88/3b

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Chemical PastTimes/Petite Chronique archéologique

JOHAN GADOLIN'S 1788 PAPER MENTIONING THE SEVERAL OXIDATION STATES OF TIN AND THEIR DISPROPORTIONATION REACTION

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ABSTRACT. — We should like to rescue from oblivion a 1788 paper by J. Gadolin on a procedure of tin plating copper vessels using tartrates. The paper clearly states, as a general principle, the possibility of several oxidation states ("degrees of calcination") of the same metal. It also contains a vivid description of a disproportionation reaction involving these oxidation states. A short biography of Johan Gadolin (1760-1852) is given.

Johan Gadolin, a short biography

Johan Gadolin[1] *was born on 5th June 1760 in Åbo (in Finnish Turku) in Finland, which at that time (1155-1809) was an integral part of Sweden, and died on 15th August 1852. His grave can still be found in Mynämäki (in Swedish Virmo), where he possessed a manor.*

His father, Jakob Gadolin, and his maternal grandfather, Johan Browallius, had both been Professors of Physics at the Royal Åbo Akademi[2]*, before being promoted to Professors of Theology and, later, Bishops of Åbo. The family name has its own history: A Finnish farm name "Maunula" was first (re)latinized to "Magnulin" when one of the sons entered the learned path and changed later, replacing the Latin "magnus" by the Hebrew "gadol", to "Gadolin".*

The young Johan Gadolin started his university studies in 1775 in Åbo and continued them in Uppsala in 1779-1783 under Torbern Bergman (1735-1784), with a dissertation "De analysi ferri" in 1781 and another one, "De problemate catenario" in mathematics in 1782. After returning to Finland, Gadolin became a titular professor of chemistry at Åbo Akademi[2] *in 1785, an "Adjunkt" (Associate Professor) in 1789 and held the Chair of Chemistry from 1797 until his retirement in 1822, declining in 1804 the offer to succeed J. F. Gmelin at Göttingen. As Professor Emeritus he still lectured on Mineralogy. He should not be confused with his nephew Axel Gadolin (1828-1892, General and Professor at the Artillery Academy in St. Petersburg, author of a treatise on crystal symmetries).*

Johan Gadolin was a member of the Academies of Stockholm, St. Petersburg and Dublin and of the scientific societies of Göttingen, Uppsala, Moscow, Marburg, etc.

His production contains 58 original publications 1781-1827, including the textbook "Inledning till Chemien" (Åbo 1798) and 22 other published items in Crells Annalen or in Annales de Chimie[1c]*. Most of these papers deal with thermochemistry*

Johan Gadolin

Figure 1. — Johan Gadolin, a Finnish chemist (1760-1852).

