Aqua regia

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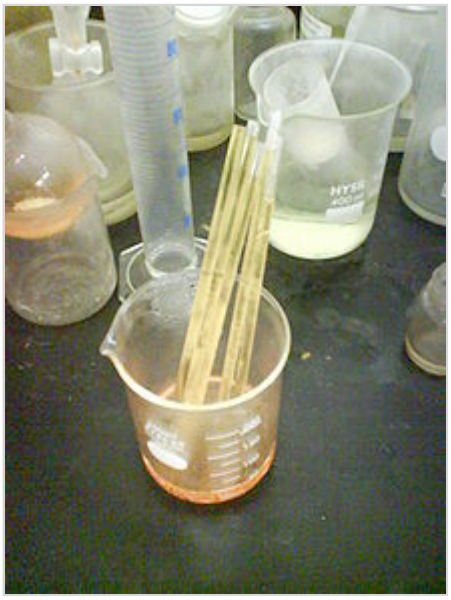
Aqua regia or **aqua regis** (Latin for **royal water** or **king's water**) is a highly corrosive, fuming yellow or red solution, also called **nitro-hydrochloric acid.** The mixture is formed by freshly mixing concentrated nitric acid and concentrated hydrochloric acid, usually in a volumetric ratio of 1:3 respectively. It was named so because it can dissolve the so-called "royal metals," or noble metals, gold and platinum. However, tantalum, iridium, osmium, titanium, rhodium and a few other metals are capable of withstanding chemical attack from it.



Freshly prepared aqua regia is colorless, but it turns orange within seconds. Here, fresh aqua regia has been added to these NMR tubes to remove all traces of organic material.

Contents

Freshly prepared aqua regia to remove metal salt deposits.

Applications

Aqua regia is primarily used to produce chloroauric acid, the electrolyte in the Wohlwill process. This process is used for refining highest quality (99.999%) gold. (See dissolving gold)

Aqua regia is also used in etching and in specific analytic procedures. It is also used in some laboratories to clean glassware of organic compounds and metal particles. This method is preferred over the "traditional" chromic acid bath for cleaning NMR tubes, because no traces of paramagnetic chromium can remain to later spoil acquired spectra.[1] Furthermore, chromic acid baths are discouraged because of the high toxicity of chromium and the potential for explosions. Aqua regia is itself very corrosive and has been implicated in several explosions due to mishandling.[2]

Due to the reaction between its components resulting in its decomposition, aqua regia quickly loses

its effectiveness. As such, its components should only be mixed immediately before use. While local regulations may vary, aqua regia may be disposed of by carefully neutralizing with an appropriate agent—such as sodium bicarbonate—before pouring down the sink. If there is a large amount of metal in solution with the acid, it may be preferable to carefully neutralize it, and absorb the solution with a solid material such as vermiculite before discarding it with solid waste.

Chemistry

Dissolving gold

Aqua regia dissolves gold, though neither constituent acid will do so alone, because, in combination, each acid performs a different task. Nitric acid is a powerful oxidizer, which will actually dissolve a virtually undetectable amount of gold, forming gold ions (Au^{3+}). The hydrochloric acid provides a ready supply of chloride ions (Cl^-), which react with the gold ions to produce chloroaurate anions, also in solution. The reaction with hydrochloric acid is an equilibrium reaction which favors formation of chloroaurate anions ($AuCl_4^-$). This results in a removal of gold ions from solution and allows further oxidation of gold to take place. The gold dissolves to become chloroauric acid. In addition, gold may be dissolved by the free chlorine present in aqua regia. Appropriate equations are

Pure gold precipitate produced by the aqua regia chemical refining process

$$Au\ (s) + 3\ NO_3^-\ (aq) + 6\ H^+\ (aq) \rightarrow Au^{3+}\ (aq) + 3\ NO_2\ (g) + 3\ H_2O\ (l)\ \text{and}$$

$$Au^{3+}\ (aq) + 4\ Cl^-\ (aq) \rightarrow AuCl_4^-\ (aq).$$

The oxidation reaction can also be written with nitric oxide as the product rather than nitrogen dioxide:

$$Au\ (s) + NO_3^-\ (aq) + 4\ H^+\ (aq) \rightarrow Au^{3+}\ (aq) + NO\ (g) + 2\ H_2O\ (l).$$

Dissolving platinum

Similar equations can be written for platinum. As with gold, the oxidation reaction can be written with either nitric oxide or nitrogen dioxide as the nitrogen oxide product.

$$Pt\ (s) + 4\ NO_3^-\ (aq) + 8\ H^+\ (aq) \rightarrow Pt^{4+}\ (aq) + 4\ NO_2\ (g) + 4\ H_2O\ (l)$$

$$3Pt\ (s) + 4\ NO_3^-\ (aq) + 16\ H^+\ (aq) \rightarrow 3Pt^{4+}\ (aq) + 4\ NO\ (g) + 8\ H_2O\ (l)$$

The oxidized platinum ion then reacts with chloride ions resulting in the chloroplatinate ion.

$$Pt^{4+}\ (aq) + 6\ Cl^-\ (aq) \rightarrow PtCl_6^{2-}\ (aq)$$

Experimental evidence reveals that the reaction of platinum with aqua regia is considerably more complex. The initial reactions produce a mixture of chloroplatinous acid (H_2PtCl_4) and nitrosoplatinic chloride ($(NO)_2PtCl_4$). The nitrosoplatinic chloride is a solid product. If full dissolution of the platinum is desired, repeated extractions of the residual solids with concentrated hydrochloric acid must be performed.

