doi:10.2533/chimia.2021.679 Chimia 75 (2021) 679–680

Chemical Education

A CHIMIA Column

Topics for Teaching: Non-existent Compounds and Fallacies in the Literature

Why We Are all Using a Nonexistent Substance: NH_4OH

Maurice Cosandey*

**Correspondence:* Dr. M. Cosandey, E-mail: maurice.cosandey@bluewin.ch, Ch. des Etourneaux 1,1162 St-Prex

Abstract: Ammonium hydroxide does not exist, but it is commercially available, although everybody knows that it should be called 'ammonia hydrate'. The reason is not scientific. It is purely commercial and will be explained in the text

Keywords: Ammonia · Ammonium · Hydroxide · Incompatibility · Mistake

If NH_4Cl is dissolved into water, its solution contains NH_4^+ and $Cl^–$ ions. If NaOH is dissolved into water, the solution contains Na^+ and $OH^–$ ions. Now if these two solutions are mixed, nearly all NH_4^+ and $OH^–$ will react and produce NH_3 and H_2O. This shows that NH_4OH cannot exist. It is decomposed into a solution of NH_3 in water, with only a few percent of NH_4^+ and $OH^–$ ions. You will certainly object and say that NH_4OH is a commercial substance, available anywhere on the market. You are correct (see Fig. 1). But you may not know that the reason for this mistake goes back to the 19th century. In the 19th century, ions were unknown. All substances had a chemical formula, whatever pure or in solution. NaOH in solution was made of NaOH and that is all. Charged ions like H_3O^+ and $OH^–$ did not exist.

In the 19th century, chemists often studied the neutralization reaction:

$$\text{Acid} + \text{Base} \rightarrow \text{Salt} + \text{Water}$$

They succeeded in carrying out this reaction with all sorts of mineral and organic acids, and with plenty of hydroxides (hydroxide was synonymous to base). When a new organic acid was discovered, they tried to make salts with all available hydroxides, and it worked. Each new series of salts deserved a publication. This was fine!

Of course, ammonia was a problem: NH_3 does react with any acid and produces a salt, but it does not produce any water. NH_3 + HCl makes NH_4Cl and that's all: no water! This was difficult to admit. So the chemists decided that, when dissolved in water, NH_3 is transformed into NH_4OH. This makes sense, because NH_3 is very soluble in water, as if a chemical reaction happens. It was fine. When neutralizing a solution of ammonia by reaction with an acid, the equation of the reaction was similar to:

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

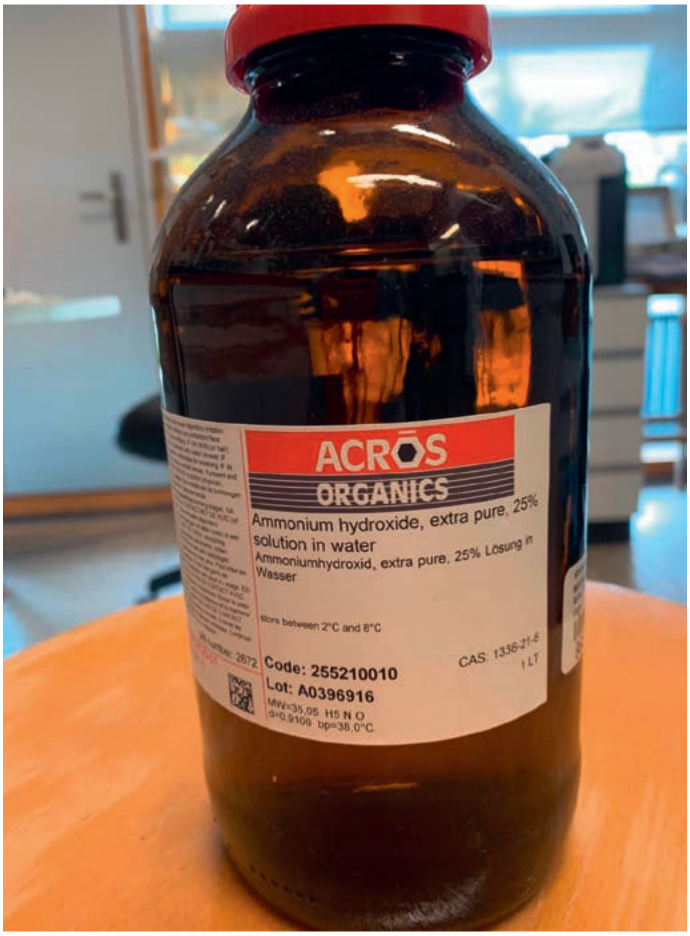

Fig. 1. Commercial bottle of concentrated ammonia solution (25% NH_3), with the incorrect label 'Ammonium hydroxide 25% in water'. If ammonium hydroxide would have existed, the concentration would have been 51.4% NH_4OH.