FINNISH CHEMICAL LETTERS – ARGUMENTTEJA PUOLESTA JA VASTAAN

6. Käännös ja kielentarkastus. On jo aika, että kaikki tutkijat osaavat kirjoittaa julkaisunsa itse!

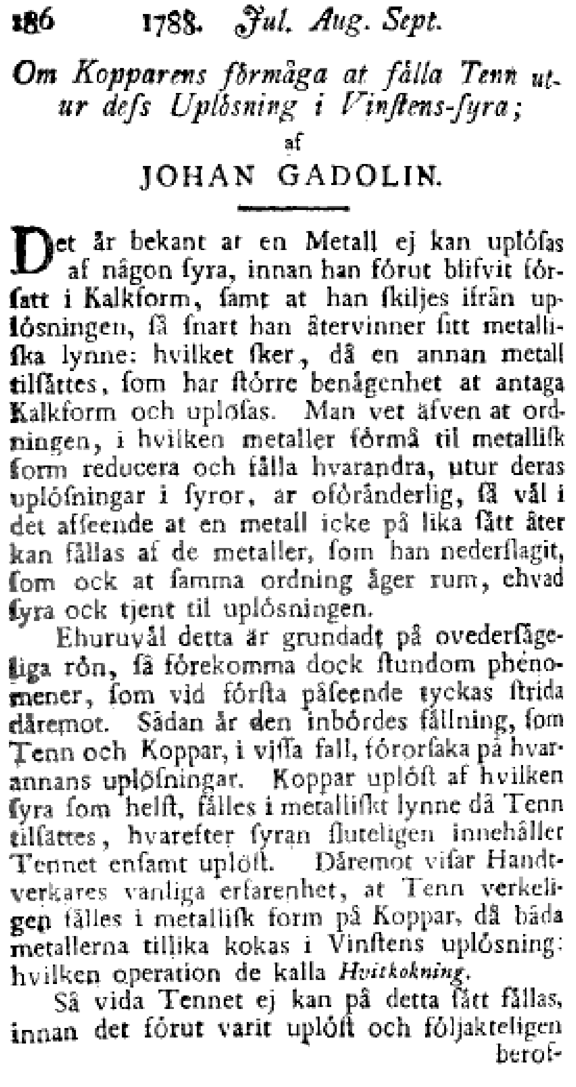
or inorganic chemistry. For instance his heat capacities and latent heats agree with later values within a few per cent (see ref. 1c, pp. xxii-xxiii). Gadolin's lectures and correspondence are also described in the 150-year memorial volume, ref. 1c. His administrative and industrial merits were only important for this own city and country, but not negligeable.

Gadolin was a student of Bergman, a good friend of Scheele (1742-1786) and still in full command of his powers when Berzelius (1779-1848) entered the scene. After the death of Scheele he probably was the most prominent chemist in Sweden. It is therefore not surprising that he was sent a sample of a new mineral, found at Ytterby near Stockholm by Captain Carl Axel Arrhenius and first reported by Geijer [3a]. Gadolin analysed the sample and reported in 1794 a new "earth" (mainly yttrium oxide)[3bc].

The mineral ($FeBe_2Y_2Si_2O_{10}$) was later named "gadolinite" and, much later, the element 64 "gadolinium". In 1788 this analysis was still six years ahead.

The 1788 paper "On the Ability of Copper to Precipitate Tin from its Solutions in Tartric Acid

In 1788 Johan Gadolin published a paper [4] in the Proceedings of the Royal Swedish Academy of Sciences on a rather practical problem, namely the procedure of tin-plating copper vessels using tartrates. We find this paper remarkable in that it enunciates, possibly for the first time, the existence of several valencies of the same metal and also the principle of disproportionation reactions. The same paper was soon translated into French [5] and German [6].



186 1788. *Jul. Aug. Sept.*

Om Kopparens förmåga at fålla Tenn utur deſs Uplösning i Vinſtens-ſyra;

af

JOHAN GADOLIN.

Det år bekant at en Metall ej kan uplóſas af någon ſyra, innan han fórut blifvit fórſatt i Kalkform, ſamt at han ſkiljes ifrån uplósningen, ſå ſnart han återvinner ſitt metalliſka lynne: hvilket ſker, då en annan metall tilſåttes, ſom har ſtórre benågenhet at antaga Kalkform och uplóſas. Man vet äfven at ordningen, i hvilken metaller fórmå til metalliſk form reducera och fålla hvarandra, utur deras uplóſningar i ſyror, ar ofóránderlig, ſå vål i det affeende at en metall icke på lika ſått åter kan fållas af de metaller, ſom han nederſlagit, ſom ock at ſamma ordning åger rum, ehvad ſyra ock tjent til uplósningen.

Ehuruvål detta är grundadt på ovederſågeliga rón, ſå fórekomma dock ſtundom phénomener, ſom vid fórſta påſeende tyckas ſtrida dåremot. Sådan år den inbórdes fållning, ſom Tenn och Koppar, i viſſa fall, fórorſaka på hvarannans uplóſningar. Koppar uplóſt af hvilken ſyra ſom helſt, fålles i metalliſkt lynne då Tenn tilſattes, hvarefter ſyran ſluteligen innehåller Tennet enſamt uplóſt. Dåremot viſar Handtverkares vanliga erfarenhet, at Tenn verkeligen fålles i metalliſk form på Koppar, då båda metallerna tillika kokas i Vinſtens uplósning: hvilken operation de kalla *Hvitkokning*.

