

17.3: Electrolysis of Brine

Three important chemicals, NaOH, Cl₂, H₂, can be obtained by **electrolyzing** an aqueous NaCl solution (brine). This forms the basis of the **chlor-alkali industry**. The diaphragm cell (also called a Hooker cell) in which the electrolysis is carried out is shown schematically in Figure 17.3.1. At the cathode, water is **reduced**:

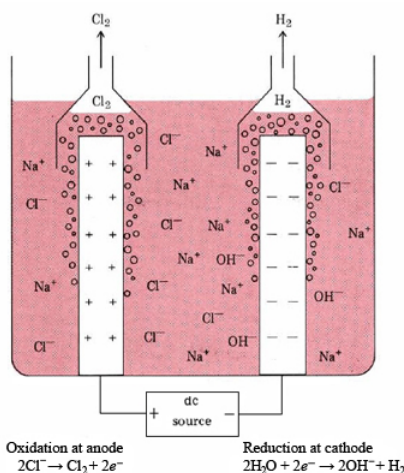
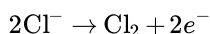


Figure 17.3.1 Diaphragm or Hooker cell for electrolysis of brine (schematic). Since chloride ions are removed and hydroxide ions produced by the electrolysis, the electrolyte gradually changes from a solution of sodium chloride to a solution of sodium hydroxide.



Chlorine is produced at the anode:



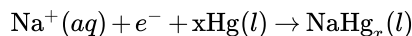
Thus the overall reaction is



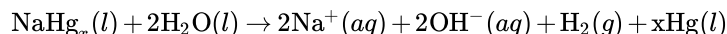
Since the H₂(g) and Cl₂(g) might recombine explosively should they come in contact, the cathode must be entirely surrounded by a porous diaphragm of asbestos. Hence the name of this type of cell.

Both the H₂(g) and Cl₂(g) produced in Eq. 17.3.1 are dried, purified, and compressed into cylinders. Fresh brine is continually pumped into the cell, and the solution which is forced out contains about 10% NaOH together with a good deal of NaCl. [Remember that the spectator ions, Na⁺(aq), are not included in a net ionic equation such as Eq. 17.3.1. H₂O is allowed to evaporate from this solution until the concentration of the solution reaches 50% NaOH, by which time most of the NaCl has crystallized out and can be recycled to the electrolysis. The NaOH is sold as a 50% solution or further dried to give crystals whose approximate formula is NaOH•H₂O.

The considerable effort required to concentrate the NaOH solution obtained from diaphragm cells can be avoided by using mercury cells. The cathode in such a cell is mercury, and the cathode reaction is



The sodium metal produced in this reaction dissolves in the liquid mercury, producing an **amalgam**. The liquid amalgam is then transferred to another part of the cell and reacted with water:



The 50% sodium hydroxide solution produced by this reaction contains no sodium chloride and can be sold directly, without being concentrated further. Up until 1970, however, chlor-alkali plants using mercury cells did not have adequate controls to prevent losses of mercury to the environment. About 100 to 200 g mercury was lost for each 1000 kg chlorine produced—apparently a small quantity until one realizes that 2 500 000 kg chlorine was produced by mercury cells *every day* during 1960 in the United States. Thus every 2 to 4 days 1000 kg mercury entered the environment, and by 1970 sizable quantities were being found in fish. Since

1970 adequate controls have been installed on mercury cells and most new alkali plants use diaphragm cells, but the very large quantities of mercury introduced into rivers and lakes prior to 1970 are expected to remain for a century or more.

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