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Chemistry of Alkali Metals. 1. A Simple Synthesis of Liquid K-Na Alloy and Few Examples of its Use in the Chemistry Education Lab

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Abstract

Upon pressing small pieces of sodium and potassium with a glass rod, the solid pieces turn into silvery liquid product – a K–Na alloy. The alloy reacts with water very vigorously (often an explosion occurs). This experiment is reserved only for chemistry instructors, providing they take all necessary precautions. Two much safer experiments are described: a novel one, where the alloy is allowed to react with mercury, giving K–Na amalgam, and the reaction of the obtained amalgam with saturated aqueous solution of ammonium chloride, where unstable ammonium amalgam is formed. Ammonium amalgam decays in several minutes to give ammonia, hydrogen and elemental mercury

Introduction

The alkali metals (the group I metals) are elements with the most pronounced metal properties of all elements in the periodic table. They all react with water, the product being hydrogen gas and alkali metal hydroxide. As the metallic character increases with the increase of atomic number (as is the general rule in the periodic table) the reaction rate increases on going from Li to Cs. Thus, the reaction of Li with water is a moderate one; that with Na is vigorous and the metal/hydrogen sometimes even ignites; K reacts very vigorously and ignition always occurs; a small piece of Rb produces a real firework, and correspondingly small piece of Cs produces almost instantaneous explosion (Bain et al., 2006), and often the beaker is shuttered into pieces. Reaction of large pieces of an alkali metal (any of the metals but lithium) with water eventually ends with a loud explosion (Petruševski & Najdoski, 2002a), (http://theodoregray.com/PeriodicTable/Stories/011.2), (http://yarchive.net/med/sodium_metal.html).

For this reason, instructors are always advised to work with small pieces of Li, Na and K only (the size of a match-head, i.e. 20-30 mg of either Na or K are as a rule considered to be the upper limit for a safe demonstration). We will mention in passing that all alkali metals are sensitive to air (as a result of chemical reactions with water vapor, CO_2, and oxygen; in case of lithium the reaction with nitrogen is also known as an important one). As a consequence, they are all kept under paraffin oil, petroleum or are covered with vaseline (lithium).

The melting temperatures of the alkali metals vary regularly: with increasing atomic number, the temperature decreasing monotonously. The melting temperatures of the two most common alkali metals are 98 °C (Na) and 63 °C (K). Both metals are therefore in the liquid state at the temperature of boiling water. Upon reaction with cold water enough heat is produced to melt the above two metals, so a small ball (Na) or a fire-ball (K)[1] is always seen whenever the experiment is performed.

It might be interesting to mention that it is very easy to prepare an alloy of the above two metals, that is liquid at room temperatures. This is known in literature (Verhovskii, 1968) where it is recommended to heat pieces of potassium and sodium (by placing a test-tube containing the metals into hot water) until they melt and the alloy is formed. A simplified and much safer procedure will be given below, followed by few recommended demonstrations with the obtained (liquid) product.

Safety Tips and Disposal

Mercury and its salts are toxic! For disposal consult local safety regulations.

Alkali metals are highly reactive and very corrosive substances. Always wear face shield and gloves when working with them. Never experiment with large pieces, unless you know exactly what you are doing and you are aware of all consequences.

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[1] This reaction releases more heat per unit time, so that the potassium spontaneously catches fire.

Never prepare larger quantities of the alloy than advised and never store any quantity of it, due to fire hazard! Use it within few minutes after the preparation.

Check whether all equipment to be used is completely dry. Don't use it if you are not aware it is.

For preventing fire hazard, always destroy all small pieces of alkali metals (like those that left during the process of the corrosion covering removal). For that purpose, use large beaker half filled with water and destroy one small piece at a time (keep in mind that the reaction is very vigorous, as mentioned above).

Always bear in mind that the K–Na alloy is more reactive than either potassium or sodium metal.

