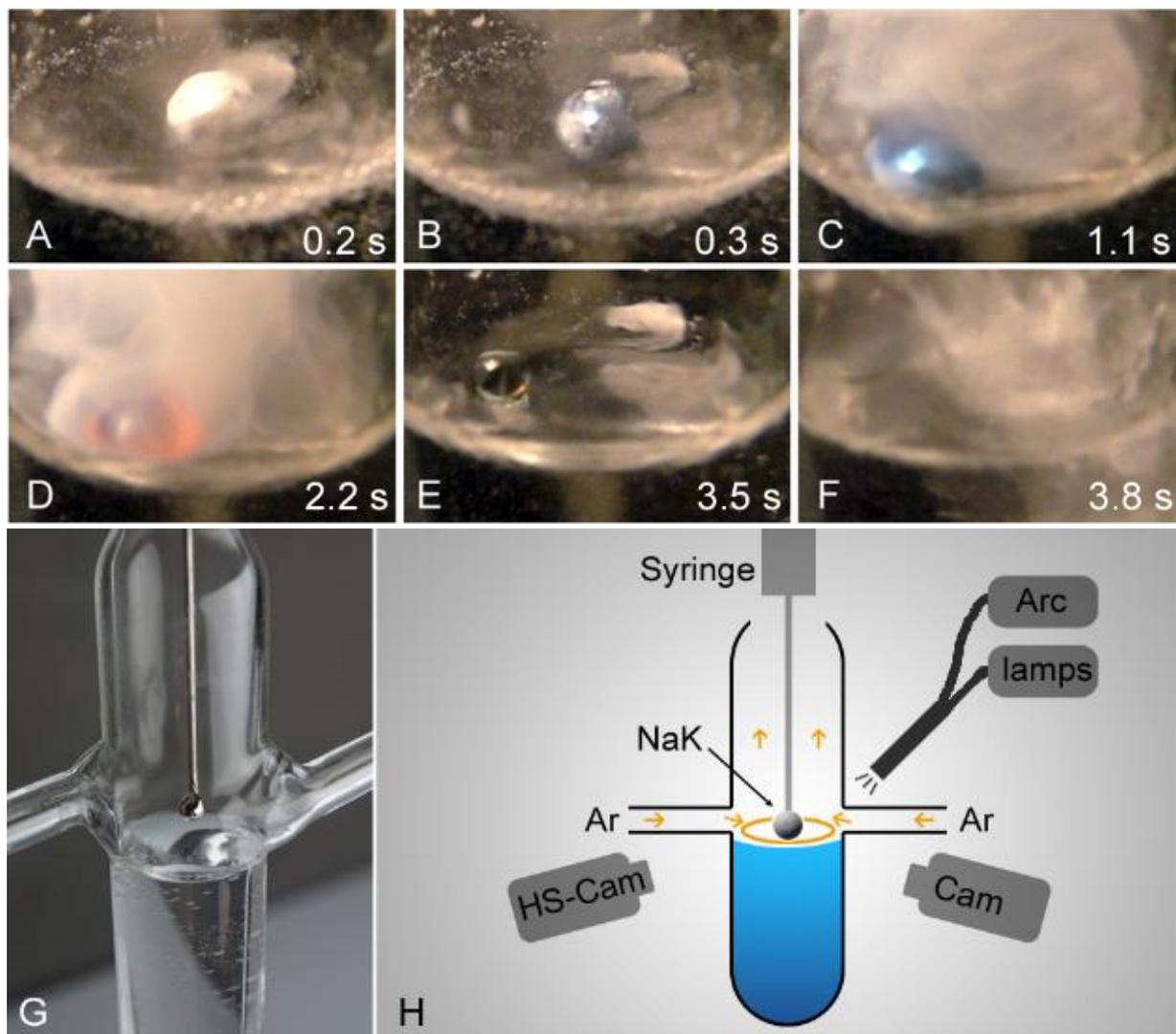


Figure 2

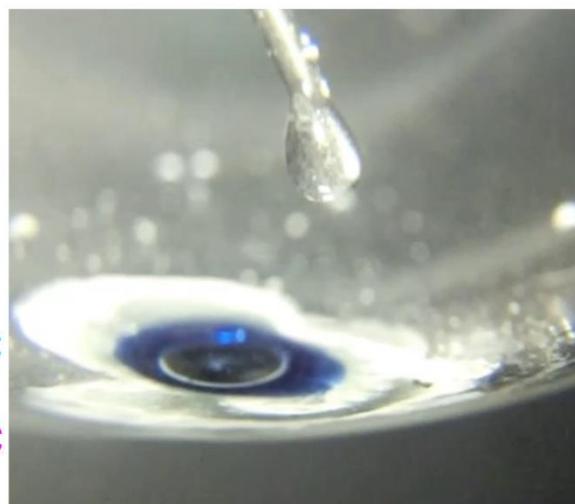
