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# Hydrogen Peroxide

*Peroxo Compounds, Inorganic and Peroxy Compounds, Organic are separate keywords.*

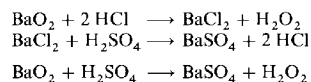
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## 1. Introduction and Historical Aspects

The industrial production of hydrogen peroxide passed through three phases, starting with wet chemical processes, followed by electrochemical processes, and then by organic autoxidation processes. Almost all hydrogen peroxide is now produced by organic autoxidation (AO) processes, primarily the anthraquinone process.

**Wet Chemical Processes.** In 1818, L. J. THENARD [9] obtained hydrogen peroxide for the first time by reacting barium peroxide [1302-29-6] with nitric acid. This process was improved by using hydrochloric acid to release hydrogen peroxide. The water-soluble barium chloride which is formed simultaneously, was precipitated with sulfuric acid.



With this reaction, THENARD established the foundation for the commercial manufacture of aqueous hydrogen peroxide solutions based on wet chemical processes, which began around 1880.

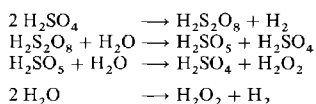
Industrial plants using the barium peroxide process were still operating until the middle of this century. Around 1900, approximately 10 000 t/a of barium peroxide was processed by this technology, yielding ca. 2000 t of hydrogen peroxide per year. Sales opportunities for the co-product barium sulfate ( $\text{BaSO}_4$ , blanc fixe) had a decisive effect on the profitability of the process.

The 3% aqueous hydrogen peroxide solutions manufactured by the barium peroxide pro-

cess had only a limited market because of their high production cost, low hydrogen peroxide content, and unsatisfactory stability due to impurities.

**Electrochemical Processes.** The introduction of electrochemical processes eliminated the disadvantages of the barium peroxide process.

In 1853, MEIDINGER discovered the formation of hydrogen peroxide during electrolysis of aqueous sulfuric acid [10]. In 1878, BERTHELOT showed that peroxodisulfuric acid [13445-49-3] is formed during this electrolysis and then hydrolyzed by water to give sulfuric acid and hydrogen peroxide via peroxomonosulfuric acid [12188-01-1] [11]:



In 1905, following the work of ELBS and SCHOENHERR [12], G. TEICHNER developed an electrolytic process at the Konsortium für Elektrochemische Industrie. The first hydrogen peroxide plant based on this new technology went on stream in 1908 at the Österreichische Chemische Werke in Weissenstein. The *Weissenstein process* was followed in 1910 by the *Münchener process* developed by A. PIETZSCH and G. ADOLPH at the Elektrochemische Werke, Munich, and then in 1924 by the *Riedel-Loewenstein process* developed by L. LOEWENSTEIN and first used by RIEDEL DE HAEN. In these processes, an ammonium sulfate solution was electrolyzed instead of free sulfuric acid, and the resulting ammonium peroxodisulfate (Riedel-Loewenstein) or potassium peroxodisulfate made from it (Pietzsch-Adolph) was hydrolyzed. After introduction of these processes, production (calculated as 100% hydrogen peroxide) increased steadily and, in 1950, reached approximately  $(30-35) \times 10^3$  t annually [13].

**Organic Autoxidation Processes.** The decisive breakthrough in industrial production of hydrogen peroxide, which enabled the construction of modern large-scale plants, came with the development of organic autoxidation processes, especially the anthraquinone process.

In 1901, MANCHOT discovered that hydroquinones (or hydrazobenzenes) react quantitatively with oxygen to form quinones (or azobenzenes) and hydrogen peroxide [14]. In

1932, WALTON and FILSON in the United States went back to this work and proposed a cyclic process for the manufacture of hydrogen peroxide based on azobenzene-hydrazobenzene [15].

PFLEIDERER of I.G. Farbenindustrie AG, Ludwigshafen (BASF), subsequently developed a process for the alkaline autoxidation of hydrazobenzene in which sodium peroxide is obtained instead of free hydrogen peroxide [16]. This process was used on an industrial scale by Kymmene AB in Kuusankoski (Finland) under BASF licence (see Section 4.4.3).

The azobenzene process showed two major technical drawbacks: hydrogenation of azobenzene was performed with sodium amalgam whereas oxidation of hydrazobenzene proceeded satisfactorily only in alkaline solution. PFLEIDERER and RIEDEL overcame these problems by using alkylated anthraquinones instead of azobenzene. Between 1935 and 1945, BASF developed the Riedel-Pfleiderer process (generally referred to as the anthraquinone or AO process) in a pilot plant with a monthly output of 30 t. At the end of World War II, this work was stopped in Germany because of Allied Control Commission Regulations, but it formed the basis for all present production processes. In 1953, Du Pont of Memphis, Tennessee, commissioned the first hydrogen peroxide production plant based on the AO process. Several other companies began to produce hydrogen peroxide by this process, and production capacity increased greatly. In 1987, it was estimated to be  $10^6$  t (calculated as 100%  $\text{H}_2\text{O}_2$ ) per year [17].

Another organic autoxidation process, the 2-propanol process, used by Shell in Norco (United States) between 1957 and 1980, made only a limited contribution to the increase of hydrogen peroxide production with an annual production capacity of about 15000 t.

## 2. Physical Properties

Hydrogen peroxide [7722-84-1],  $M_r$  34.016, is a clear, colorless liquid which is miscible with water in all proportions. Hydrogen peroxide and highly concentrated aqueous solutions (> 65 wt%) are soluble in a variety of organic solvents such as carboxylic esters.

Hydrogen peroxide and water do not form an azeotropic mixture and, in theory, can be sepa-

**Table 1.** Physical properties of hydrogen peroxide and water

Property	Value	
	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O
<i>mp</i> , °C	−0.43	0
<i>bp</i> (101.3 kPa), °C	150.2	100
Heat of melting, J/g	368	334
Heat of vaporization, J g <sup>−1</sup> K <sup>−1</sup>		
At 25 °C	1519	2443
At <i>bp</i>	1387	2258
Specific heat, J g <sup>−1</sup> K <sup>−1</sup>		
Liquid (25 °C)	2.629	4.182
Gas (25 °C)	1.352	1.865
Relative density, g/cm <sup>3</sup>		
0 °C	1.4700	0.9998
20 °C	1.4500	0.9980
25 °C	1.4425	0.9971
Viscosity, mPa · s		
0 °C	1.819	1.792
20 °C	1.249	1.002
Critical temperature, °C	457	374.2
Critical pressure, MPa	20.99	21.44
Refractive index <i>n</i> <sub>D</sub> <sup>20</sup>	1.4084	1.3330

**Table 2.** Physical properties of aqueous hydrogen peroxide solutions

Property	H <sub>2</sub> O <sub>2</sub> concentration, wt%			
	35	50	70	90
Relative density, g/cm <sup>3</sup>				
0 °C	1.1441	1.2110	1.3071	1.4136
20 °C	1.1312	1.1953	1.2886	1.3920
25 °C	1.1282	1.1914	1.2839	1.3867
Viscosity, mPa · s				
0 °C	1.82	1.87	1.93	1.88
20 °C	1.11	1.17	1.23	1.26
Refractive index				
<i>n</i> <sub>D</sub> <sup>20</sup>	1.3563	1.3672	1.3827	1.3995
<i>mp</i> , °C	−33	−52.2	−40.3	−11.9
<i>bp</i> (101.3 kPa), °C	107.9	113.8	125.5	141.3
H <sub>2</sub> O <sub>2</sub> partial pressure (30 °C), kPa	0.05	0.11	0.17	0.29

rated completely by distillation. In practice, 100 wt% hydrogen peroxide is obtained by fractional crystallization of highly concentrated (ca. 90 wt%) aqueous solutions. Pure 100 wt% hydrogen peroxide is of scientific interest only and is not produced on an industrial scale.

Data pertaining to molecular structure (obtained by neutron diffraction of solid H<sub>2</sub>O<sub>2</sub>) are as follows [18]:

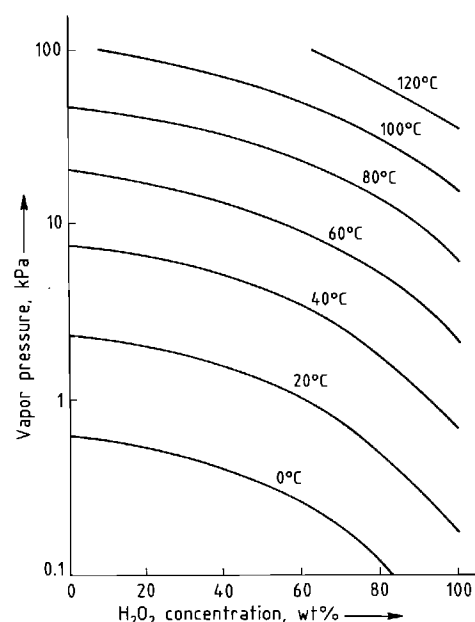
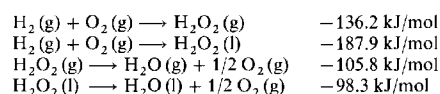
Bond length, O—O	0.1453 ± 0.0007 nm
Bond length, O—H	0.0998 ± 0.0005 nm
Bond angle, O—O—H	102.7 ± 0.3°
Azimuthal angle	90.2 ± 0.6°

Physical constants of hydrogen peroxide and water are compared in Table 1. Physical constants of some aqueous hydrogen peroxide solutions in commercially available concentrations are listed in Table 2.

The vapor pressure and partial pressure of aqueous hydrogen peroxide solutions are shown as a function of temperature in Figures 1 and 2, respectively. Figure 3 shows the vapor–liquid equilibrium curve for aqueous hydrogen peroxide solutions [19].