The first three demonstrations are potentially dangerous, particularly the first one. It should be performed only by careful and experienced instructors. Anyway, have at hand few kilos of dry sand (as a precaution; in case of accident it is to be used as a fire extinguisher).

We are always willing to advise and help the instructors that feel they might need it.

Preparation and Properties of K–Na Alloy

Materials. Pieces of potassium and sodium, glass test-tube (standard size), glass rod, watch glass, scalpel, dry filter paper.

Procedure. One piece of potassium (the size of a corn grain) and one piece of sodium (about half the size of the potassium piece) are put in a dry test tube (Figure 1).[2] Freshly cut pieces freed of the corrosion covering are used (that's why the razor is necessary). The pieces are pressed by a glass rod. Ask students to carefully observe the changes from that point on. After few minutes, a metallic liquid (K–Na alloy) is obtained in the test tube (cf. Figure 2).

Physical and chemical properties of the obtained alloy. Simple pressing brings the particles in close (intimate) contact, and the atoms of both kinds interpenetrate giving in few minutes liquid product, the K–Na alloy. This is, in a way, a 'forced diffusion' reaction (diffusion is, originally, a spontaneous process). The product resembles mercury, for it is liquid and has silvery metallic luster. One important difference is noticed immediately: in mercury the cohesion forces are larger than the adhesion forces between mercury and the glass walls of the test-tube. In the K–Na alloy, it is quite the opposite – a liquid metal film covers the glass. Also, mercury is very heavy (relative density with respect to water is 13.6), while the alloy is very light (the relative density is estimated to be close to 0.9).

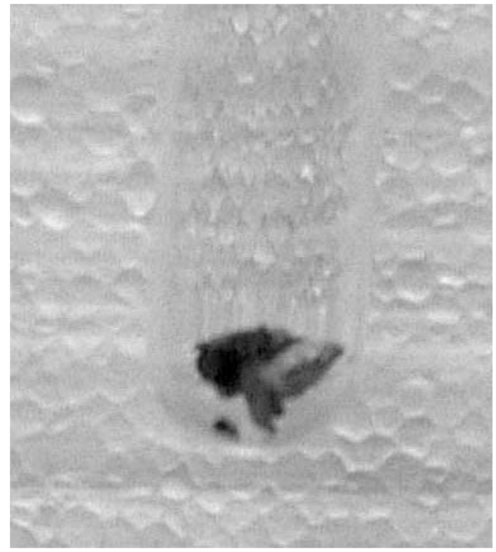

Figure 1. Pieces of potassium (left, dark) and sodium (right, grey) used for the alloy synthesis. Although the corrosion covering was removed, a new one is formed within seconds and this gives the dark color

There exist several types of alloys. Alloys of the substitutional type are formed between chemically similar metals, where the atomic radii are also rather close (the allowed differences are roughly within the 15% limit). The above mixtures are in most cases truly isomorphous (the Au–Ag alloy might be mentioned as an example of this type, http://www.hooverandstrong.com/articles/?id=41). Another type of alloys are intermetallic compounds e.g. Na_3Hg (Greenwood & Earnshaw, 1998). Interstitial alloys make yet another type (these have the solute metal atoms occupying holes in the close-packed structure of the solvent metal, http://www.wwnorton.com/chemistry/overview/ch18.htm). Some binary alloys like the Au–Sn (Matijasevic, et al., 1993) rep-

Figure 2. K–Na alloy covers the test-tube glass due to strong adhesion forces

[2] The ratio of the quantities of K and Na affects somewhat the melting temperature of the product, but its general properties will basically be the same in a wide composition range.

resent eutectic systems (Atkins, 1982). Finally, there are alloys that belong to systems showing incongruent melting (due to so–called peritectic reaction), as is the case with the K–Na alloys (Atkins, 1982). Namely, a reaction is possible between the two metals giving 'a feeble product' (Atkins, 1982), Na_2K, that can survive only in the solid state, but not in the liquid where it immediately dissociates back to the components.

