RSC | Advancing the Chemical Sciences

Historical Group

NEWSLETTER
and
SUMMARY OF PAPERS

August 2010

(3) *Journal de Toulouse*, 12 September 1860. http://images.jdt.bibliotheque.toulouse.fr/1860/B315556101_JOUTOU_1860_09_12.pdf (accessed 16 March 2010)

4) *Daily Southern Cross*, 25 December 1860, Volume XVII, Issue 1361, p. 6, http://paperspast.natlib.govt.nz/cgi-bin/paperspast?a=d&d=DSC18601225.2.24&l=mi&e=-------10--1----0-all (accessed 16 March 2010)

5) The early chemical investigations are described in Cooksey, C.J., Dronsfield, A.T. and Kirby, J., (2005) Chinese green, an enduring mystery, *Dyes in History and Archaeology* 20, pp. 155–164

6) Cooksey, C.J., Dronsfield, A.T. and Kirby, J., (2008) Chinese green: Experimental Investigations, *Dyes in History and Archaeology* 21, pp. 167–179

Chris Cooksey
Watford

What happened in Thomsen's kiln? – a detective story

Julius Thomsen, the Danish chemist (1826-1909) was recently commemorated in a *Chemistry World* article by Mike Sutton (1). After the discovery of the noble gases helium and argon, Thomsen correctly located them in the Periodic Table and thereby predicted the existence and relative atomic masses of neon, krypton, xenon, and radon. He made 3500 meticulous thermochemical measurements. In addition, without giving up his academic career, Thomsen made a fortune in the chemical industry with the help of Carl Frederik Tietgen, who, according to Helge Kragh (2), was then 'on his way to becoming the leading [Danish] industrialist, banker, and entrepreneur'. Thomsen retired as professor of chemistry at Copenhagen University in 1901.

Working mostly from primary sources in Danish, Kragh gives a detailed description (in English) of the keystone of Thomsen's commercial success, namely the use of cryolite (Na_3AlF_6) as the source of sodium for the manufacture of washing soda ($Na_2CO_3.10\ H_2O$). The cryolite was mined at Ivigtut in Greenland, a Danish possession. Thomsen's 'cryolite soda process' began commercially in 1857, and factories were built in Denmark, at five sites elsewhere in Europe, and in Pennysylvania, USA. It competed for a long time with the established Leblanc process and later with the Solvay process, both of which used common salt as their source of sodium. Its end came in 1900 when the Pennysylvania factory was last to stop using the process. Over forty-three years, an estimated 100 000 tons of washing soda had been made from cryolite. By this time, the use of molten cryolite as the solvent for alumina in the electrolytic commercial production of aluminium metal had become established, and the Ivigtut mine continued to be worked until 1962.

The present essay examines the chemistry of Thomsen's cryolite soda process by the use of modern thermodynamic data. It also raises the intriguing possibility that one or more compounds believed to have been first discovered in the 1980s were in fact produced a century before, on an industrial scale, as an intermediate in Thomsen's process. Echoing Henry Rzepa (3), one can hope that somewhere there is a sample tube containing the intermediate so that this possibility can be checked archaeologically.

Thomsen's process consisted of four steps, which, if the cryolite was pure, gave, overall, 96.5 % of the theoretical yield of washing soda based on the cryolite used (though in normal practice, crude cryolite was used). The steps were as follows, beginning with the kilning of a mixture of limestone and cryolite:-

---

kiln, care taken to avoid melting

$6\ CaCO_3\ (s) \rightarrow 6\ CaO\ (s) + 6\ CO_2(g)$ (step I, reaction i)

$2\ Na_3AlF_6\ (s) + 6\ CaO\ (s) \rightarrow$ new solid phases (step I, reaction ii)

boiling, probably

new solid phases + water (l) $\rightarrow 2$ "Na_3AlO_3" (aq) + $6\ CaF_2\ (s)$ (step II)

2 "Na_3AlO_3" (aq) + $3\ CO_2\ (g) \rightarrow 3\ Na_2CO_3\ (aq) + 2\ Al(OH)_3\ (s)$ (step III)

evaporate

$3\ Na_2CO_3\ (aq) \rightarrow 3\ Na_2CO_3.10\ H_2O\ (s)$ + water (g) (step IV)