The solid–liquid phase diagram (Figure 4) shows eutectic points for the mixtures ice–H<sub>2</sub>O<sub>2</sub> · 2 H<sub>2</sub>O at 45.2 wt% hydrogen peroxide and for solid H<sub>2</sub>O<sub>2</sub>–H<sub>2</sub>O<sub>2</sub> · 2 H<sub>2</sub>O at 61.2 wt% hydrogen peroxide with a congruent melting point for the compound H<sub>2</sub>O<sub>2</sub> · 2 H<sub>2</sub>O between them.

Heat of formation and of decomposition of hydrogen peroxide are

**Figure 1.** Vapor pressure of aqueous hydrogen peroxide solutions

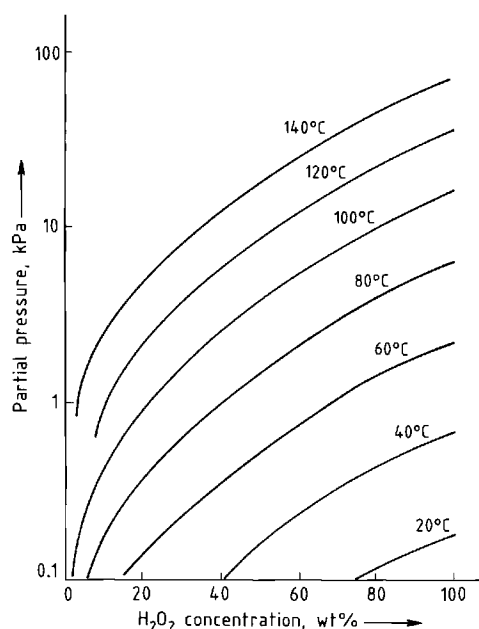


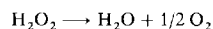
Figure 2. Partial pressure of hydrogen peroxide over aqueous hydrogen peroxide solutions

### 3. Chemical Properties

**Dissociation.** Hydrogen peroxide is weakly acidic in aqueous solution, with a dissociation constant of  $1.78 \times 10^{-12}$  ( $pK$  11.75) at 20°C. As a weak acid, hydrogen peroxide forms salts with various metals.

**Oxidation and Reduction.** Hydrogen peroxide can behave both as an oxidizing and as a reducing agent (Tables 3 and 4). Systems with a redox potential  $E_0 < -1.80$  V at pH 0 cannot be oxidized by hydrogen peroxide; systems with a redox potential  $E_0 > -0.66$  V at this pH cannot be reduced by hydrogen peroxide [6], [20].

**Decomposition** of hydrogen peroxide occurs with disproportionation



and is extremely important in handling hydrogen peroxide during storage and in the laboratory. This reaction is highly exothermic (see Chap. 2) and takes place in the presence of small amounts of catalyst even in aqueous solution. In the ab-

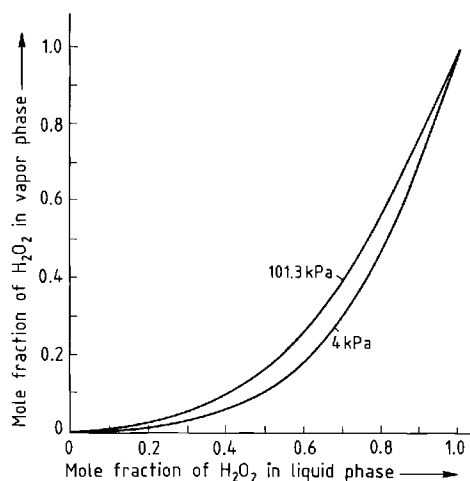


Figure 3. Vapor-liquid equilibrium curve for water-hydrogen peroxide

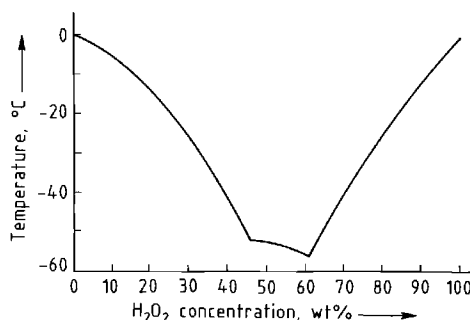


Figure 4. Freezing point curve for water-hydrogen peroxide

Table 3. Hydrogen peroxide as an oxidizing agent [20]

Redox reaction	Standard potential $E_0$ , V*
pH 0	
$\text{HOOH} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{HOH}$	+1.80
$\text{HSO}_3^- + \text{HOH} \rightarrow \text{SO}_4^{2-} + 3 \text{H}^+ + 2 \text{e}^-$	-0.17
$\text{NO}_2^- + \text{HOH} \rightarrow \text{NO}_3^- + 2 \text{H}^+ + 2 \text{e}^-$	-0.94
$2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$	-1.36
$2 \text{Br}^- \rightarrow \text{Br}_2 + 2 \text{e}^-$	-1.07
$2 \text{I}^- \rightarrow \text{I}_2 + 2 \text{e}^-$	-0.54
pH 14	
$\text{HOOH} + 2 \text{e}^- \rightarrow 2 \text{OH}^-$	+0.87
$\text{Mn}(\text{OH})_2 + 2 \text{OH}^- \rightarrow \text{MnO}(\text{OH})_2 + \text{HOH} + 2 \text{e}^-$	+0.05

\* Standard potential of redox reactions measured against a hydrogen electrode (25°C, 100 kPa).

**Table 4.** Hydrogen peroxide as a reducing agent [20]

Redox reaction	Standard potential $E_0$ , V*
pH 0	
$\text{HOOH} \longrightarrow 2 \text{H}^+ + \text{O}_2 + 2 \text{e}^-$	- 0.66
$5 \text{e}^- + \text{MnO}_4^- + 8 \text{H}^+ \longrightarrow \text{Mn}^{2+} + 4 \text{HOH}$	+ 1.51
$1 \text{e}^- + \text{Ce}^{4+} \longrightarrow \text{Ce}^{3+}$	+ 1.61
pH 14	
$\text{HOOH} + 2 \text{OH}^- \longrightarrow 2 \text{HOH} + \text{O}_2 + 2 \text{e}^-$	+ 0.08
$1 \text{e}^- + \text{ClO}_2^- \longrightarrow \text{ClO}_2$	+ 1.16
$2 \text{e}^- + \text{ClO}^- + \text{HOH} \longrightarrow \text{Cl}^- + 2 \text{OH}^-$	+ 0.89

\* Standard potential of redox reactions measured against a hydrogen electrode (25 °C, 100 kPa).

sence of catalyst, it occurs only in the gas phase at high temperature.

Decomposition can be catalyzed both homogeneously by dissolved ions (especially of the heavy metals iron, copper, manganese, and chromium) and heterogeneously by suspended oxides and hydroxides (e.g., manganese, iron, copper, palladium, or mercury) and by metals such as platinum, osmium, and silver.

**Substitution.** The hydrogen atoms of hydrogen peroxide can be substituted by alkyl and acyl groups, leading to the formation of

H—O—O—alkyl	alkyl hydroperoxides
alkyl—O—O—alkyl	dialkyl peroxides
H—O—O—acyl	percarboxylic acids
acyl—O—O—acyl	diacyl peroxides

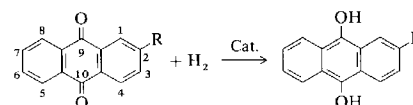
Hydrogen peroxide forms peroxohydrates with a number of compounds. Addition compounds with sodium carbonate (sodium carbonateperoxohydrate [15630-89-4]) and with urea (urea peroxohydrate [124-43-6]) are industrially important. For a detailed description of peroxo compounds see → Peroxo Compounds, Inorganic; → Peroxy Compounds, Organic.

## 4. Production

### 4.1. Anthraquinone Process (AO Process)

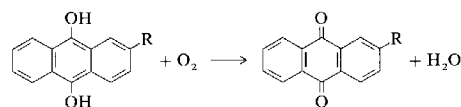
#### 4.1.1. Principles

In the AO process, 2-alkyl-9,10-anthraquinones react with hydrogen in the presence of a catalyst to form the corresponding hydroquinones.



R = alkyl

After the catalyst is removed (otherwise, the hydrogen peroxide would decompose), the hydroquinones are oxidized to quinones with oxygen (usually air) with simultaneous quantitative formation of hydrogen peroxide:



Hydrogen peroxide is extracted with water, and the quinones are returned to the hydrogenator to complete the loop.

The AO process, therefore, leads to the net formation of hydrogen peroxide from gaseous hydrogen and oxygen.

**Solvents.** Anthraquinones must be dissolved in a suitable solvent for hydrogenation, oxidation, and extraction (the so-called working solution).