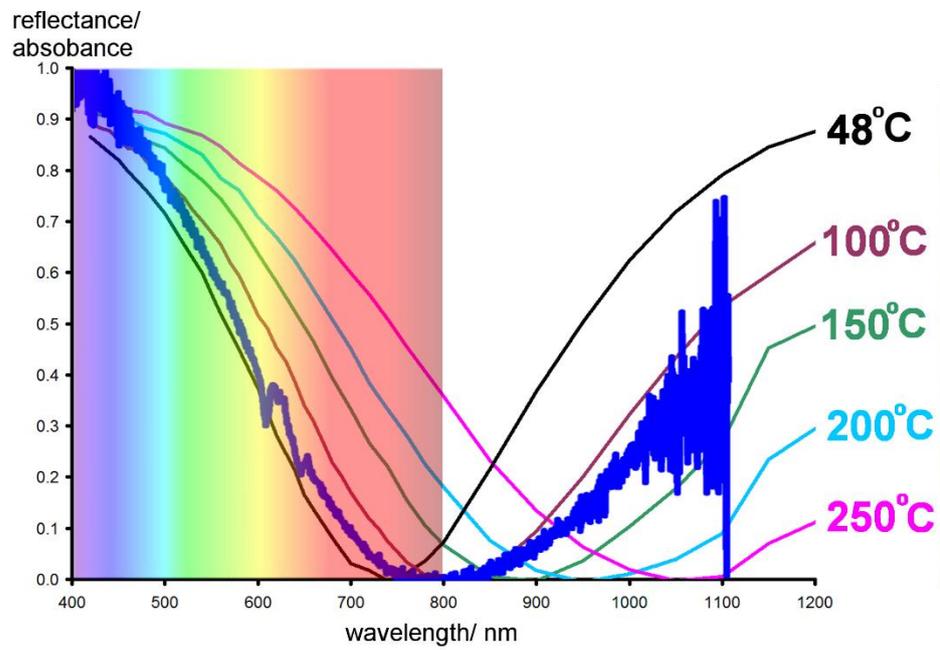


Figure 3

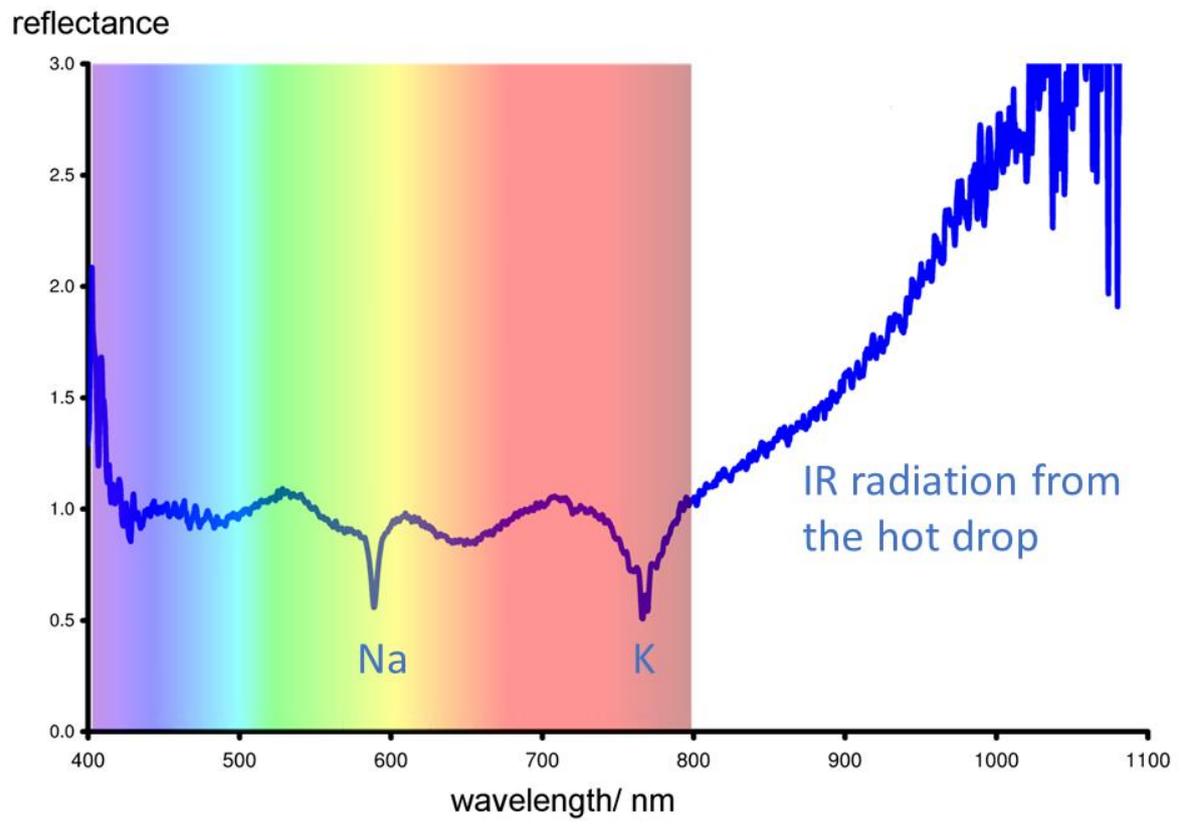


Figure 4