$$Pt\ (s) + 2\ HNO_3\ (aq) + 4\ HCl\ (aq) \rightarrow (NO)_2PtCl_4\ (s) + 3\ H_2O\ (l) + 1/2\ O_2\ (g)$$

$$(NO)_2PtCl_4\ (s) + 2\ HCl\ (aq) \rightarrow H_2PtCl_4\ (aq) + 2\ NOCl\ (g)$$

The chloroplatinous acid can be oxidized to chloroplatinic acid by saturating the solution with chlorine while heating.

$$H_2PtCl_4\ (aq) + Cl_2\ (g) \rightarrow H_2PtCl_6\ (aq)$$

Dissolving platinum solids in aqua regia was the mode of discovery for the most dense metals. Iridium and osmium, both of which are found in platinum ore and will not be dissolved by the acid, instead collecting on the base of the vessel.

Reactions with other metals

Aqua regia reacts with tin to form tin(IV) chloride, containing tin in its highest oxidation state:

$$4\ HCl + 2\ HNO_3 + Sn \rightarrow SnCl_4 + NO_2 + NO + 3\ H_2O$$

Decomposition of aqua regia

Upon mixing of concentrated hydrochloric acid and concentrated nitric acid, chemical reactions occur. These reactions result in the volatile products nitrosyl chloride and chlorine as evidenced by the fuming nature and characteristic yellow color of aqua regia. As the volatile products escape from solution, the aqua regia loses its potency.

$$HNO_3\ (aq) + 3\ HCl\ (aq) \rightarrow NOCl\ (g) + Cl_2\ (g) + 2\ H_2O\ (l)$$

Nitrosyl chloride can further decompose into nitric oxide and chlorine. This dissociation is equilibrium-limited. Therefore, in addition to nitrosyl chloride and chlorine, the fumes over aqua regia contain nitric oxide.

$$2\ NOCl\ (g) \rightarrow 2\ NO\ (g) + Cl_2\ (g)$$

History

Aqua regia is mentioned in the world's first encyclopedia, published in AD 77 by Pliny the Elder (Gaius Plinius Secundus, AD 23-79).

Aqua regia was used around the year 800 by the alchemist Jābir ibn Hayyān (Geber). Jabir's use of gold-dissolving aqua regia, consisting of hydrochloric acid and nitric acid, was used to in the fruitless efforts of alchemists to find the philosopher's stone.[3]

Lavoisier called it nitro-muriatic acid in 1789.[4]

When Germany invaded Denmark in World War II, the Hungarian chemist George de Hevesy dissolved the gold Nobel Prizes of Max von Laue and James Franck in aqua regia to prevent the Nazis from stealing them. He placed the resulting solution on a shelf in his laboratory at the Niels Bohr Institute. It was subsequently ignored by the Nazis who thought the jar—one of perhaps hundreds on the shelving—contained common chemicals. After the war, de Hevesy returned to find the solution undisturbed and precipitated the gold out of the acid. The gold was returned to the Royal Swedish Academy of Sciences and the Nobel Foundation who recast the medals and again presented them to Laue and Franck.[5]

In literature

- *Cryptonomicon,* by Neal Stephenson - The fuel for the "Galvanick Lucipher" (a sort of specialized lantern) used by the butler Ghnxh on Qwghlm.
- *The Crying of Lot 49,* by Thomas Pynchon - During *The Courier's Tragedy,* the faithful servant Ercole pours aqua regia into a steel box around the traitor Domenico's head.
- *Octopussy,* a James Bond film; Bond is provided by Q with a fountain pen containing a mixture of hydrochloric and nitric acids, which Bond utilizes to cut his way through metal prison bars.
- In the children's novel *Pigeon Post,* by Arthur Ransome, Dick Callum dissolves the ore they have discovered in Aqua Regia, and thinks it is gold, not an ore of copper. But copper is what Captain Flint and Timothy wanted to find.
- In "The Devil In The Dark," an episode of *Star Trek's* first season in the Original Series, as James Blish wrote in his script novelizations, the silicon-based *horta* exudes aqua regia naturally as it tunnels through rock.

See also

- Aqua fortis
- Aqua vitae
- Chromic acid
- Digger gold
- Sulfuric acid
- Nitric acid

References

1. ^ Hoffman, R., How to make an NMR sample (http://chem.ch.huji.ac.il/nmr/preparation/preparation.html) , Hebrew University, 10 Mar 2005. Accessed 31 Oct 2006.
2. ^ American Industrial Hygiene Association, Laboratory Incidents: Explosions (http://www2.umdnj.edu/eohssweb/aiha/accidents/explosion.htm) , 8 Dec 2004. Accessed 31 Oct 2006.
3. ^ Hassan, Ahmad Y. "Technology Transfer in the Chemical Industries" (http://www.history-science-technology.com/Articles/articles%2072.htm) . *History of Science and Technology in Islam*. http://www.history-science-technology.com/Articles/articles%2072.htm. Retrieved 2008-03-29.
4. ^ *Elements of Chemistry*, p. 116
5. ^ Birgitta Lemmel (2006). "The Nobel Prize Medals and the Medal for the Prize in Economics" (http://nobelprize.org/nobel_prizes/medals/) . The Nobel Foundation. http://nobelprize.org/nobel_prizes/medals/.

External links

- Chemistry Comes Alive! Aqua Regia (http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA3/MAIN/AQREGIA/PAGE1.HTM)
- The Columbia Encyclopedia: Aqua Regia (http://www.bartleby.com/65/aq/aquaregi.html)

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