Although a number of individual solvents have been proposed (e.g., aromatic alcohols or their esters [21]), solvent mixtures are almost always used because the quinones and hydroquinones formed during the synthesis loop have different solubilities. Quinones dissolve readily in nonpolar, aromatic solvents (quinone solvents). Hydroquinones dissolve well in polar solvents, especially alcohols and esters (hydroquinone solvents). Proposed solvents or solvent mixtures are

#### Quinone solvents

Benzene [22]  
*tert*-Butylbenzene [23]  
*tert*-Butyltoluene [24]  
 Trimethyl benzene [25]  
 Polyalkylated benzenes [26]  
 Methylnaphthalene [27]

#### Hydroquinone solvents

Alkyl phosphates [28]  
 Alkyl phosphonates [29]  
 Nonyl alcohols [27]  
 Alkylcyclohexanol esters [30]  
*N,N*-Dialkyl carbonamides [31]  
 Tetraalkyl ureas [32]  
*N*-Alkyl-2-pyrrolidones [33]

*Solvent mixtures*

- Polyalkylated benzenes and alkyl phosphates [26]
- Polyalkylated benzenes and tetraalkyl ureas [32]
- Trimethyl benzenes and alkylcyclohexanol esters [25]
- Methylnaphthalene and nonyl alcohols [27]

The following criteria must be fulfilled when choosing solvents and preparing solvent mixtures:

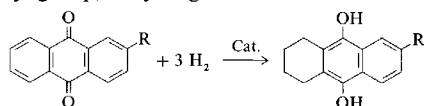
- 1) good solubility of both quinone and hydroquinone
- 2) good stability in the hydrogenator and oxidizer
- 3) low solubility in water and aqueous hydrogen peroxide solutions
- 4) sufficiently higher density than water to ensure separation of the two phases during extraction
- 5) low volatility, i.e., high boiling point and flash point
- 6) high distribution coefficient for hydrogen peroxide in the solvent-water system
- 7) low toxicity

**Quinones.** Criteria similar to those used for selecting solvents also apply to the quinone or quinone mixture, which is used as the working compound:

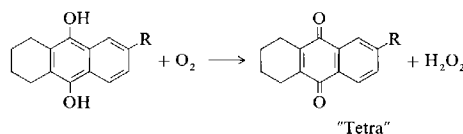
- 1) good solubility of the quinone form
- 2) good solubility of the hydroquinone form
- 3) good resistance to oxidation
- 4) good availability

The choice of quinone, depends mainly on the properties, especially the solubility, of the products formed in the AO process. Examples of working compounds proposed in the patent literature are 2-ethylantraquinone [84-51-5] [34], 2-*tert*-butylantraquinone [84-47-9] [35], eutectic mixtures of alkylantraquinones [36], and mixtures of 2-amylantraquinones [37].

The formation of degradation products and their ability to be regenerated to active quinones also play a role in the decision. In addition to hydroquinone formation, a number of secondary reactions occur during the hydrogenation step; of these, hydrogenation of the anthraquinone ring system is particularly important. One ring of the anthraquinone molecule, preferably the one that is not substituted by an alkyl group, is hydrogenated.



2-Alkyl-5,6,7,8-tetrahydro-9,10-dihydroxyanthracene is formed, which is also oxidized by oxygen to regenerate the 2-alkyl-5,6,7,8-tetrahydroanthraquinone (known as "tetra"), with simultaneous quantitative formation of hydrogen peroxide.



Although "tetra" is more readily hydrogenated than a 2-alkylantraquinone, the resulting "tetra" hydroquinone is much more difficult to oxidize than the readily oxidizable anthrahydroquinone.

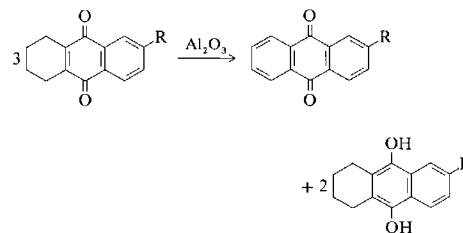
The formation of "tetra" in the synthesis loop depends on process conditions and has led to two methods for carrying out this process—the "anthra" system and the "all-tetra" system.

**Anthra System.** The slower oxidation rate of the "tetra" hydroquinone causes difficulties in the oxidizer. Actions have, therefore, been proposed which suppress the formation of "tetra" or to dehydrogenate it to anthraquinone.

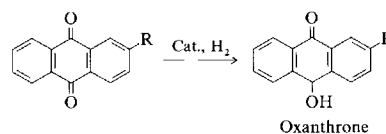
When the "tetra" content of the working solution is kept low (i.e., if 2-alkylantrahydroquinone is formed almost exclusively during hydrogenation), the process is referred to as the "anthra" system.

"Tetra" formation is suppressed by using selective catalysts [38], special solvents [39], special working compounds [40], and mild hydrogenation conditions [41] (e.g., the use of olefins has been recommended for the steady dehydrogenation of "tetra" [42]).

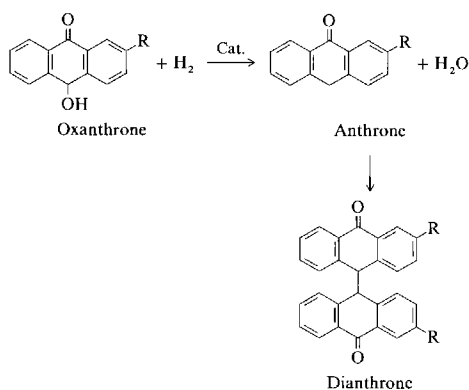
"Tetra" can be dehydrogenated in the presence of active aluminum oxide:



When the "anthra" system is used, tautomeric 2-alkyl-10-hydroxy-9-anthrone (oxanthrone) is also formed during hydrogenation [13], [43]:

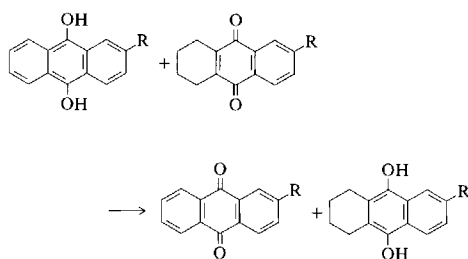


Oxanthrone is not oxidized by oxygen to form hydrogen peroxide and, therefore, leads to loss of active quinone. Although oxanthrone can be regenerated to active quinone, further hydrogenation leads to anthrone and, subsequently, dianthrone which cannot be regenerated and thus represent a loss of quinone [13].

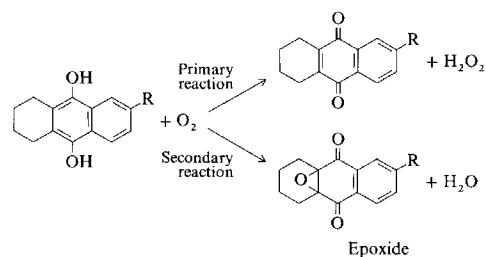


**“All-Tetra” System.** If “tetra” formation is not suppressed during hydrogenation or “tetra” is not dehydrogenated, an equilibrium is reached, in which the hydroquinone charged to the oxidizer consists exclusively of 2-alkyl-5,6,7,8-tetrahydroanthrahydroquinone. Such a system is called an “all-tetra” system.

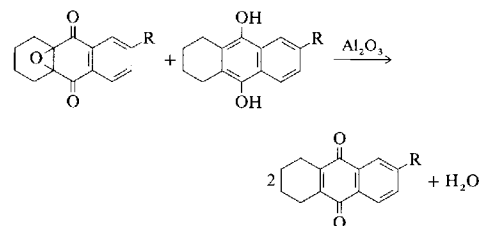
If anthraquinone is hydrogenated in addition to “tetra” during the hydrogenation step, hydrogen transfer occurs:



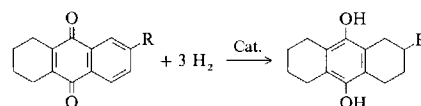
This means that the hydroquinone leaving the hydrogenation step is always the “tetra” hydroquinone. Dianthrone formation does not occur in the “all-tetra” system, but oxidation of “tetra” hydroquinone leads to a byproduct, the so-called epoxide:



The epoxide does not participate in the formation of hydrogen peroxide and leads to a loss of active quinone. Measures have, therefore, been suggested for regenerating “tetra” from the epoxide [44].



If the “tetra” content of the “all-tetra” system is high, another byproduct can be formed, namely, 2-alkyl-1,2,3,4,5,6,7,8-octahydroanthraquinone [13]:



Although this “octa” hydroquinone is oxidized by oxygen to quinone with the formation of hydrogen peroxide, the reaction is too slow to be important in the formation of hydrogen peroxide. “Octa” thus represents a decomposition product that cannot be regenerated to quinone.

#### 4.1.2. Process Description

The cyclic Riedel–Pfleiderer or BASF process (Chap. 1) forms the technological basis for all modern AO processes. Developments include improvement of the individual process steps, use of stable working solutions, and use of selective hydrogenation catalysts.

The basic principles of the process are illustrated in Figure 5.

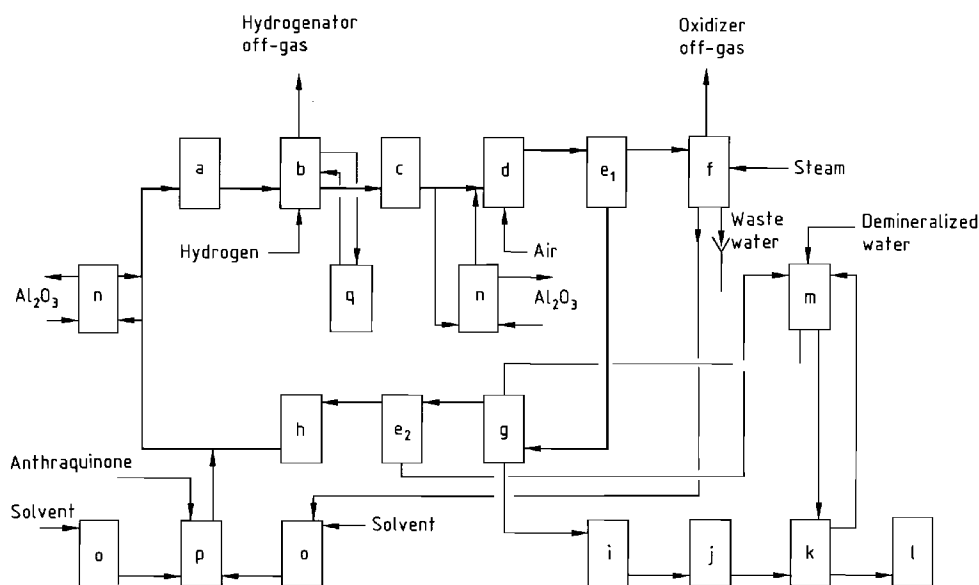


Figure 5. Production of hydrogen peroxide by the anthraquinone (AO) process

a) Storage tank for working solution or hydrogenator feed tank; b) Hydrogenator; c) Safety filtration; d) Oxidizer; e) Separator; f) Activated carbon adsorber; g) Extraction; h) Drying; i) Prepurification; j) Crude product storage tank; k) Hydrogen peroxide concentration; l) Hydrogen peroxide storage tank; m) Demineralized water feed tank; n) Regeneration and purification; o) Solvent storage tank; p) Working solution make up tank; q) Catalyst regeneration

**Hydrogenation.** From the storage tank or hydrogenation feed tank (a), the working solution enters the hydrogenator (b) where it is hydrogenated in the presence of a suspended, supported, or fixed-bed catalyst.

