Reaction of aluminium with dilute nitric acid containing dissolved sodium chloride: on the nature of the gaseous products

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A recent paper on the reactivity of aluminium in mineral acids, particularly nitric acid (Petruševski *et al.*, 2010) rediscovers some all but forgotten chemical behavior of this metal:

"It is really unusual that some elementary chemistry of such well-known metals as aluminium is either missing from the chemistry textbooks, or is simply wrong. The reactions of aluminium with concentrated and diluted acids may serve as a good example for the above assertion. In many of the standard textbooks of general/inorganic chemistry (Parkes, 1961; Wiberg, 1967; Nekrasov, 1971; Glinka, 1986; Brady, 1990; Greenwood & Earnshaw, 1998) one finds that aluminium does not react with concentrated nitric acid and this is indeed true. However, regarding other strong acids one finds quite a number of various statements. Some of the above textbooks (Parkes, 1961; Wiberg, 1967; Nekrasov, 1971) were rather old, and for that reason their reliability was initially considered as being questionable. The information found in the newer ones (Glinka, 1986; Brady, 1990; Greenwood & Earnshaw, 1998) are not consistent. Thus, according to Glinka (1986) and Brady (1990), aluminium reacts with diluted acids displacing hydrogen, while Greenwood & Earnshaw (1998) say that the protective oxide cover prevents any reaction with diluted acids. On the other hand, the experiments of Najdoski & Petruševski (2002) show that the only reaction that occurs in real time with diluted acids at room temperature is the reaction with HCl(aq), giving rise to hydrogen gas and aqueous solution of aluminium chloride. Therefore, the simple chemical reaction based on the equation

$$2Al_{(s)} + 6H^+ = 3H_{2(g)} + 2Al^{3+}_{(aq)}$$
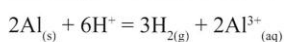
seems not to be operative for strong acids other than HCl! That being so, one is faced with a widespread preconception about the negligible role of the spectator ions in reactions of hydrogen displacement, at least for reactions including aluminium. This problem is addressed elsewhere (Stojanovska & Petruševski, 2011). At this point it may be interesting to say that, although an old one, Mellor's textbook (Parkes, 1961) gives information that seems to be the most accurate and the most relevant ones.

"In the course of the reinvestigation of the reactions of aluminium with strong inorganic acids (concentrated and diluted) one fact soon became obvious: aluminium is readily dissolved in practically all strong acids, providing the solution contains chloride ions (obviously acting as a catalyst). Traces of Cu^{2+} ions further catalyse the process."

Partington's (1947) textbook notes that aluminum is attacked by seawater. The pitted aluminium window joinery seen in buildings located in windy coastal areas of New Zealand shows the truth of this statement (see also: "Corrosion of Aluminium and Aluminium Alloys", n.d.). Moreover, aluminum is not the only metal that can be corroded in this way. Non-marine grades stainless steel used as sheathing of the Michael Fowler Centre corroded under the onslaught of Wellington's salt laden southerly winds (Rawding, 1985), and corrosion of stainless steel hot water tanks containing water with significant amounts of chloride-ion is well known (e.g., Krady, 2008).

"The [gaseous] product thus obtained is practically pure hydrogen, in all cases except where one deals with nitric acid. The product of the reaction with diluted nitric acid is again, a gas (depending on the quantity of the added Cu^{2+} ions the reaction may be somewhat vigorous). In all instances but one, where a minor puff occurred, the product gas was nonflammable, thus suggesting that hydrogen is far from being the principal component. One of us proposed to analyse the product using FT-IR spectroscopy."
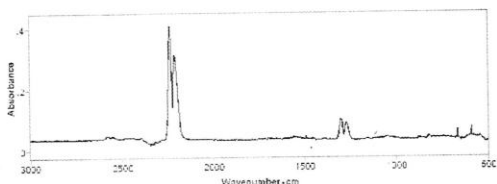
"The spectra were obtained using the Perkin Elmer System 2000 FT-IR interferometer in the 3000-500 cm^{-1} region. A Perkin Elmer gas cell was used (cell length ~10 cm, CsBr windows for the measurements. For measuring the background spectrum, the cell was filled with air and the sample spectrum was recorded. Low resolution spectra (resolution of 4 cm^{-1}) perfectly served the purpose. 16 scans were accumulated for both the background and the sample

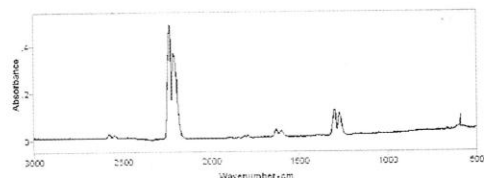spectra. GRAMS 32 programme package was used for spectra manipulation."

