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Aqua regia

Aqua regia (/ˈreɪgiə, ˈriːdʒiə/; from Latin, lit. "regal water" or "king's water") is a mixture of nitric acid and hydrochloric acid, optimally in a molar ratio of 1:3.[note 2] Aqua regia is a yellow-orange (sometimes red) fuming liquid, so named by alchemists because it can dissolve the noble metals, gold and platinum, though not all metals.

Contents

Manufacture and decomposition

Upon mixing of concentrated hydrochloric acid and concentrated nitric acid, chemical reactions occur. These reactions result in the volatile products nitrosyl chloride and chlorine gas:

$$HNO_{3\,(aq)} + 3\,HCl_{\,(aq)} \rightarrow NOCl_{\,(g)} + Cl_{2\,(g)} + 2\,H_2O_{\,(l)}$$

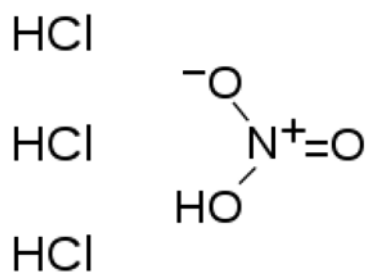
as evidenced by the fuming nature and characteristic yellow color of aqua regia. As the volatile products escape from solution, the aqua regia loses its potency. Nitrosyl chloride can further decompose into nitric oxide and chlorine:

$$2\,NOCl_{\,(g)} \rightarrow 2\,NO_{\,(g)} + Cl_{2\,(g)}$$

This dissociation is equilibrium-limited. Therefore, in addition to nitrosyl chloride and chlorine, the fumes over aqua regia contain nitric oxide. Because nitric oxide reacts readily with atmospheric oxygen, the gases produced also contain nitrogen dioxide, NO_2:

$$2\,NO_{\,(g)} + O_{2\,(g)} \rightarrow 2\,NO_{2\,(g)}$$

Aqua regia[note 1]



Names	
IUPAC name nitric acid hydrochloride	
Other names Aqua regis Nitrohydrochloric acid Royal water	
Identifiers	
CAS Number	8007-56-5 (http://www.commonchemistry.org/ChemicalDetail.aspx?ref=8007-56-5)
3D model (JSmol)	Interactive image (https://chemapps.stolaf.edu/jmol/jmol.php?model=%5BN%2B%5D%28%3DO%29%28O%29%5BO-%5D.Cl)
PubChem CID	90477010 (https://pubchem.ncbi.nlm.nih.gov/compound/90477010)
CompTox Dashboard (EPA)	DTXSID50893666 (https://comptox.epa.gov/dashboard/DTXSID50893666)
SMILES	
[N+](=O)(O)[O-].Cl	
Properties	

Applications

Aqua regia is primarily used to produce chloroauric acid, the electrolyte in the Wohlwill process for refining the highest quality (99.999%) 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 among most over the more traditional chromic acid bath for cleaning NMR tubes, because no traces of paramagnetic chromium can remain to spoil spectra.[1] While 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 (yet remains a strong acid), so its components are usually only mixed immediately before use.

While local regulations may vary, aqua regia may be disposed of by careful neutralization, before being poured down the sink. If there is contamination by dissolved metals, the neutralized solution should be collected for disposal.[3][4]

Chemical formula	HNO_3+3 HCl
Appearance	Red, yellow or gold fuming liquid
Density	1.01–1.21 g/cm^3
Melting point	−42 °C (−44 °F; 231 K)
Boiling point	108 °C (226 °F; 381 K)
Solubility in water	Miscible
Vapor pressure	21 mbar
Hazards	
NFPA 704 (fire diamond)	
Except where otherwise noted, data are given for materials in their standard state (at 25 °C [77 °F], 100 kPa).	
Infobox references	

Chemistry

Freshly prepared aqua regia to remove metal salt deposits

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 tetrachloroaurate(III) anions, also in solution. The reaction with hydrochloric acid is an equilibrium reaction that 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 chlorine present in aqua regia. Appropriate equations are:

$$Au + 3\ HNO_3 + 4\ HCl \rightleftharpoons [AuCl_4]^- + 3\ [NO_2] + [H_3O]^+ + 2\ H_2O$$

or

$$Au + HNO_3 + 4\ HCl \rightleftharpoons [AuCl_4]^- + [NO] + [H_3O]^+ + H_2O.$$

If the aqua regia solution only contains gold, solid tetrachloroauric acid may be prepared by boiling off excess aqua regia, and removing residual nitric acid by repeatedly heating with hydrochloric acid. That step reduces nitric acid (see decomposition of aqua regia). If elemental gold is desired, it may be

selectively reduced with sulfur dioxide, hydrazine, oxalic acid, etc.[5] The equation for the reduction of gold by sulfur dioxide is:

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.

$$2\ AuCl_4^-{}_{(aq)} + 3\ SO_{2(g)} + 6\ H_2O_{(l)} \rightarrow 2\ Au_{(s)} + 12\ H^+{}_{(aq)} + 3\ SO_4^{2-}{}_{(aq)} + 8\ Cl^-{}_{(aq)}.$$

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:

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

Pure gold precipitate produced by the aqua regia chemical refining process

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:

$$2Pt_{(s)} + 2HNO_{3\ (aq)} + 8\ HCl_{(aq)} \rightarrow (NO)_2PtCl_{4\ (s)} + H_2PtCl_{4\ (aq)} + 4\ H_2O_{(l)}$$

and

$$(NO)_2PtCl_{4\ (s)} + 2\ HCl_{(aq)} \rightleftharpoons H_2PtCl_{4\ (aq)} + 2\ NOCl_{(g)}.$$

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.

A platinum Soviet commemorative coin being dissolved in aqua regia.

4 days later.

Precipitating dissolved platinum

As a practical matter, when platinum group metals are purified through dissolution in aqua regia, gold (commonly associated with PGMs) is precipitated by treatment with iron(II) chloride. Platinum in the filtrate, as hexachloroplatinate(IV), is converted to ammonium hexachloroplatinate by the addition of ammonium chloride. This ammonium salt is extremely insoluble, and it can be filtered off. Ignition (strong heating) converts it to platinum metal:[6]

$$3\ (NH_4)_2PtCl_6 \rightarrow 3\ Pt + 2\ N_2 + 2\ NH_4Cl + 16\ HCl$$

Unprecipitated hexachloroplatinate(IV) is reduced with elemental zinc, and a similar method is suitable for small scale recovery of platinum from laboratory residues.[7]

Reaction with tin

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

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

Reaction with other substances

It can react with iron pyrite to formed nitrogen oxide:

$$FeS_2 + 5\ HNO_3 + 3\ HCl \rightarrow FeCl_3 + 2\ H_2SO_4 + 5\ NO + 2\ H_2O$$

History

Aqua regia was first mentioned in the works of Islamic alchemists such as Muhammad ibn Zakariya al-Razi (854-925),[8] and then later mentioned in a work of Pseudo-Geber (ca. 1300).[9] The third of Basil Valentine's keys (ca. 1600) shows a dragon in the foreground and a fox eating a rooster in the background. The rooster symbolizes gold (from its association with sunrise and the sun's association with gold), and the fox represents aqua regia. The repetitive dissolving, heating, and redissolving (the rooster eating the fox eating the rooster) leads to the buildup of chlorine gas in the flask. The gold then crystallizes in the form of gold(III) chloride, whose red crystals were known as dragon's blood. The reaction was not reported again in the chemical literature until 1890.[9]

Antoine Lavoisier called aqua regia nitro-muriatic acid in 1789.[10]

The fox in Basil Valentine's Third Key represents aqua regia, *Musaeum Hermeticum*, 1678

When Germany invaded Denmark in World War II, Hungarian chemist George de Hevesy dissolved the gold Nobel Prizes of German physicists Max von Laue (1914) and James Franck (1925) in aqua regia to prevent the Nazis from confiscating them. The German government had prohibited Germans from accepting or keeping any Nobel Prize after jailed peace activist Carl von Ossietzky had received the Nobel Peace Prize in 1935. De Hevesy 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. They re-cast the medals and again presented them to Laue and Franck.[11][12]

See also

- Nitric acid
- Hydrochloric acid
- Piranha solution is sometimes also used to clean glassware.

Notes

1. The information in the infobox is specific to a molar ratio of 1:3 between nitric acid and hydrochloric acid.
2. The relative concentrations of the two acids in water differ; values could be 65% w/v for nitric acid and 35% w/v for hydrochloric acid – that is, the actual HNO_3:HCl mass ratio is less than 1:2,

References

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12. Birgitta Lemmel (2006). "The Nobel Prize Medals and the Medal for the Prize in Economics" (http://nobelprize.org/nobel_prizes/about/medals/). The Nobel Foundation.

External links

- Chemistry Comes Alive! *Aqua Regia* (http://jchemed.chem.wisc.edu/JCESoft/CCA/CCA3/MAIN/AQREGIA/PAGE1.HTM)
- Aqua Regia (http://www.periodicvideos.com/videos/mv_aqua_regia.htm) at *The Periodic Table of Videos* (University of Nottingham)
- Demonstration of *Gold Coin Dissolving in Acid (Aqua Regia)* (https://www.youtube.com/watch?v=XoqU1GfIOkI)