If a suspended catalyst (e.g., palladium black or Raney nickel) or a supported catalyst (e.g., palladium) is used, the hydrogenation step includes a main filtration stage which retains the catalyst and allows it to be returned to the hydrogenator. The heat of reaction released during hydrogenation can be removed (1) before hydrogenation (by cooling the oxidized working solution), (2) during hydrogenation (by cooling the reactor) or (3) after hydrogenation (by cooling the hydrogenated working solution).

**Oxidation.** Before the hydrogenated working solution that contains hydroquinone can be fed to the oxidation step, it must pass through a safety filtration stage (c). This is particularly important because the hydrogenation catalysts used in the AO process (palladium and Raney nickel) also catalyze the decomposition of hydrogen peroxide. Even a small amount of these catalysts in the oxidation and extraction steps would

lead to considerable loss of hydrogen peroxide and serious disturbances.

During the oxidation step (d), the hydrogenated working solution is gassed with air. Dissolved hydroquinones are oxidized to quinones, and hydrogen peroxide is formed.

After the working solution has been separated (e<sub>1</sub>), air from the oxidation step passes over activated carbon adsorbers (f), and adsorbed solvent is recovered from them. Several adsorbers are usually loaded and regenerated alternately, for example, with steam.

**Extraction and Recovery of the Working Solution.** The oxidized working solution is then treated with water to extract hydrogen peroxide (g).

The working solution leaving the extraction unit must be adjusted to a specific water content before being returned to the hydrogenation step. Free water taken up by the working solution during extraction is separated (e<sub>2</sub>) and the water content is adjusted to the desired level in the drier (h).

To purify the working solution and regenerate the quinone decomposition products into ac-

tive quinones, some or all of the working solution is passed through a regeneration step (n).

**Hydrogen Peroxide Concentration.** Crude aqueous hydrogen peroxide from the extraction stage ( $\text{H}_2\text{O}_2$  concentration 15–35 wt%) is fed into the crude product storage tank (j) via a pre-purification unit (i).

From the crude product storage tank, aqueous hydrogen peroxide goes to the concentration unit (k) where it is distilled. Here, hydrogen peroxide is freed from most of its impurities and concentrated to the commercial concentration of 50–70 wt%; it is then collected in a storage container (l).

Water vapor produced during distillation is condensed and fed into the water storage tank (m).

**Auxiliary Processes.** A number of additional processes are required to maintain the AO operation. For example, to maintain hydrogenation activity, part of the catalyst is removed, regenerated in the catalyst regeneration area (q), and returned to the hydrogenator. To compensate for quinone and solvent losses, working solution is periodically made up with anthraquinone and solvent (o, p).

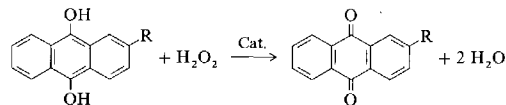
#### 4.1.2.1. Hydrogenation

The hydrogenation step is the most important step of modern AO processes. Quinone de-

composition products that cannot be regenerated into active quinone are formed during this step (cf. Section 4.1.1). New hydrogenation catalysts and hydrogenation reactors have been developed that deviate totally from the BASF principle. Here, design of the hydrogenator depends largely on the type of catalyst used.

Four typical reactors for the three usual catalyst systems (suspended, supported, and fixed-bed catalysts) are discussed in this section.

**BASF Hydrogenation Step.** The hydrogenation step in the BASF plant (Fig. 6) uses a Raney nickel catalyst at a slight excess pressure of approximately 0.2 MPa and at 30–36 °C. Because Raney nickel is sensitive to oxygen, the working solution from the extraction or drying and purification steps cannot be fed directly into the hydrogenator. This working solution still contains residual hydrogen peroxide and must pass over a decomposition catalyst (e.g., supported Ni–Ag), together with a fraction of the hydrogenated working solution (which also contains hydroquinone), to remove hydrogen peroxide completely:



The solutions are passed through the precontact column (Fig. 6, a) and collected in the hydrogenator feed tank (b). The working solu-

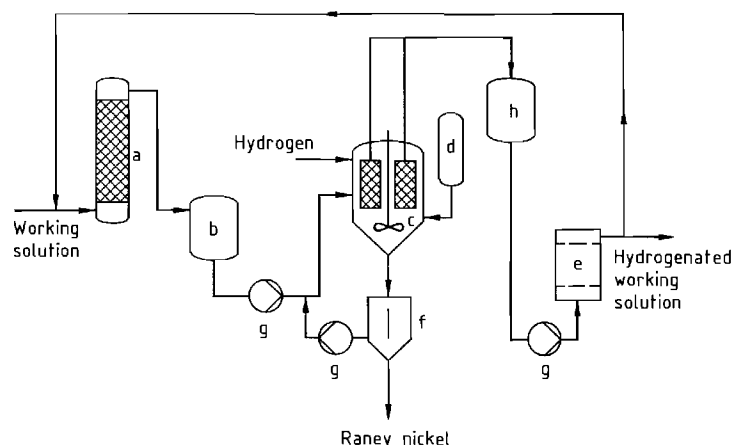


Figure 6. BASF hydrogenation step

a) Precontact column; b) Hydrogenator feed tank; c) Stirred vessel reactor with internal filters; d) Catalyst feed tank; e) Safety filtration; f) Catalyst separator; g) Pump; h) Oxidizer feed tank

tion is then pumped into the stirred vessel reactor (c) and is gassed with hydrogen in the presence of Raney nickel. Periodic addition of small amounts of hydrogenation catalyst from the catalyst feed tank (d) allows a constant rate of hydrogen conversion in the hydrogenator. Hydrogenated working solution is collected in the oxidizer feed tank (h) through the internal filters in the stirred vessel, thus exploiting the excess pressure in the reactor. The solution is then led into the oxidation step via the safety filter (e). A side stream of hydrogenated working solution is withdrawn and recycled to the precontact column (a).

When the concentration of Raney nickel in the hydrogenation reactor reaches a certain limit, the content of the reactor is drained into the catalyst separator (f). Raney nickel settles to the bottom, and catalyst-free supernatant is pumped back to the hydrogenator.

A significant disadvantage of Raney nickel as catalyst is its limited selectivity, i.e., the ratio of hydroquinone formation to "tetra" formation. BASF largely eliminated this by pretreating the catalyst with ammonium formate [45].

Alternatives were subsequently suggested for pretreating Raney nickel (e.g., nitriles [46], amines [47], and aldehyde solutions [48]).

The pyrophoric properties of Raney nickel also require more stringent safety procedures when handling the material. Raney nickel is still used today in some AO plants, but palladium catalysts are preferred because of their higher selectivity and simpler handling.

**Degussa Hydrogenation Step.** Degussa has proposed the use of palladium black as the hydrogenation catalyst. This exploits the advantages offered by a suspended catalyst and avoids the disadvantages of Raney nickel. Equipment that allows good conversion of hydrogen with very finely distributed palladium black is shown in Figure 7 [49].

The most important feature of the loop reactor (c) is the connection in series of pipes with different diameters. The working solution flows downward in the large pipes at a rate of 0.7–1.5 m/s and flows upward in the narrower pipes at 1.5–3 m/s.

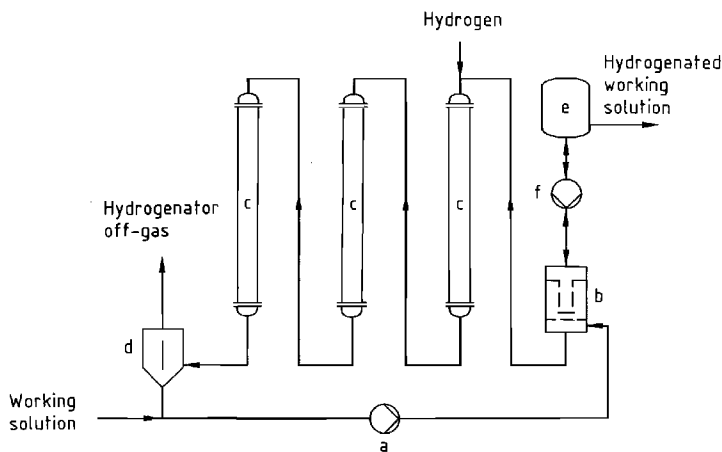
Degussa proposed a carbon filter [50]. A decline in filter performance can be overcome by periodic back flush with hydrogenated working solution through the filter into the hydrogenator.

Advantages of this hydrogenation system are

- 1) almost complete conversion of hydrogen,
- 2) nonpyrophoric catalyst,
- 3) easy exchange of palladium black, and
- 4) easy regeneration of the catalyst.

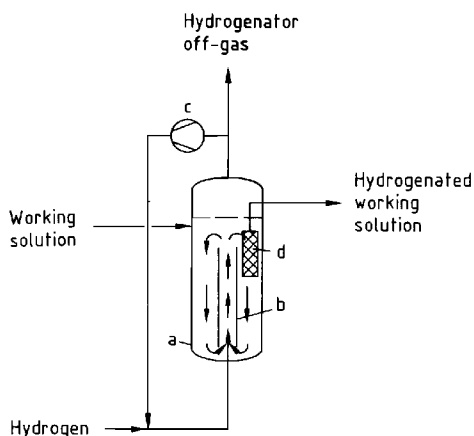
**Laporte Hydrogenation Step.** Laporte Chemicals and other companies proposed the use of supported palladium catalysts [51]. These catalysts have the advantage that their particle diameter of 0.06–0.15 mm makes their filtration and recirculation to the reactor simpler than those of palladium black.