According to literature data, there exists an eutectic mixture (Nekrasov, 1976; BASF, 2004), i.e. a mixture with a lowest melting temperature that melts without changing its composition. It is formed for $w(K) = 0.78$ and $w(Na) = 0.22$, corresponding to a composition that is very close to K_2Na. For the latter composition, the melting temperature (the eutectic temperature) is −12.6 °C, i.e. much lower than the melting temperature of any of its components. Also, the product is reported to be liquid at room temperature in a rather wide range of compositions, namely for $w(K)$ between 40 and 90% (BASF, 2004). This is interesting but not surprising. Indeed, it is quite possible to have an alloy with a melting temperature appreciably lower than the melting temperatures of its components (68 °C for potassium and 96 °C for sodium), as in this case. Let us briefly mention here one of the more familiar examples – Wood's alloy (http://www.jtbaker.com/msds/englis html/w3500.htm), composed of tin, lead, cadmium and bismuth, with a melting temperature at 70 °C (i.e. again, much lower then the melting temperature of any of its components). By the way, the composition of the K–Na system obtained as advised above may be estimated as $w(K)$ 0.65 and $w(Na)$ 0.35, meaning it is well within the limits for which the product is liquid at room temperature. Some of its properties will be discussed below.

The K–Na alloys (typically the eutectic mixture) find various uses. One is as a coolant in nuclear reactors (Siborov, 1961). Another use might be as a strong reducing agent (like the alkali metals in general, see e.g. Ohsawa et al., 1981; Stowe, 1989). One should perhaps mention here that it is possible to prepare K–Na alloys that are much more stable in air, by making a mixture with silica and then heating to 150 °C (http://www.signachem.com/SiGNa_science_highlight_p21.pdf). This might be important from a viewpoint of safe handling of the above materials.

The alloy corrodes in air even faster than the individual metals it is composed of (question of reactivity, see below). Still, it is easy to note its metallic luster due to the fact that it adheres firmly to the glass, thus preventing the air contact. The alloy is extremely reactive. This high reactivity may be best pictured through its reaction with water.

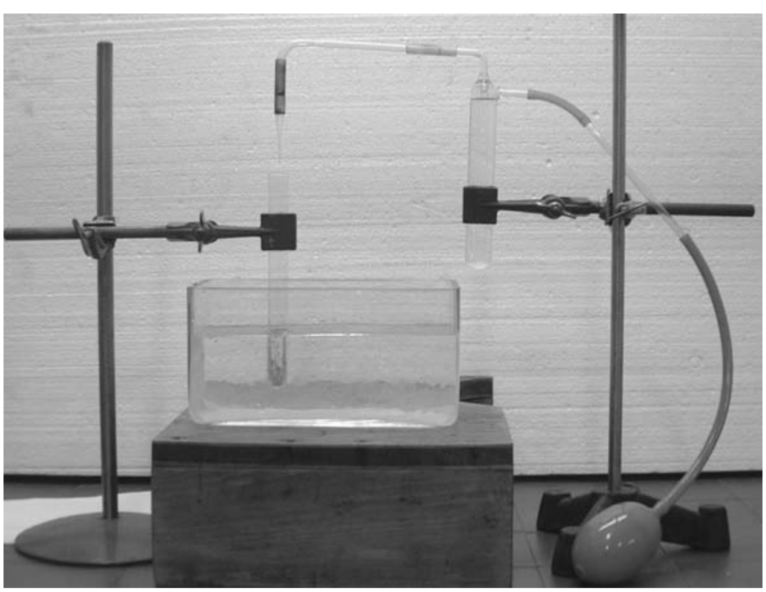

Figure 3. Reaction of the K-Na alloy with water – setup for experiment.

Reaction of the K–Na Alloy with Water

Note from experience. When the K–Na alloy is brought in contact with water, very often small explosions occur. In order to perform this reaction safely (for both the audience and the instructor), we recommend the use of the safety dropper. Its construction is given elsewhere (Petruševski & Najdoski, 2002b).