Together, steps I to IV amount to -

$2\ Na_3AlF_6\ (s) + 6\ CaCO_3\ (s)$ + water (l) $\rightarrow$

$3\ Na_2CO_3.10\ H_2O\ (s) + 2\ Al(OH)_3\ (s) + 6\ CaF_2\ (s) + 3\ CO_2\ (g)$ + water (g)

We can infer the occurrence of step I, reaction ii because, without it, the above scheme would not differ significantly from an earlier, abandoned scheme in which CaO and Na_3AlF_6 were boiled up with water. According to this earlier scheme, large amounts of water were needed to enable a reaction between the only slightly soluble $Ca(OH)_2$ and the insoluble Na_3AlF_6 (4); the excess water had to be removed later, at a high cost in fuel. It is reasonable to suppose that step I, reaction ii transferred at least the sodium content of Na_3AlF_6 into one or more relatively water-soluble phases. This would explain why Thomsen found he needed to use less water than according to the earlier scheme, saving on fuel.

The question posed in this paper is *'What happened in Thomsen's kiln, and in particular what were the new solid phases produced in step I, reaction ii and constituting the key intermediate in Thomsen's successful industrial process?'*

As Kragh points out, Thomsen, despite his academic devotion to thermochemistry, did not apply thermochemistry to his own process. However, considering initially only those potential products for which thermodynamic data are available today (5, 6), we can now calculate that the plausible candidates for step I, reaction ii are the following, all of which transfer the sodium content of the Na_3AlF_6 into NaF, or else NaF and $NaAlO_2$, both of these compounds being, as desired, water-soluble (7).

$2\ Na_3AlF_6(s) + 6CaO\ (s) \rightarrow 6\ NaF\ (s) + Al_2O_3\ (s) + 3\ CaF_2\ (s) + 3\ CaO^*\ (s)$

$\Delta G = -260$ kJ/mol at 298 K and 1 bar (a)

$2\ Na_3AlF_6\ (s) + 6\ CaO\ (s) \rightarrow 6\ NaF\ (s) + Ca_3Al_2O_6\ (s) + 3\ CaF_2\ (s)$

$\Delta G = -280$ kJ/mol at 298 K and 1 bar (b)

$2\ Na_3AlF_6\ (s) + 6\ CaO\ (s) \rightarrow 6\ NaF(s) + CaAl_2O_4\ (s) + 3\ CaF_2\ (s) + 2\ CaO^*\ (s)$

$\Delta G = -283$ kJ/mol at 298 K and 1 bar (c)

$2\ Na_3AlF_6(s) + 6\ CaO(s) \rightarrow 6\ NaF(s) + 0.5\ CaAl_4O_7(s) + 3\ CaF_2(s) + 2.5\ CaO^*\ (s)$

$\Delta G = -272$ kJ/mol at 298 K and 1 bar (d)

$2\ Na_3AlF_6(s) + 6\ CaO(s) \rightarrow 4\ NaF(s) + 2NaAlO_2(s) + 4\ CaF_2(s) + 2CaO^*\ (s)$

$\Delta G = -295$ kJ/mol at 298 K and 1 bar (e)

*The inclusion of unused CaO on the right-hand side (instead of cancelling out the two sides) preserves the same left-hand side throughout (a) to (e), for consistency with step I, reaction ii above and to facilitate comparison among (a) to (e).

All of these reactions are highly favourable at 298 K as indicated by the ΔGs, and there can be no doubt that they would be highly favourable also at Thomsen's kilning temperature, perhaps 1200 K. The last reaction, (e), in which NaF and $NaAlO_2$ are formed, has the most negative ΔG and is therefore the most favourable at 298 K. However, because we lack high-temperature heat capacity data on several of the compounds, and because the range of ΔGs across (a) to (e) is small, we cannot predict for certain that (e) would be the most likely to occur also at the kilning temperature.