Laporte proposed the apparatus shown in Figure 8 for industrial hydrogenation [52]. The



**Figure 7.** Degussa hydrogenation step

a) Reactor circulating pump; b) Filter; c) Loop reactor; d) Separator; e) Oxidizer feed tank; f) Back flush pump

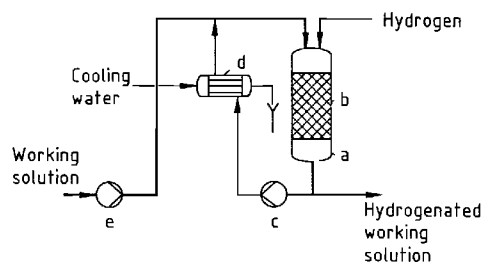


**Figure 8.** Laporte hydrogenation step  
a) Hydrogenator; b) Reactor tubes; c)  $H_2$  compressor; d) Internal filter

reactor contains a series of tubes whose lower ends lie just above the bottom of the reactor and whose top ends are just below the liquid surface. Hydrogen is fed into the bottom of each tube, and very small gas bubbles are formed by distributors. Upward flow occurs in the tube due to the density difference between the solutions in the tube and in the reactor. The catalyst suspension is drawn into the pipe by the continuous flow of working solution. To obtain a sufficiently high airlift effect in the tube, hydrogen must be circulated continuously.

**FMC Hydrogenation Step.** Fixed-bed hydrogenation represents a simple solution for the hydrogenation step; it involves a palladium catalyst and avoids the problem of filtration and recirculation of catalyst into the reactor [55]. The first industrial fixed-bed hydrogenation unit for the AO process was commissioned by FMC (Fig. 9) [53], [54].

The fixed-bed catalyst should have a diameter of 0.2–5 mm, a surface area less than  $5 \text{ m}^2/\text{g}$ , and a pore volume smaller than  $0.03 \text{ cm}^3/\text{g}$  [55]. The working solution is pumped to the top of the reactor. A side stream of the hydrogenated working solution is also fed into the fresh working solution after the heat of reaction has been removed in a heat exchanger (d). This operation results in optimal cross-sectional loading of the fixed bed, which should be  $12\text{--}120 \text{ m}^3$  of working solution per square meter per hour. The cat-



**Figure 9.** FMC hydrogenation step  
a) Fixed-bed reactor; b) Catalyst; c) Reactor circulating pump; d) Heat exchanger; e) Hydrogenator feed pump

alyst must fulfill a number of requirements such as

- 1) high abrasion resistance to allow simplification of the filtration step,
- 2) a long working life because replacing a fixed-bed catalyst is more complicated than replacing a suspended catalyst,
- 3) good productivity, and
- 4) easy regeneration of the catalyst.

#### 4.1.2.2. Oxidation

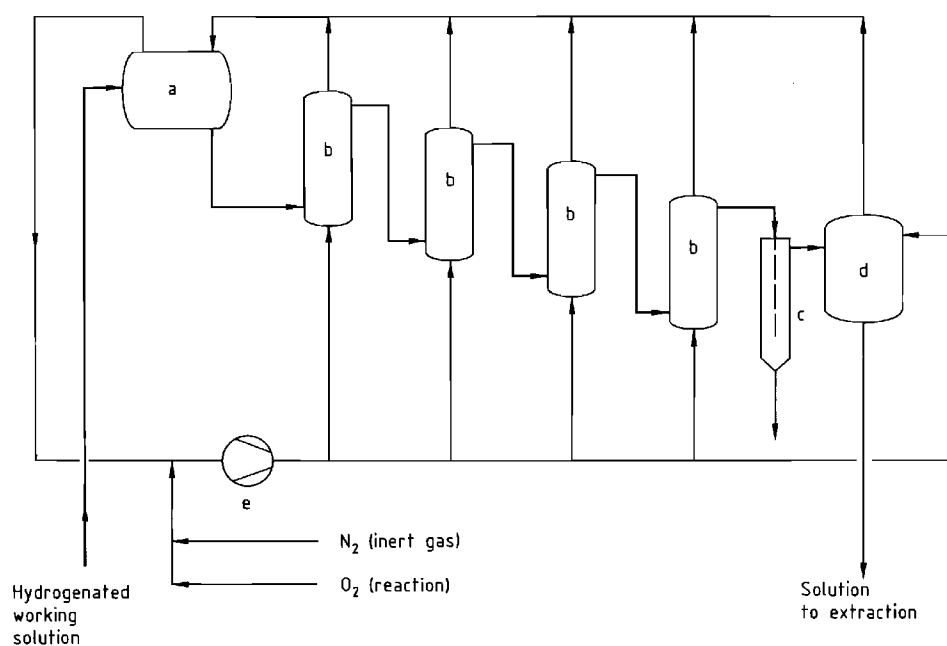
In industrial plants, the catalyst-free hydrogenated working solution is usually oxidized with slightly pressurized air (up to 0.5 MPa). The oxidizer off-gas is then directed to a series of activated carbon adsorbers to purify it and recover the solvents escaping with it.

For economic reasons, the following objectives are sought in designing industrial oxidation reactors:

- 1) efficient utilization of atmospheric oxygen to reduce the volume of the off-gas and the size of activated carbon adsorbers;
- 2) low compressor pressure to decrease energy costs; and
- 3) small reactor volume or reduced holdup of working solution to lower investment costs for equipment and working solution.

**BASF Oxidation Step** (Fig. 10). A working solution containing benzene as the quinone solvent has been used at BASF. For safety reasons and to minimize the volume of off-gas, the BASF oxidation step uses a nitrogen–oxygen mixture. The mixture is cycled in a closed circuit, and its composition is kept constant by adding pure oxygen to compensate for the amount consumed in the formation of hydrogen peroxide.

Hydrogenated working solution enters a separator (a) and then flows through four oxidation columns (b) arranged in series as a cascade. Oxi-



**Figure 10.** BASF oxidation step

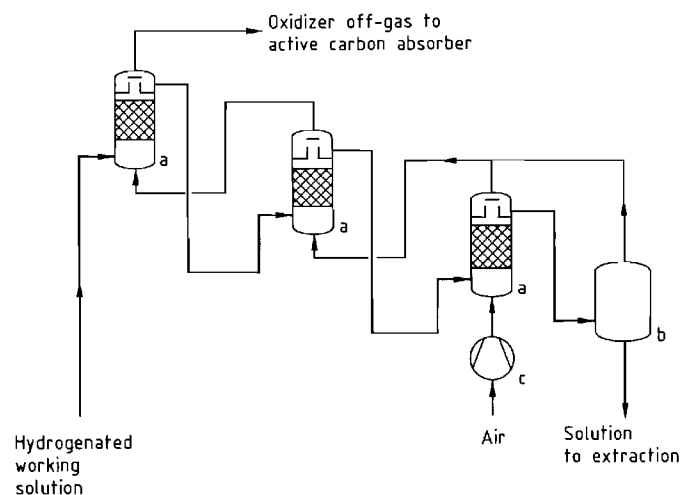
a) Separator; b) Oxidation columns; c) Siphon; d) Extractor feed tank; e) Compressor

dized working solution flows into the extractor feed tank (d) via a siphon (c). The nitrogen–oxygen mixture is compressed and fed into each of the four reactors.

Off-gas from the reactors is collected in a pipe and separated from entrained droplets of working solution. After compensation for con-

sumed oxygen, the gas mixture is returned to the compressor (e).

**Degussa Oxidation Step** (Fig. 11) [56]. The hydrogenated working solution flows cocurrently upward with the oxidizing air through the first reactor. The working solution and air are sepa-



**Figure 11.** Degussa oxidation step  
a) Concurrent-flow oxidation reactors; b) Separator; c) Air compressor

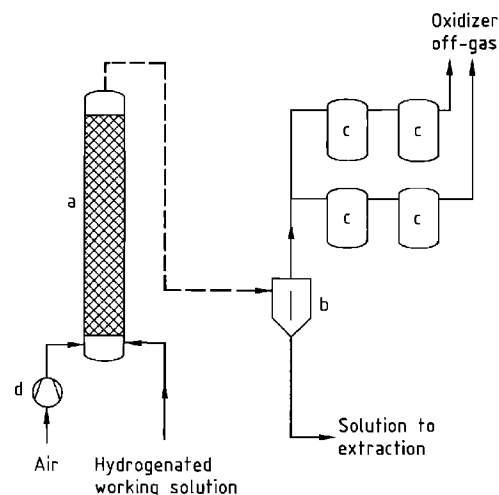
rated in the upper part of the reactor. Off-gas from the reactor is fed to the activated carbon adsorption unit, and working solution flows into the second and third reactors which are installed in series. The air needed for oxidation is pressurized with a compressor (c) and fed to the third reactor. The working solution and air flow countercurrently, but both streams are divided into cocurrent flow segments.

**Laporte Oxidation Step** (Fig. 12). In Laporte's Warrington plant, oxidation is carried out in a cocurrent flow column [57]–[61]. The entire volume of the oxidation reactor (a) is used for air gassing. The air and the working solution leaving the top of the column are fed together into a separator (b). The air then reaches the alternately operated two-stage activated carbon adsorbers (c), and the working solution passes to the extraction stage.

**Allied Chemical Oxidation Step.** To shorten the residence time of the working solution in the oxidation step, Allied Chemical suggested a counterflow reactor in which residence times are less than 2.5 min at a partial oxygen pressure of 70–90 kPa [62].

#### 4.1.2.3. Extraction and Drying

In the BASF plant, a sieve-tray extraction column extracts hydrogen peroxide from the



**Figure 12.** Laporte oxidation step  
a) Oxidation reactor; b) Separator; c) Activated carbon adsorber; d) Air compressor

working solution. A number of other extractors, such as packed columns, pulsed packed columns, and Podbielniak extractors, have been proposed.