Så vida Tennet ej kan på detta ſått fållas, innan det fórut varit uplóſt och fóljakteligen

berof-

Figure 2. – The title page of ref. 4.

This paper describes a series of experiments, started with J. G. Gahn earlier during the same summer. The puzzle was that "the order in which metals are able to reduce into metallic form and precipitate each other, from their solutions in acids, is unchanged...". In the case of copper and tin, tin reduces copper. Yet, "the common experience of Artisans shows that Tin indeed is precipitated in metallic form upon Copper when both metals are simultaneously boiled in Wine Stone solution, which operation they call White Cooking".

In the paper Gadolin describes sixteen experiments, of which we have repeated one (No 8. of the original paper):

1.88 g (10 mmol) of tin(II) chloride, dissolved in water, was added to a hot saturated aqueous solution of potassium hydrogen tartrate. After boiling the solution fór about three hours, a thin layer of tin was deposited on the copper plate.

The complexation chemistry of both copper and with tartrates is complex [7]. What is remarkabke, are the "two general statements that nobody should dispute:

1. That each metal is calcinated when he combines himself with a substance which is a common constituent of all metal chalks and also exists in air and water which I call the calcinating substance.

2. That a metal may take a chalk form to varying extent by combining himself with a larger or smaller amount of the calcinating substance; and thereby obtains a varying inclination to give back a part, or to combine itself with a larger amount thereof".

Evidently, in 1788, oxygen was not a new discovery. In fact, in an appendix to Gadolin's paper [4], Baron N. von Gedda quotes "le Principo Oxigene". What is remarkable, though, is the clear enunciation of the possibility of several oxidation states ("degrees of calcination") of the same metal [8]. The quantum mechanical (and possibly partially relativistic) explanation of the existence of Sn(II) and Sn(IV) is still being discussed by theoretical chemists [9]. The first scientist who experimentally demonstrated the existence of two oxidation states of tin seems to have been B. Pelletier in 1792 [10].

Galodin drew in his paper five conclusions (A - E). Of these, B) contains a clear description of a disproportionation reaction:

"When Tin, at the moment of dissolution, touches another metal, for instance Copper, which strongly attracts Metallic Tin, then on one hand this attraction of Copper towards the dissolved Tin closest to it, and on the other hand, the inclination of the other dissolved tin particles to still combine themselves with the amount of the calcinating substance, contained by the Tin nearest to Copper cause a disproportionation ("söndring") through which the last-mentioned Tin lays itself on the Copper surface, while the rest, which forms the majority, undergoes a greater degree of calcination."

While we have not tried to investigate whether

$$2\ Sn(II) \rightarrow Sn(IV) + Sn(0) \qquad (1)$$

is the reaction of central importance in the procedure mentioned, we find this description of a disproportionation process a vivid one.

Acknowledgement

We became aware of Gadolin's paper[4] *through a memorial article written by the late Professor Lars Sjöblom.*

REFERENCES

[1] (*a*) Asimov I., "*Biographical Encyclopedia of Science and Technology*", Avon Books, New York, 1976, p. 223 ; (*b*) Enkvist T., "*The History of Chemistry in Finland 1828-1918*", Soc. Sci. Fennica, Helsinki, 1972 ; (*c*) Hjelt E., Tigerstedt R., Eds, "*Johan Gadolin 1760-1852 in Memoriam*", Acta Soc. Sci. Fenn., **39**, 1910, xcviii + 287 p. ; (*d*) Klinge M., Knapes R., Leikola A. and Strömberg J., "*Kuninkaallinen Turun Akatemia 1640-1808*" ("The Royal Academy at Åbo 1640-1808", in Finnish), Otava, Helsinki, 1987.

[2] The old Åbo Akademi, established 1640, was moved to Helsinki in 1828. Gadolin's chair (established 1761) is now the Chair of Organic Chemistry at the University of Helsinki. A new, Swedish-speaking university named Åbo Akademi was founded at the original site in 1918.

[3] (*a*) Geijer B. R., *Crells chem. Annal.*, 1788, **I**, 229-230 ; (*b*) Gadolin J. *Kungl. Svenska Vetenskapsakademiens Handlingar*, 1794, 137-155 ; (*c*) Gadolin J., *Crells chem. Annal.*, 1796, 313-329.

