The Origin of the Brin Process

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Question

What is the origin of the Brin Process for the industrial manufacture of oxygen?

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Answer

The Brin process for the industrial manufacture of pure dioxygen gas was based on the thermal reversibility of the reaction between barium oxide (BaO) and dioxygen gas (O_2) to produce barium peroxide (BaO_2):

$$2BaO(s) + O_2(g) \leftrightarrow 2BaO_2(s) \quad [1]$$

Since the reaction as written is exothermic ($\Delta H°$ = -143.1 kJ/mol rx) combination of the barium oxide with the dioxygen gas of the air is favored at low temperatures, whereas its reverse, the decomposition of the resulting peroxide to give pure O_2 and the original oxide, is favored at high temperatures. The regenerated oxide can then be reused to produce more peroxide and the cycle repeated indefinitely.

Reaction 1 was discovered by the French chemists, Joseph-Louis Gay-Lussac and Louis-Jacques Thenard, in 1811 (1), and was first explored as a method for the industrial separation of dioxygen gas from air by the French chemist, Jean-Baptiste Boussingault, in 1852 (2). However, Boussingault found that the barium oxide became inactive after the process had been repeated about a dozen times and so did not succeed in making it industrially viable.

In 1879 the French team of Quentin and Arthur Brin discovered that this deactivation was primarily due to the barium oxide reacting with the carbon dioxide content of the air to produce barium carbonate:

$$BaO(s) + CO_2(g) \leftrightarrow BaCO_3(s) \quad [2]$$

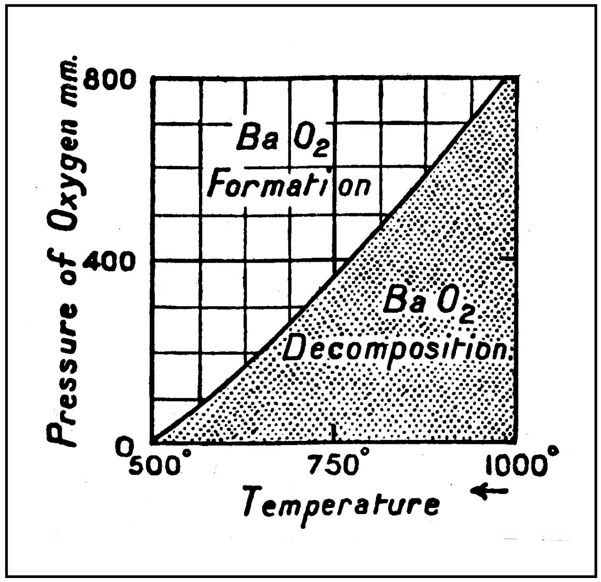

Figure 1. A plot of pressure versus temperature showing the regions corresponding to the favorable production of barium oxide versus barium peroxide (7).

and that if one first removed the carbon dioxide by passing the air over lime ($Ca(OH)_2$) or through a solution of potassium or sodium hydroxide:

$$CO_2(g) + 2NaOH(aq) \leftrightarrow Na_2CO_3(aq) + H_2O(l) \quad [3]$$

one could then recycle the barium oxide indefinitely. The next year the Brin brothers were granted a British patent for their process (3) and in 1886 the Brins Oxygen Company was incorporated, which continued to produce industrial quantities of dioxygen gas using the barium peroxide process until 1906, when the name was changed to the British Oxygen Company Ltd. and they began to produce dioxygen gas more economically using the fractionation of liquid air (4, 5).

It should be noted that the industrial use of reaction 1, like the more famous Haber ammonia synthesis, is an excellent textbook example of the practical application of Le Chatelier's principle. Indeed, in 1880, Boussingault, inspired by the earlier work of Henri Sainte-Claire Deville on thermal dissociation reactions, returned to the study of reaction 1 and showed that it could be reversed not only by a change in temperature at constant air pressure, but also by a change in pressure at constant temperature - high pressures favoring the formation of the peroxide and low pressures favoring the formation of the oxide (6). Though, as summarized in figure 1, one can in principle optimize the equilibrium shift by simultaneously manipulating both temperature and pressure, in actual practice it was far easier and more economical to shift the pressure than to shift the temperature. Consequently, when applied industrially, the latter was kept constant at about 700°C while the air pressure was set at 2 atm for peroxide production and then reset at about 0.05 atm for its subsequent decomposition, the gas obtained under these conditions being about 90-96% dioxygen and 4-10% dinitrogen (7).

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4. D. W. F. Hardie, J. D. Pratt, *A History of the Modern British Chemical Industry*, Pergamon Press: Oxford, 1966, pp. 59-60, 280-281.

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6. J. B. Boussingault, "Sur la décomposition du bioxyde de baryum dans le vide, a la température de rouge sombre," *Ann. chim. phys.* **1880**, *19 (5th series)*, 464-472.

7. J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry,* Vol. 1, Longmans, Green & Co: London, 1922, p. 355.

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