Working solution leaving the extraction unit contains dispersed water droplets and is led into coagulators and separators to separate free water. The working solution is then dried to a specific water content.

Because the solubility of water in the working solution depends on temperature, its moisture content can be adjusted by carrying out the extraction at low temperature, separating the dispersed water, and then increasing the temperature of the working solution by about 30 °C before it reaches the hydrogenation step [63].

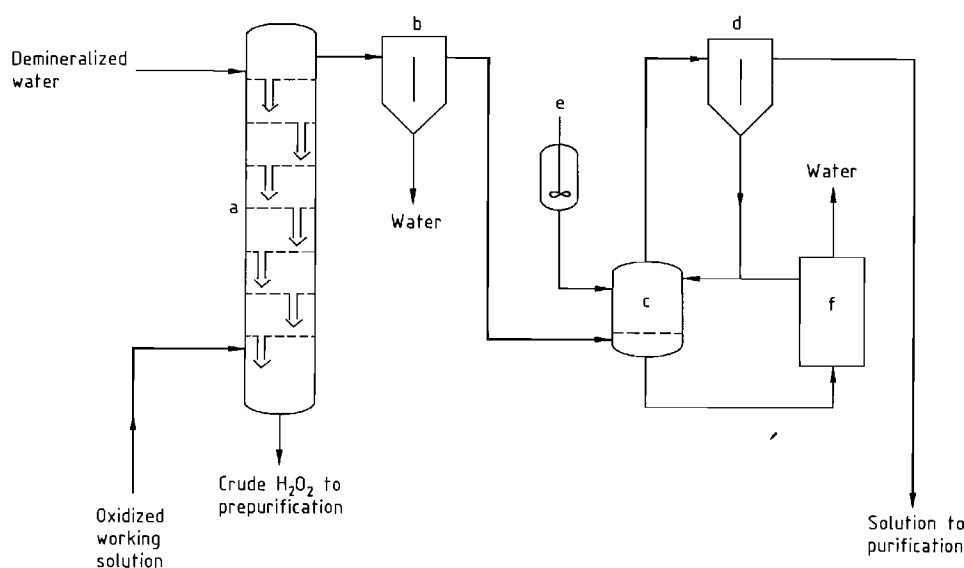
In extraction and drying according to BASF (Fig. 13), working solution leaving the head of the extraction column (a) is initially freed from entrained water in a water separator (b). The working solution then passes through aqueous potassium carbonate solution for drying (c).

#### 4.1.2.4. Working Solution Purification and Regeneration

During the constant circulation of working solution, degradation products are formed not only from the working compound, but also from the solvents. These degradation products must be removed from the working solution to prevent (1) deterioration of the crude hydrogen peroxide (color, smell, dissolved organic compounds), (2) an increase in density and viscosity of the working solution, and (3) a decrease in surface tension of the working solution, which promotes the formation of an emulsion during extraction. In addition, degradation products decrease the activity and life time of the hydrogenation catalysts.

Numerous methods have been suggested for purifying the working solution and regenerating active quinone from the quinone degradation products. Examples include the following:

- 1) Treatment of the hydrogenated working solution with alkaline substances [44]
- 2) Treatment of the working solution with sodium aluminum silicates at 50–200 °C [64]
- 3) Treatment of the working solution with active aluminum oxide or magnesium oxide at 90–150 °C [65]
- 4) Treatment of the hydrogenated or, preferably, the oxidized working solution at 75–150 °C with calcium, magnesium, or zinc silicates [66]
- 5) Treatment with alkali hydroxide, calcium hydroxide, ammonia, or amines in the presence of oxygen or hydrogen peroxide [67]
- 6) Treatment with concentrated sulfuric acid [68]



**Figure 13.** BASF extraction and drying step

a) Sieve-tray extraction column; b) Water separator; c) Drier; d) Potassium carbonate solution separator; e) Potassium carbonate solution make-up and feed tank; f) Potassium carbonate concentration

- 7) Treatment with alkaline hyposulfite solutions, followed by oxidation [69]
- 8) Treatment of the working solution with aqueous sodium hydroxide or potassium hydroxide solution (8–17 mol/L) in the presence of oxidants [70]

#### 4.1.2.5. Purification of Crude Hydrogen Peroxide

The aqueous hydrogen peroxide leaving the extraction is impure. Separators are usually installed after extraction (Section 4.1.2.4). Measures for reducing the amount of dissolved organic compounds include treatment of the crude product with polyethylene [71], ion exchangers [72], or hydrocarbons [73], [74]. Water-soluble organic compounds can also be oxidized by heating and then extracted with suitable solvents (e.g., the quinone solvent) [75]. The effect of purification on carbon content of crude hydrogen peroxide is illustrated in Table 5.

Purified crude product is then usually fed to a distillation unit where it is purified further and concentrated to the usual commercial concentration of 50–70 wt% hydrogen peroxide. This product can be used directly in a number of applications.

**Table 5.** Processes for purifying crude hydrogen peroxide

Process	Carbon content of H <sub>2</sub> O <sub>2</sub> , mg/L		Reference
	Before purification	After purification	
Extraction with xylene	580	450	[76]
Extraction with methylcyclohexanol acetate	580	390	[76]
Extraction with xylene and methylcyclohexanol acetate	580	370	[76]
Brief treatment with 0.5 wt% activated carbon	134	11	[77]
Treatment with adsorber resin	320	140	[78]

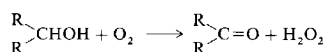
#### 4.1.2.6. Concentration of Hydrogen Peroxide

Water and hydrogen peroxide do not form an azeotrope; their boiling point difference at atmospheric pressure is 50.2 °C (Table 1, p. 445). Distillation of water from aqueous hydrogen peroxide can, therefore, be used to concentrate the solution or to completely separate hydrogen peroxide from water. A number of technical safety requirements must be observed. Distillation of dilute solutions has been used industrially to produce commercial 50–70 wt% hydrogen peroxide

solution in electrochemical processes; the technology is described in [3], [5], [79]–[82].

#### 4.2. 2-Propanol Process (Shell Process)

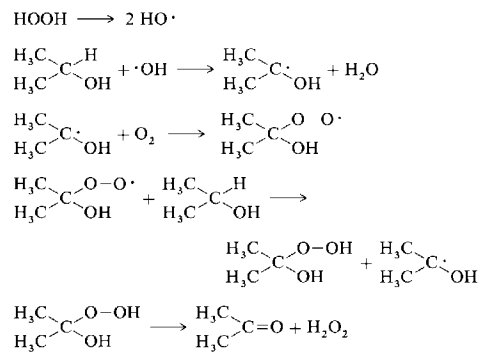
In 1945 HARRIS discovered that primary and secondary alcohols react with oxygen to form hydrogen peroxide and an aldehyde or ketone, respectively [83]:



Oxidation of the alcohol can be carried out in the liquid or the gas phase. Because aldehydes formed in the reaction with primary alcohols are oxidized easily, only the oxidation of secondary alcohols, especially 2-propanol [67-63-0], has industrial importance.

A process for the simultaneous production of hydrogen peroxide and acetone [67-64-1] by atmospheric oxidation of 2-propanol was first suggested by RUST [84], [85]. BRODSKI demonstrated that oxygen in the hydrogen peroxide product originates exclusively from atmospheric oxygen and not from the alcohol [86].

Reaction of 2-propanol with oxygen in the liquid phase does not require a special catalyst because it is catalyzed by the hydrogen peroxide product. However, a small amount (0.5–1 wt%) of hydrogen peroxide is added to 2-propanol to shorten the induction period. The reaction proceeds as follows:



Secondary reactions also take place but are not discussed here. To reduce the formation of byproducts, particularly acetic acid which affects the quality of hydrogen peroxide, only part of

the 2-propanol is oxidized and oxidation is carried out in several consecutive steps at decreasing temperatures [87].

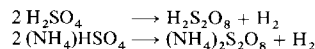
The 2-propanol process is used only in two plants in the Soviet Union, which have been operating since 1968 and 1972. The Shell Oil Company decommissioned its plant in Norco, Louisiana in 1980 [88], [89]; that plant had been in operation since 1957. The technology of the Shell 2-propanol process is described in [6]. The hydrogen peroxide yield of the Russian plants, relative to 2-propanol or atmospheric oxygen, is 90–94%; the acetone yield is 92–94% [90].

#### 4.3. Electrochemical Processes

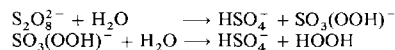
Electrochemical production of hydrogen peroxide is of minor industrial importance compared to the AO process. A few plants still produce hydrogen peroxide by electrolytic processes, for instance the Biochemie Gesellschaft mbH in Austria.

Because electrochemical processes played an important part in the development of hydrogen peroxide and their technology reached a high standard, essential features of the three known cyclic processes are described below. These processes are described in detail in [3], [5].

The basis of electrochemical processes is anodic oxidative coupling of sulfate ions to persulfate ions. Sulfuric acid is oxidized in the Degussa–Weissenstein process, whereas ammonium hydrogen sulfate solutions are used in the Münchner process.



Hydrogen peroxide is formed by hydrolysis of the persulfate ion via the peroxomonosulfate anion:



In the Degussa–Weissenstein and Riedel–Loewenstein processes, persulfuric acid or ammonium persulfate derived from the electrolysis is hydrolyzed directly. In the Münchner process, ammonium persulfate is converted to potassium persulfate which is then hydrolyzed. The Münchner process, therefore, consists of several coupled cyclic processes.

**Table 6.** Yields and energy consumption of electrochemical processes

Yield or consumption*	Degussa–Weissenstein process	Münchener process	Riedel–Loewenstein process
Current yield, %	73	83	83
Hydrolysis and distillation yield, %	93–96	87	82–85
Total yield, %	68–70	72	68–70.5
Electrical energy, kW·h	1280	1760	1700
Steam, t	1.85	2.5	4.5–4.8
Cooling water, m <sup>3</sup>	200	240	250

\* Parameters are expressed per 100 kg of hydrogen peroxide (calculated as 100 wt%) in the form of a distilled 35 wt% solution.