A further possibility is that water-soluble sodium aluminates were formed, but more sodium-rich than the $NaAlO_2$ produced according to (e) above, as follows:

$$2\ Na_3AlF_6\,(s) + 6\ CaO\ (s) \rightarrow 2\ \text{'}Na_3AlO_3\text{'}\ (s) + 6\ CaF_2\,(s) \qquad \text{(f)}$$

In (f), 'Na_3AlO_3' (s) represents a mixture of sodium aluminate phases of the formula x Na_2O, Al_2O_3 ($x > 1$) in such proportions as to achieve the overall stoichiometry $x = 3$. Such phases were obtained in the 1980s by Barker *et al* (8) by heating mixtures of Na_2O and Al_2O_3 in argon at 700 to 800 °C; the products were phases with $x = 2.33$, 3.40, and 5.00, plus one other which they did not fully characterise. Unfortunately, no one seems to have followed up their work with thermodynamic measurements that would allow us to judge whether they were in fact produced in Thomsen's kiln among his 'new solid phases' of step I, reaction ii.

Barker *et al* believed that they were the first to obtain sodium aluminates

x Na_2O, Al_2O_3 in which x exceeded 1. If a sample of the 'new solid phases' produced in Thomsen's step I still exists, despite their being an intermediate consumed in step II and despite their water-sensitivity, then X-ray powder diffraction, which gives 'lines' for each phase present independently of the others, would show which of (a) to (f) was in fact Thomsen's step I, reaction ii. If (f), then Thomsen anticipated Barker *et al* on a vast scale, his 100 000 tons of washing soda involving the production and consumption of over 30 000 tons of 'Na_3AlO_3' (s).

The author acknowledges gratefully correspondence with Dr Mike Sutton and Professor Helge Kragh.

References

1) Mike Sutton, *Chemistry World*, September 2009, 56.

2) Helge Kragh, *Annal. Sci.*, 1995, 52, 285.

3) Henry S Rzepa, *Newsletter*, February 2010, 8.

4) *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton FL, 2008, 89th edition, page 4-55, entry 590 and page 4-90, entry 2578.

5) *CRC Handbook of Chemistry and Physics*, pages 5-5 (AlF_3, Al_2O_3), 5-8 (CaF_2, CaO), 5-11 ("FNa"), and 5-16 (Na_2O).

6) O Kubachewski and C B Alcock, *Metallurgical thermochemistry*, Pergamon, 5th edition (1979), 298 (Na_3AlF_6, $NaAlO_2$) and 276 ($Ca_3Al_2O_6$, $CaAl_2O_4$, $CaAl_4O_7$).

7) *CRC Handbook of Chemistry and Physics*, page 4-89, entry 2531 and page 4-90, entry 2568.

8) Martin G Barker, Paul G Gadd, and Michael J Begley, *J. Chem. Soc. Dalton Trans.*, 1984, 1139, together with earlier shorter communications referenced therein.

The spreadsheet containing the author's calculations is available online.

Michael Jewess
Harwell, Oxfordshire
michaeljewess@tiscali.co.uk

Charles Darwin and Raphael Meldola

Bill Griffiths' item on "Darwin, chemistry and the age of the earth" in the February 2010 *Newsletter* is a timely reminder of the way in which early studies on evolution involved a variety of scientific activities and, in particular, attracted the interests of a number of prominent chemists. Perhaps there was no greater a devotee to the theory of evolution based on natural selection among chemists than Raphael Meldola (1849-1915), from 1885 professor of chemistry at Finsbury Technical College. Though his name often appears in historical accounts of the pioneers of evolutionary studies, it is invariably without explanation of his role, apart from as a correspondent of Charles Darwin, and supporter of natural selection. This aspect of the scientific career of Meldola emerged from his love of entomology during his teenage years, when he spent days, and sometimes nights, in Epping Forest, observing insects, particularly moths and butterflies. Encouraged to place his interest on more scientific lines, he quickly appreciated the role of similar studies made on Lepidoptera in the 1860s as providing the first concrete evidence for the theory of natural selection.

Relevant to his role as an evolutionary selectionist is the fact that Meldola had made his early reputation from engagement with an industry, the