Materials. A test-tube with the K-Na alloy, safety dropper filled with water, a pneumatic trough filled with tap water, stands, clamps, screw-holders, transparent shield for protection of the audience.

Procedure & observations. The test-tube with the alloy is clamped and fastened on a stand. Then its lower part is dipped in the trough filled with water (this is just a precaution: if the reaction goes as violently as to shatter the test-tube – it never did like that in reality – the pieces will be safely shattered under the water). The safety dropper is clamped and fastened on the other stand, so that the capillary tube ends just above the mouth of the test-tube. A view of the experimental setup using the safety dropper is given in Figure 3.

The transparent shield is placed between the setup and the audience. The demonstration starts simply by pressing the rubber pump (lower right on Figure 3). This enables the instructor to add water in the test-tube containing the K–Na alloy, from a safe distance. An instantaneous explosion occurs due to the violent reaction of the alloy with water. Part of the alloy reacts with water, part of it burns and small part is shattered on the test-tube walls. By carefully adding more water to the test-tube, all small pieces of the alloy are converted into potassium and sodium hydroxides that remain dissolved in the water.

From what has been mentioned/demonstrated above, it becomes clear that the alloy reacts more vigorously with water than the individual metals. At first sight this is really peculiar. It might be explained, however, on the basis of what is generally known about electrochemical corrosion. When two metals are brought into contact (and the contact is a very intimate one in the homogenous liquid alloy) then the corrosion (the reaction with water in our case) of the less noble metal (K in our case) may be significantly enhanced.

It should be mentioned that more than half a century ago, this reaction was carefully researched both in the presence and in the absence of oxygen (Kilpatrick et al., 1953).

Reaction of the K-Na Alloy with Mercury

Note from experience. The reaction of K-Na alloy with mercury is much safer than the previous one. To the best of our knowledge, it has been reported in the literature only once (Najdoski & Petruševski, 2002).

Material. A test-tube with freshly prepared K–Na alloy, mercury, dropper, stand with clamp and screw-holder, transparent shield for protection of the audience (just as a precaution).

Procedure & observations. The test-tube with the alloy is clamped and fastened on a stand. The instructor takes ≈ 1 mL mercury from the bottle with the dropper (**Caution! Mercury is apt to run out of the dropper!**). Students are asked for attention and the mercury is quickly transferred to the test-tube with the K-Na alloy. Somewhat vigorous reaction occurs instantaneously (sparks are often seen). Heat is being released and in few seconds the formation of a solid (!) product occurs – potassium sodium amalgam. The product is usually of irregular shape and can be easily inspected (after cooling) by simply inverting the test-tube over a piece of paper. Very seldom, however, the product may be stuck on the test-tube walls (cf. Figure 4).

It is relatively safe to conclude that the amalgam

Figure 4. K–Na amalgam is occasionally stuck on the test-tube walls.

is intermetallic compound (or an alloy of two such compounds – one of sodium and one of potassium). However, it would be better to encourage students to explain their observations (two metallic liquids are mixed that in a vigorous reaction give solid product).

The obtained K–Na amalgam might be used to demonstrate that it reacts with water rather slowly (!), if compared with the rate of reaction of Na or K with water. However, there is a much more spectacular demonstration – the synthesis of ammonium amalgam.[3]

Synthesis and Properties of Ammonium Amalgam

Ammonium amalgam is well-known in the educational chemistry literature (Reedy, 1929; http://www.1911encyclopedia.org/Ammonia). However, in all reports its synthesis has always been based on previous preparation of sodium amalgam. Surprisingly, the preparation of the latter is more hazardous than the preparation of K–Na amalgam. This comes as a consequence of the fact that Na amalgam is generated from a solid Na and liquid Hg, where the contact is severally restricted. The reaction is usually performed by pressing pieces of Na with Hg in a mortar (this is much less appreciative method than the one described in the previous demonstration, where two metallic liquids are simply mixed).

Materials. A test-tube with K–Na amalgam (see previous demonstration), a beaker with concentrated aqueous solution of ammonium chloride, stand with clamp and screw-holder.