All three processes have a very high energy consumption and an unsatisfactory yield of ca. 70% (Table 6).

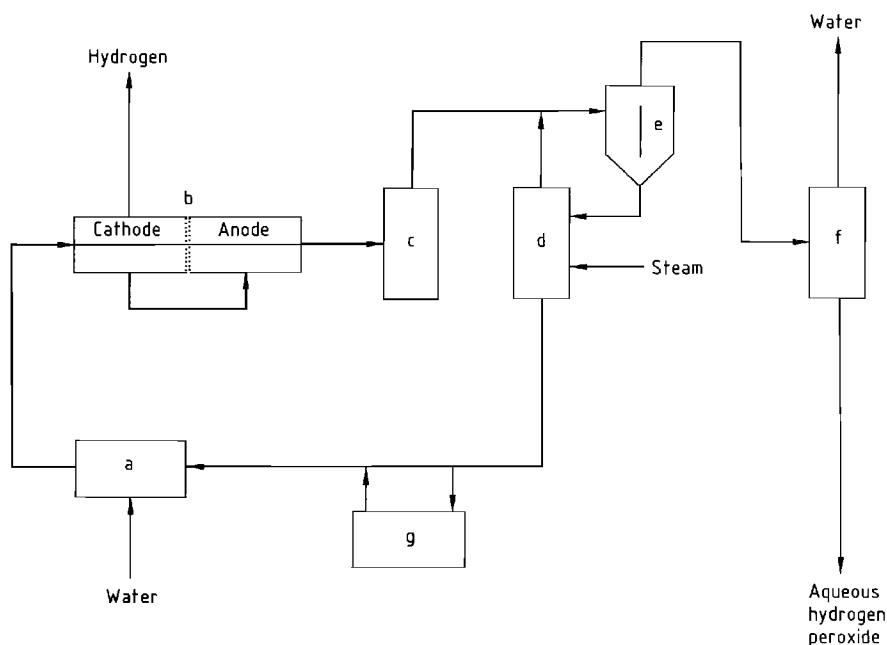
#### 4.3.1. Degussa–Weissenstein Process

In the Degussa–Weissenstein process (Fig. 14), sulfuric acid is adjusted to a concentration of 550–570 g/L (a) before flowing through

the catholyte chamber (b) where residual peroxide is destroyed and heavy-metal ions are precipitated. After addition of chemicals to raise the electrochemical potential (e.g., ammonium rhodanide or hydrochloric acid), sulfuric acid passes to the anolyte chamber where persulfuric acid is formed. Hydrolysis of persulfuric acid and distillation of hydrogen peroxide are carried out in two steps (c, d). Hydrolysis is 80–90% completed in (c), and distillation is achieved in approximately equal parts in two steps (c, d). In the expulsion column (d), hydrogen peroxide is expelled from the concentrated sulfuric acid solution by countercurrent steam. Entrained acid is separated in an acid separator (e), and hydrogen peroxide–water vapors are separated in a fractionating column (f). An aqueous solution with a maximum content of 45 wt% hydrogen peroxide is obtained. To purify the circulating solution, part of the stream is distilled constantly (g).

#### 4.3.2. Münchner Process

In the Münchner process (Fig. 15), acid ammonium sulfate is electrolyzed in electrolyzers without diaphragms.

**Figure 14.** Degussa–Weissenstein process

a) Electrolyzer feed tank; b) Electrolyzer; c) Evaporation and hydrolysis; d) Hydrogen peroxide expulsion and hydrolysis; e) Acid separator; f) Water–hydrogen peroxide fractionating column; g) Acid purification

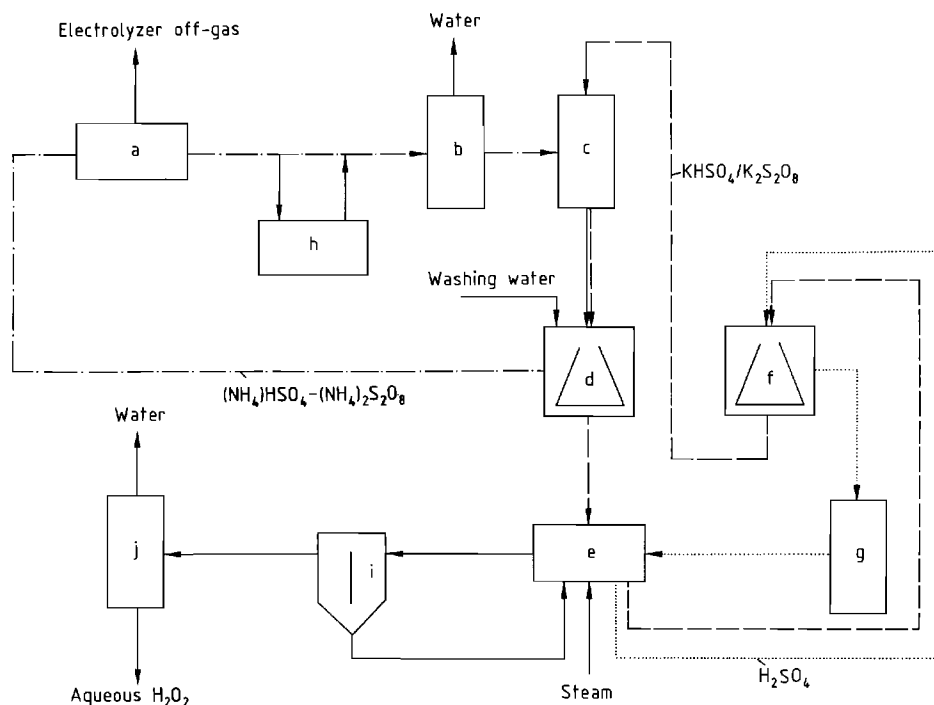


Figure 15. Münchner process

a) Electrolyzer; b) Vacuum cooler; c) Conversion (crystallization); d) Centrifuge; e) Hydrolysis–distillation; f) Centrifuge; g) Sulfuric acid purification; h) Purification of cycle solution; i) Acid separator; j) Fractionating column

The circulating solution contains 300 g of  $(\text{NH}_4)_2\text{SO}_4$ , 40 g of  $\text{K}_2\text{SO}_4$ , 100 g of  $\text{H}_2\text{SO}_4$ , and 57.6 g of  $\text{S}_2\text{O}_8^{2-}$  per liter before entering the electrolyzer. Its persulfate concentration is increased to 115.2 g/L by the electrolytic process. After electrolysis, the circulating solution is cooled and concentrated in a vacuum cooler (b) by evaporation of water and then fed into a crystallizer (c). Half of the persulfate is precipitated as potassium persulfate by addition of potassium hydrogen sulfate and separated in a centrifuge (d). The supernatant mother liquor diluted with washing water is returned to the electrolyzer. Solid potassium persulfate is hydrolyzed (e) and hydrogen peroxide is steam distilled.

The remaining potassium hydrogen sulfate–sulfuric acid residue is separated in a centrifuge (f). Sulfuric acid is recycled to the hydrolysis and distillation stage (e) via a purification stage (g). Potassium hydrogen sulfate is returned to the crystallizer (c) for precipitation of persulfate.

To purify the circulating solution, a side stream is mixed with ammonia in the purification

step (h) to precipitate iron. The hydrogen peroxide–water vapors formed during hydrolysis and distillation are led through an acid separator (i) and separated in the rectification step (j). Because hydrolysis is carried out batchwise, the initial vapor mixture is rich in hydrogen peroxide, giving a distillate of 60 wt% which then drops to 20 wt%.

#### 4.4. Other Processes

A number of reactions and processes for the production of hydrogen peroxide are described in the literature. Some of them are no longer economical (e.g., the barium peroxide, azobenzene, and Krusch processes). Others (e.g., production from hydrogen and oxygen or cathodic reduction of oxygen) have no industrial importance.

Only a few examples can be described here; detailed information may be found in the literature [1], [3], [5].

#### 4.4.1. Production from Peroxy Compounds

Peroxy compounds can be decomposed to form hydrogen peroxide. Examples of such reactions, which include the historically important Thenard reaction of barium peroxide with nitric or sulfuric acid, are listed in Table 7.

#### 4.4.2. Production from Hydrogen and Oxygen

Direct reaction of hydrogen and oxygen to form hydrogen peroxide can be achieved in a number of ways but is not industrially important. Available processes are either uneconomical or difficult to execute. However, the most important hydrogen peroxide manufacturing process—the AO process—also allows production of hydrogen peroxide from its elements.

