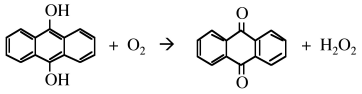
9.4: Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a very pale blue liquid but appears colorless in dilute solution. It is prepared by the oxidation of anthraquinol (shown below). The hydrogen peroxide is extracted with water from the anthraquinone solution and the 20 - 40% solution is purified by solvent extraction. An alternative process involves the oxidation of isopropanol in either the vapor or liquid phase at 100 °C and *ca*. 15 atm, (9.4.1). The products are separated by fractional distillation.



$$Me_2C(H)OH + O_2 \rightarrow Me_2C(OOH)OH \rightarrow Me_2C{=}O + H_2O_2 \tag{9.4.1}$$

In the gas phase H_2O_2 adopts a gauche conformation (Figure 9.4.1), but there is only a low barrier to rotation about the O-O bond.

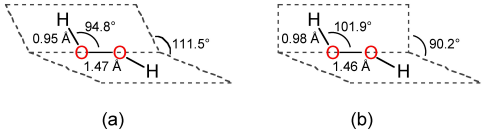


Figure 9.4.1: Structure of hydrogen peroxide in (a) the vapor phase and (b) the solid (crystal) phase.

Hydrogen peroxide is a liquid at standard temperature and pressure (25 °C, 1 atm) due to the presence of strong hydrogen bonding similar to found in water. In fact, the liquid range for H_2O_2 (Mp = -0.43 °C, Bp = 150.2 °C) is actually broader than water, and it is slightly more viscous than water. Hydrogen peroxide has a density of 1.44 g/cm^3, and is 10^6 times less basic that water.

As with water, H_2O_2 is a good solvent because of its polar nature and broad liquid temperature range, however, it is dangerous in its pure state due to its facile (ΔH = -99 kJ/mol) auto decomposition, (9.4.2), as well as its strong oxidizing nature.

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{9.4.2}$$

Hydrogen peroxide is usually sold as 3 - 12% solution for home use; however, laboratory and certain industrial applications require 30% solutions.

Note

Hydrogen peroxide should be stored in a cool, dry, well-ventilated area and away from any flammable or combustible substances. It should be stored in a container composed of non-reactive materials such as stainless steel or glass (other materials including some plastics and aluminum alloys may also be suitable). Because it breaks down quickly when exposed to light, it should be stored in an opaque container, and pharmaceutical formulations typically come in brown bottles that filter out light.

Aqueous solution are weakly acidic (K = 1.5 x 10^{-12}), (9.4.3). However, there is no exchange of oxygen atoms between H_2O_2 and H_2O in the liquid phase.

$$H_2O_2 + H_2O \rightleftharpoons HO_2^- + H_3O^+ \tag{9.4.3}$$

As expected hydrogen peroxide is a strong oxidizing agent, (9.4.4), however, it can also act as a reducing agent, (9.4.5).

$$H_2O_3 + 2HI \rightarrow I_2 + 2H_2O \tag{9.4.4}$$

$$5H_2O_2 + 2MnO_4 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2 \uparrow \tag{9.4.5}$$