[4] Gadolin J., "Om kopparens förmåga at fälla tenn utur dess uplösning i vinstens-syra", *Kungl. Svenska Vetenskapsakademiens Handlingar*, 1788, 186-197.

[5] Gadolin J., "Expériences sur la cause de la propriété du cuivre de précipiter l'étain dissous dans l'acide de tartre" Traduit du Suédois par Dollfuss *Observ. sur la physique, sur l'histoire naturelle et sur les arts, par Rozier, Mongez et de La Métherie*, 1789, **34**, 363-369. (As quoted in ref. 1*c*.)

[6] Gadolin J., "Von dem Vermögen des Kupfers das Zinn aus seinen Auflösungen in der Weinsteinsäure zu fällen", *Crells chem. Annalen*, 1790, **I**, 260-273. (Reprinted in ref. 1*c*.)

[7] Johansson L., *Acta Chem. Scand.*, 1980, **A34**, 495 and references there.

[8] Any claim of originality is left to the original author. In the summer of 1788 Gadolin had just returned from a two-year trip (1786-1788) to Denmark, Germany, Holland and the British Isles. Ref. 4 does not have a single reference.

[9] Pyykkö P., *Chem. Rev.*, 1988, **88**, 563.

[10] See Kopp, *Geschichte der Chemie*, Vol. 4, p. 129 (as quoted in ref. 1c, p. xliv).

Note: In the original journal version the Figure 1 was printed as a negative! The correct version was published in NJC 13 (3) (1989) 269, and in this reprinted reprint.

88/3 b

ERRATA

I. Oxygenation of hydrocarbons by $KHSO_5$ catalyzed by manganese porphyrin complexes.

A. Robert, B. Meunier, *New J. Chem.*, 1989, **12**, 885.

1. All the paper long (TCPP) or (TCDPP) should be read as (TDCPP) and (OFPP) as (oFPP).
2. p. 886, left column, the paragraph "Results and Discussion" should begin as follows: "The ability of $KHSO_5$ to behave as a single oxygen atom donor..."
3. p. 888, left column, 1 st paragraph, 6 lines before the end, should be read as follows: "*i.e.* with Mn(TMP) Cl and Mn(TDCPP) Cl regioselectivity increases: 85/15 and 90/10 respectively...".
4. p. 888, left column, last paragraph, 3 lines before the end, should be read as follows: "furthermore the rates are at least 5 to 20 times higher with Mn(TPP)OAc than with Mn(TDCPP) Cl or Mn(TMP) Cl..."
5. p. 889, right column, first paragraph, line 4: "At higher olefin concentrations (above 0.6 M), the order with respect to the olefin decreased from one partial order."
6. p. 892, right column, first paragraph, line 8 should be read "$k_H/k_D = 11.5$" in place of $k_H k_D$.
7. p. 892, right column, second paragraph, line 3: "in the hydroxylation of perdeuterated cyclohexane...".
8. p. 893, right column, 1 st paragraph, line 4 should be read: "to recover the manganese catalyst at the end of each run."
9. p. 894, paragraph 2, lines 7 and 8 of the column should be read as follows: "(iii) aromatic derivatives, except..."
10. p. 894, paragraph 3, lines 4 to 7 of the left column should be read as follows: "except for *cis*-stilbene, an olefin sensitive to stereochemical change in manganese-porphyrin catalyzed epoxidations,...".
11. p. 895, left column, title of paragraph **B** should be read as follows: "Oxidation of Various Pyridines by $KHSO_5/Mn(TPP)OAc$ (Figure 2).

II. Chemical Past Times: Johan Gadolin's 1788 paper mentioning the several oxidation states of tin and their disproportionation reaction.

P. Pyykkö, O. Orama, *New J. Chem.*, 1988, **12**, 881.

The figure 1 should have been printed as follows:

Johan Gadolin

Figure 1. – Johan Gadolin, a Finnish chemist (1760-1852).

New Journal of Chemistry
13 (3) 269 (?) (1989)