Procedure & observations. The test-tube with the alloy is clamped and fastened on a stand. The ins-

[3] In case the K–Na amalgam is not to be used the same day, it is best to keep it in a sealed evacuated tube.

tructor pours slowly the NH_4Cl solution in the test tube till it is half-filled. A series of spectacular events occurs, lasting ~ 10 minutes (cf. Figure 5).

Upon the very first contact of the K–Na amalgam with the saturated N $_4$Cl(aq), a grey, voluminous sponge-like substance forms. Its volume increases with time, and at certain point the substance floats on the surface of the solution (obviously the density becomes lower and lower, cf. Figure 5). This is ammonium amalgam. According to some authors, it should be considered as a mixture of mercury, ammonia and hydrogen. Others claim that many of its properties indicate it is true (although unstable) amalgam.

After a while, the grey voluminous mass starts to shrink. Bubbles are being emitted all the time. Slowly, the metallic luster reappears, the substance settles down to the test-tube bottom, and finally pure mercury is recovered.

Students are asked to think about the possible chemical changes and to write down chemical equations for each change.

Objectives

Briefly on the general objectives of these demonstrations: every experiment (individual or a demonstration one) leads to increasing of students' interest and to positive attitude to the subject and learning. Students simply need to see chemical phenomena, to carry out (wherever possible) their own experiments, and to feel in that way the chemistry and its benefits. Students are expected to develop ability for perception of the relevant changes during the experiment, to make correct description of the above and to interpret the results. One would also expect that they make correct predictions of the changes in a system under some given set of circumstances, to perceive the relation between the experiment and theory etc.

In the demonstrations offered below, there are several specific objectives:

(1) offering a simple and safe method for preparation of liquid K–Na alloy;
(2) showing that by simple pressing of two metals, a metallic liquid (an alloy) may be formed;
(3) demonstration of a safe method for the alloys' reaction with water;
(4) presentation of a rather safe method for synthesis of K–Na amalgam;
(5) showing that by simply mixing of two liquids (the alloy and mercury), a solid is formed (K–Na amalgam);
(6) using the synthesized K–Na amalgam to obtain NH_4 amalgam and demonstration of its properties.

The instructor should discuss with the students all of the above advantages in the proposed demos. The students are expected to notice that the alloy's properties (both physical and chemical) differ from those of the individual metals and to be capable to make correct interpretations of their observations. Students should also be capable to write down the chemical equations corresponding to the observed changes. They may also be given assignments (e.g. "Explain the increase of reactivity of K–Na alloy with respect to that of pure metals" and also "Explain the decrease of reactivity of K–Na amalgam, when compared to the reactivity of pure metals or their alloy" etc.).

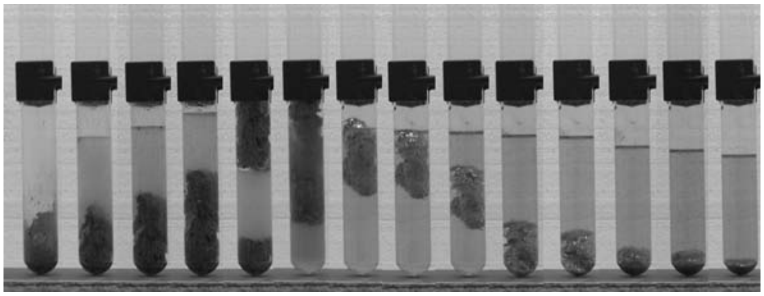

Figure 5. Spectacular changes upon addition of saturated NH_4Cl(aq) to K–Na amalgam (photos taken at 40 s interval)

Conclusions

Alkali metals experiments are one of the most interesting in chemistry and one of the most dangerous at the same time. For that reason this kind of experiments must always be carried out with caution.

The demonstration given in this paper is appropriate for students of the final year in high school or for university students.