"Concentrated nitric acid was diluted to 1:2 with distilled water (volume ratios of acid and water). 10 mL of the diluted acid were taken and ~ 1 g of NaCl [added]. After the salt was dissolved a grain of aluminium was added together with a drop of copper(II) chloride solution with $w(CuCl_2) = 0.05$. After the evolution [of gas] becomes vigorous enough, the gas was collected in the cell (precautions were taken for preventing microscopic droplets of the liquid to enter the cell). Another sample with several drops of copper(II) chloride was also prepared (this reacts more vigorously with the aluminum). The [gaseous] product was again collected and its spectrum was analysed."

"The spectrum of the product (presumably a gaseous mixture) is given in Figs 1 and 2. The wavenumbers of the three strongest bands (v_3, 2223; v_1, 1285 and v_2, 589 cm^{-1}) are in excellent agreement with those reported for nitrous oxide (Nakamoto, 1986). The band at *ca* 2563 cm^{-1} can be safely attributed to the $2v_1$ mode. Further check and comparison with the spectrum of N_2O taken from metal cylinder show beyond any doubt that the polyatomic molecules belong to N_2O (nitrous oxide). The presence of H_2 or N_2 cannot be precluded in this way (being homonuclear diatomics, they are IR inactive)."

The authors of the original article proposed a mechanism that involved the production of atomic hydrogen by the reaction of aluminum and hydrochloric acid and its subsequent reaction with nitric acid to produce nitrous oxide. An alternative mechanism is for aluminium oxide on the aluminium metal to be initially dissolved by the acid, perhaps itself catalyzed by Cl$^-$, i.e.,

$$Al_2O_3 + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3H_2O$$
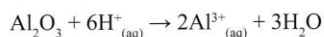
… followed by the oxidation of the exposed aluminium metal by nitrate ion, represented by the following half-reactions:

$$Al \rightarrow Al^{3+}_{(aq)} + 3e^-$$

$$10H^+_{(aq)} + 8e^- + 2NO_3^- \rightarrow N_2O_{(g)} + 5H_2O$$
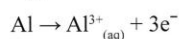
"The product obtained from the reaction mixture containing several drops of copper(II) chloride (Fig. 2) contains N_2O as the major component, as well as traces of other gases (like NO_2, evidenced by the band at 1617 cm^{-1}, again in excellent agreement with the literature value (Arakawa & Nielsen, 1958)."

In explanation, the authors of the original article suggest:

"The appearance of the NO_2 impurities, in the presence of higher concentrations of Cu^{2+} ions in solution, might be explained by the displacement of copper with aluminium

$$2Al_{(s)} + 3Cu^{2+}_{(aq)} = 3Cu_{(s)} + 2Al^{3+}_{(aq)}$$
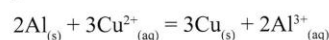
and subsequent reaction of the elemental copper with the diluted HNO_3

$$3Cu_{(s)} + 8HNO_{3(aq)} = 2NO_{(g)} + 3Cu(NO_3)_{2(aq)} + 4H_2O"$$
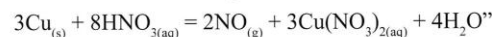
Since all nitrates are highly soluble, the species $Cu(NO_3)_{2(aq)}$ seems unlikely to exist in water, so that this latter reaction could be perhaps better expressed as the combination of the half-reactions:

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$$

$$6H^+_{(aq)} + NO_3^-_{(aq)} + 5e^- \rightarrow NO_{(g)} + 3H_2O$$
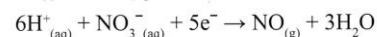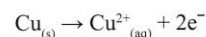
In any event this reaction is "followed by the immediate oxidation of the NO gas with atmospheric oxygen

$$2NO_{(g)} + O_{2(g)} = 2NO_{2(g)}"$$
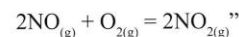
"The principal product of the reaction, N_2O, is also one of the products in the reaction of zinc with nitric acid (together with NO, NO_2 and perhaps N_2). However, there is no reaction at all between aluminium and diluted nitric acid (most probably due to the protective covering of aluminium oxide (Greenwood & Earnshaw, 1998)), unless the solution contains chloride ions."