NH_3 only exists in a gaseous state. It was considered as a sort of 'dehydrated ammonium hydroxide'. A little bit like other hydroxides, which can easily lose water. At high temperature, $Cu(OH)_2$ becomes CuO and $Al(OH)_3$ becomes Al_2O_3.

So the merchants started to sell ammonia solution with the label NH_4OH. It was soon discovered that this solution is helpful unblocking blocked-up pipes. Everything was OK!

Unfortunately at the end of the 19th century, Arrhenius discovered the ions, and showed that NH_4^+ and $OH^–$ ions cannot exist simultaneously in solution. Disaster! The so-called 'ammonium hydroxide' did not exist any more. It mainly contained NH_3 and H_2O, with only a few percent of remaining NH_4^+ and OH^- ions. So the merchants changed their labels and started to sell 'concentrated ammonia solution 25%'. It was OK for the chemists.

But this change was not accepted by the caretakers, managers and contractors. They protested to the manufacturers against this

Would you like to publish a Chemical Education topic here?
Please contact: Prof. Catherine Housecroft, University of Basel, E-mail: Catherine.Housecroft@unibas.ch

new 'ammonia solution' which was useless to unblock blocked pipes. They said they have tried the new and the old solutions. They demanded to get the old ammonium hydroxide, which was 'much better' than this 'miserable' ammonia solution. Well! The merchants were not stupid. They want to sell their product and get money. So they renounced the modernization of their labels, and continued to print NH_4OH on NH_3 solutions. This was accepted by chemists and non-chemists, although the label mentions 25% for the concentration. But this concentration is related to NH_3 and not to NH_4OH. The reader is probably supposed to correct the label. See the mistake in Fig. 1.

This is why NH_4OH is still on sale today. I am an old man, 84. This story was reported to me by my father, who was a chemist in the beginning of the 20th century and who remembered this old time. It is even surprising that the preceding story has not been published in the past. Several reports[1–4] have been published about the strange non-existence of a commercial product like NH_4OH, but without giving the origin of this peculiarity. Is the present publication the first one to propose an explanation?

As a more recent complement, new arguments have been published. The geometry and bond lengths of NH_4OH have been calculated using Gaussian,[5] the D95 basis set and the B3LYP method.The bond lengths are as follows :

- Three N–H bonds in NH_3: 102 pm
- N–H hydrogen bonds between N and H-O-H: 179 pm
- Two O–H bonds in H2O: 98 and 100 ppm.

According to S. J. Hawke,[5] the hydrogen bond between H from water and N from ammonia is much longer (179 pm) and therefore weaker than the covalent bond N–H in ammonia (102 pm). So, it is misleading to speak of it as part of a NH_4 group, as if the four bonds were similar. Moreover the length of the two OH bonds in H_2O are almost identical, the one that is hydrogen bonded to the N is 2% longer than the other. There is no neutral NH_4 group in the ammonia solution. As a consequence, the NH_4 group does not exist in the ammonia solution. Only a few per cent of the ammonia is transformed into ammonium and hydroxide ions.

Received: January 29, 2021

[1] T. R. Tuttle, *J. Chem. Educ*. **1991**, *68*, 533.
[2] G. B. Kauffman. *J. Chem. Educ*. **1991**, *68*, 534.
[3] J. Yoke, *J. Chem. Educ*. **1989**, *66*, 310.
[4] M. Laing, *Education in Chem*. **1992**, July, 116.
[5] S. J. Hawkes, *J. Chem. Educ*. **2004**, *81*, 1569, https://doi.org/10.1021/ed081p1569.3

For further reading:

F. F. Rupert, 'Hydration of Ammonia', *J. Am. Chem. Soc.* **1909**, *31*, 866.
J. B. Davis, 'About the Fiction of the Ammonium Hydroxide', *J. Chem. Educ.* **1953**, *20*, 511.
P. A. Kollmann, 'Complex Water - Ammonia', J. Am. Chem. Soc. 1971, 93, 4991
J. B. Dill, 'About ammonia and Water', *J. Am. Chem. Soc.* **1975**, *97*, 7220
B. Nelander, 'Complex Between Water and Ammonia', *J. Phys. Chem.* **1982**, *86*, 4375
J. A. Young, 'Aqueous Ammonia', *J. Chem. Educ.* **2003**, *80*, 24.