There are several important aspects arising from the above demonstrations:

- all of the above demonstrations are very interesting for students;
- the demonstrations do not take too much time of the class;
- each demonstration is easy to perform and simple apparatus is being used, which is one of the main advantages;

- the chemical changes are easily perceptible;
- a much safer method for preparation of K–Na amalgam (as compared to the preparation of Na amalgam) is offered;
- the amalgam is used to synthesize the unstable NH_4 amalgam that is itself a spectacular demonstration;
- as always, an experiment is a much better tool for strengthening the knowledge system than a monotonous lecture.

References

Atkins, P. W., *Physical Chemistry*, 2nd edition, Oxford University Press, p. 298–301, 1982.

BASF, *Sodium-Potassium Alloy (NaK)*, Technical data sheet, December, 2004 (http://www. basf.com/inorganics/pdfs/tech_datasheet/NaK.pdf, accessed October 2006).

Bain, G., Bruce, K., Jacobsen, J. J., Moore, J. W., *Chemistry comes alive*, Vol. 4, JCE, http://jchemed.chem.wisc.edu/jcesoft/cca/CCA4/MAINPT/Cm Cz_elt/Cs.HTM#Water accessed October, 2006).

Greanwood, N. N., Earnshaw, A., *Chemistry of the Elements*, 2nd edition, Butterworth-Heinemann, Oxford, p. 1206, 1998.

http://theodoregray.com/PeriodicTable/Stories/011.2/ (accessed October, 2006).

http://yarchive.net/med/sodium_metal.html (accessed October, 2006).

http://www.1911encyclopedia.org/Ammonia (accessed October, 2006)

http://www.hooverandstrong.com/articles/?id=41 (accessed October, 2006)

http://www.jtbaker.com/msds/englishhtml/w3500. htm (accessed October, 2006).

http://www.signachem.com/SiGNa_science_highlight_p21.pdf (accessed October, 2006).

http://www.wwnorton.com/chemistry/overview/ch18.htm (accessed October, 2006).

Kilpatric, M., Baker, L. L. Jr., McKinney, C. D. Jr., Studies of Fast Reactions Which Evolve Gases. The Reaction of Sodium-Potassium Alloy with Water in the Presence and Absence of Oxygen, *Journal of Chemical Physics*, **57**, 385–390, 1953.

Matijasevic G. S., Lee C. C., Wang C. Y., Au-Sn Alloy Phase Diagram and Properties Related to its Use as a Bonding Medium, *Thin Solid Films,* **223**, 276–287, 1993.

Najdoski, M. Ž, Petruševski, V. M., *The Experiment in the Chemistry Education II*, Magor, Skopje, p. 67–68, 2002 (in Macedonian).

Nekrasov, B. V., *General Chemistry Course*, 6th edition, Nauçna knjiga, Beograd, p. 521, 1976 (translation from Russian into Serbian).

Ohsawa, T., Takagaki, T., Haneda, A., Oishi, T., *Tetrahedron Letters* **27**, 2583-2586, 1981.

Petruševski, V. M., Najdoski, M. Ž., A Safe Way of Performing Some Dangerous Experiments. I. Construction of a Safety Spoon, *The Chemical Educator*, **7**, 81–83, 2002a.

Petruševski, V. M., Najdoski, M. Ž., A Safe Way of Performing Some Dangerous Experiments. II. Construction of a Safety Dropper, *The Chemical Educator*, **7**, 220–222, 2002b.

Reedy, J. H., Lecture Demonstration of Ammonium Amalgam, *Journal of Chemical Education,* **6**, 1767–1769.

Siborov, E. I., On the Question of the Choice of Heat Carriers for Nuclear Reactors, *Atomic Energy*, **8**, 224–226, 1961.

Stowe, J. A., *Synthesis,* **6**, 495–496, 1989.

Verhovskii, V. N., *Techniques and Methods of Performing Chemistry Experiments in a College, Vol. 2, Zavod za izdavanje udžbenika SR Srbije, Beograd, p. 552, 1968 (translation from Russian into Serbian).*