The original article draws attention to some rather overlooked matters of metal-acid interactions,

Fig. 1: *FT-IR spectrum of the product of the reaction between Al and diluted HNO_3 containing one drop of $CuCl_2(aq)$. The spectrum matches the spectrum of N_2O; the sharp peak at ~667 cm^{-1} is attributed to CO_2 uncompensations (Petruševski et al., 2010).*


Fig. 2: *FT-IR spectrum of the product of the reaction between Al and diluted HNO_3 containing several drops of $CuCl_2(aq)$. The spectrum matches the spectrum of N_2O; the peak at ~1617 cm^{-1} is attributed to traces of NO_2, and the nature of that at ~1800 cm^{-1} is open to discussion (Petruševski et al., 2010).*

which could be the subject of some simple experiments for science classes, comparing, for example, the behavior of 'unscraped' and 'scraped' aluminium (i.e., with oxide coating removed) in acids of varying strengths and in different acids. The article suggests that the rates of release of hydrogen will be seen to differ markedly, even if it is not possible to determine the existence and composition of other gaseous products.

The overall reactivity of aluminum under various pH and oxidising conditions can be represented on a Pourbaix diagram (Fig. 3, based on "Aluminum E-pH diagram" (n.d.)). While the boundaries of the regions on this diagram are concentration-dependent, it is clear that on thermodynamic grounds dissolution of aluminum would be expected in acidic environments with pH < 4.0. That this does not always occur suggests that some of these reactions are slow.

Secondly, the article introduces the idea of catalytic dissolution of metals. As the authors note, addition of $Cu^{2+}(aq)$ affects not only the type of gases produced when aluminum reacts with nitric acid, but also appears to affect the rate of production of hydrogen. This latter observation may be a manifestation of a colleague's observation:

"A fascinating demonstration of a redox reaction is to join a copper wire to a piece of zinc and drop it into dilute acid. Bubbles of hydrogen pour off the copper, but it is the zinc that dissolves – demonstrat-ing that the reduction and oxidation sites can be well separated providing there is a metallic connection." (Jim Pearce, personal communication).

These observations again provide opportunities for a number of simple experiments, for which the explanations might admittedly be complex. Finally, the article reminds us that 'old' chemistry textbooks may be worth mining for interesting tidbits of forgotten or overlooked chemical phenomena.

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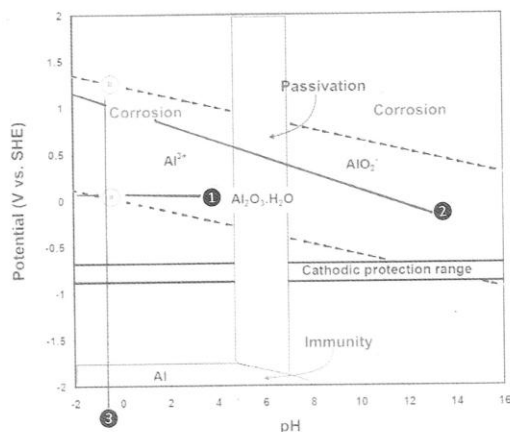
Fig. 3: *Pourbaix diagram for aluminium showing the expected Eh and pH where the metal has total immunity from corrosion and where it is totally or partially covered by oxide of hydroxide. Also shown are: ❶, Eh and pH relationships for the oxidation of Cu to $Cu^{2+}(aq)$; and ❷, reduction of $NO_3^-(aq)$ to $N_2O(g)$, concentrations of the aqueous species assumed to be $10^{-6}M$. Vertical line ❸ is the pH of the inferred 4.7M nitric acid used in the experiments The lines marked (a) and (b) are the lower and upper limits of Eh and pH in the natural environment.*