**Table 7.** Production of hydrogen peroxide from peroxy compounds

Peroxide	Reaction	Reference
BaO <sub>2</sub>	reaction of barium peroxide with H <sub>2</sub> SO <sub>4</sub> in the presence of a small amount of HCl allows quantitative conversion; ca. 6% aqueous H <sub>2</sub> O <sub>2</sub> solutions are obtained	[91]
BaO <sub>2</sub>	as above, but in the presence of HCl and H <sub>3</sub> PO <sub>4</sub>	[92]
Na <sub>2</sub> O <sub>2</sub>	sodium peroxide solutions are passed through acidic ion exchangers to exchange Na <sup>+</sup> for H <sup>+</sup>	[93]
(CH <sub>3</sub> ) <sub>3</sub> CO—OH	<i>tert</i> -butyl hydroperoxide is hydrolyzed to <i>tert</i> -butanol and H <sub>2</sub> O <sub>2</sub> in the presence of H <sub>2</sub> SO <sub>4</sub> in a fractionating column	[94]
(CH <sub>3</sub> ) <sub>3</sub> CO—OH	H <sub>2</sub> O <sub>2</sub> and di- <i>tert</i> -butyl peroxide are formed from <i>tert</i> -butyl hydroperoxide in 50% H <sub>2</sub> SO <sub>4</sub>	[95]
$\text{H}_3\text{C}-\text{C} \begin{array}{l} \text{O}-\text{OH} \\ \text{O} \end{array}$	peracetic acid is hydrolyzed to CH <sub>3</sub> COOH and H <sub>2</sub> O <sub>2</sub> in the presence of H <sub>2</sub> SO <sub>4</sub> ; to shift the equilibrium to H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> COOH is reacted with an alcohol and the ester is distilled	[96]
$\text{H}_3\text{C}-\text{C} \begin{array}{l} \text{O}-\text{OH} \\ \text{O} \end{array}$	peracetic acid is hydrolyzed with acidic ion exchangers, and the equilibrium mixture is separated by distillation	[97]

Examples of hydrogen peroxide synthesis from hydrogen and oxygen follow:

- 1) Silent electrical discharge into a reaction gas containing 95% hydrogen and 5% oxygen, in the presence of water vapor at 150–160 °C and 100 kPa, and subsequent condensation of hydrogen peroxide result in a 10% aqueous solution. The minimum electrical energy needed to produce 1 kg of hydrogen peroxide is 40 kW·h [98].
- 2) Addition of hydrogen, oxygen, and nitrogen to acetone in the presence of hydrochloric acid, sulfuric acid, and palladium–silica gel catalyst results in hydrogen peroxide yields of 50% relative to hydrogen [99].
- 3) Hydrogen and oxygen react to form hydrogen peroxide in a biphasic liquid system (water–organic solvent) with a catalyst of the L<sub>2</sub>PdX<sub>2</sub> type (L = phosphorus-containing ligand, X = halogen, preferably chlorine). The catalyst is soluble in organic solvents but generally insoluble in water [100].
- 4) Reaction of hydrogen and oxygen proceeds in the presence of a nitrile or a nitrogen-containing organic compound, a strong acid, and a palladium catalyst [101].
- 5) Homogeneously catalyzed reaction of hydrogen and oxygen occurs in a biphasic liquid system (water–organic solvent) in the presence of a promoter. Compounds of the IrClCO(XR<sub>3</sub>)<sub>2</sub> type are used as catalysts (X = P, As, or Sb; R = phenyl, alkyl, or cyclohexyl) [102].

#### 4.4.3. Production by Autoxidation of Organic Compounds

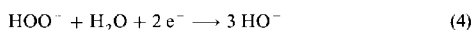
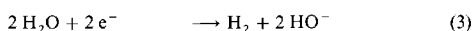
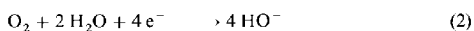
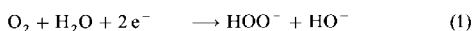
Autoxidation processes for the production of hydrogen peroxide include the AO process and the 2-propanol process discussed in Sections 4.1 and 4.2. The azobenzene process has occasionally been used on a commercial scale. Analogous to the AO process, azobenzene is reduced to hydrazobenzene which is then oxidized to azobenzene. The reaction proceeds at alkaline pH and results in formation of Na<sub>2</sub>O<sub>2</sub>·8 H<sub>2</sub>O [103]–[105].

Other autoxidation processes have been suggested, such as the oxidation of hydrocarbons, alcohols, and hydrazine, but they have no commercial significance. They are usually carried out in the gas phase at high temperature and give a multicomponent reaction mixture due to subsequent secondary reactions.

#### 4.4.4. Production by Cathodic Reduction of Oxygen

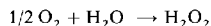
The formation of hydrogen peroxide (max. 1% solution) by cathodic reduction of oxygen was reported by TRAUBE in 1882 [106]. The process was improved by FISCHER and PRIESS who introduced pressurized electrolysis (ca. 10 MPa),

which gave 1.3–2.7% hydrogen peroxide solutions with current efficiencies of 83–90% [107]. Although BERL attempted to bring cathodic oxygen reduction to technological maturity [108], [109], this process is not yet used on an industrial scale. Apart from the desired reduction of oxygen to hydrogen peroxide according to Equation (1)

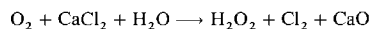


Equations (2) and (3) occur, which reduce current efficiency, and the hydrogen peroxide formed can be destroyed by reduction (Eq. 4). Equation (3) ultimately leads to the formation of a detonating gas atmosphere in the electrolyzer. Work on cathodic reduction with oxygen has been resumed [110], [111]. Gas cathodes and > 3500 h of operation allow current efficiencies > 90%. The following methods are suggested for industrial use and yield a 10% aqueous hydrogen peroxide solution which must be brought to the commercial concentration of 50–70 wt% by distillation.

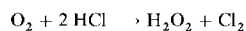
- 1) Use of caustic potash as the working electrolyte, anodic oxygen production, precipitation of peroxide as calcium peroxide, reaction of calcium peroxide with carbon dioxide and water to form hydrogen peroxide and calcium carbonate, and conversion of the latter into carbon dioxide and calcium oxide results in the net reaction:



- 2) Use of potassium chloride solution as the working electrolyte with anodic chlorine production, otherwise follows method 1.



- 3) Use of potassium chloride as the working electrolyte with anodic chlorine production, precipitation of peroxide with calcium chloride, release of hydrogen peroxide by reaction of calcium peroxide with carbon dioxide and water, and conversion of calcium carbonate with hydrochloric acid to calcium chloride. The net reaction is



## 5. Storage and Transportation [4]

The decomposition of hydrogen peroxide caused by catalytic impurities and the associated release of heat have been described in Chapters 2 and 3. Great care must be taken in production,

storage, and transportation to prevent these impurities from entering the hydrogen peroxide solution and to ensure that hydrogen peroxide is put only into perfectly clean containers. Because commercial hydrogen peroxide always contains small quantities of catalytic impurities, the stabilization of peroxide solutions is extremely important. The stabilizing effects of inorganic and organic compounds are described in detail in [3].

Sodium pyrophosphate [7722-88-5] and sodium stannate [12058-66-1] are the preferred stabilizers and are added separately or together [112], [113]. Organic compounds are not stable enough for use with concentrated hydrogen peroxide; they are preferred for dilute solutions [114], [115].

Aluminum (99.5%), aluminum–magnesium alloys, or stainless steels are good construction materials. Because of their corrosion resistance, polyethylene containers and storage tanks are preferred for hydrogen peroxide concentrations up to 50 wt%. Before metallic tanks and containers can be used, their surfaces must be passivated. Iron particles may become attached to the surface during the rolling of aluminum, and they must be removed. Aluminum is, therefore, treated with dilute sodium hydroxide and then passivated with dilute nitric acid. Because hydrogen forms during the caustic treatment of aluminum with sodium hydroxide, safety precautions must be taken to avoid a detonating gas atmosphere. It is extremely important to ensure that no hydrogen peroxide is trapped, e.g. between closed valves. If decomposition occurs, extremely high pressures result which lead to very serious explosions.

Hydrogen peroxide is admitted for air transport only up to a concentration of 40 wt% (IATA regulations).

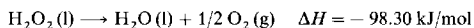
No special regulations apply to the transport of solutions of up to 8 wt% hydrogen peroxide. Table 8 lists international regulations for rail (RID), road (ADR), and sea (IMDG code) transport of more highly concentrated solutions.

**Table 8.** Transport regulation for hydrogen peroxide

	H <sub>2</sub> O <sub>2</sub> concentration, wt%		
	8–20	20–60	> 60
RID/ADR	8, No. 62c	8, No. 62b	5.1, No. 1
IMDG Code	5.1	5.1	5.1
UN No.	2984	2014	2015
	package group III	package group II	package group I

## 6. Safety

Hydrogen peroxide has a high energy content:

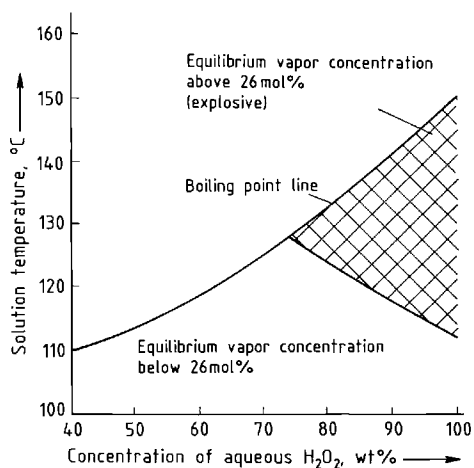


Furthermore, its high oxygen content (47 wt%) is available for combustion reactions and the oxidation of organic compounds. This means that special safety conditions apply in handling hydrogen peroxide. Safety studies can be divided into three groups:

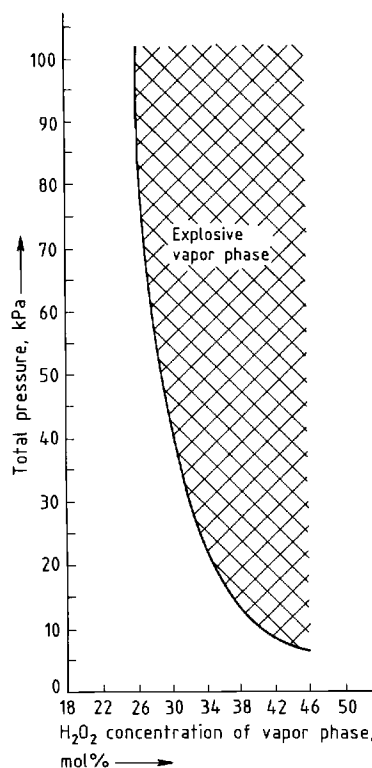
- 1) examination of the pure vapor phase,
- 2) examination of the pure liquid (aqueous) phase, and
- 3) examination of mixtures or solutions of organic compounds with or in aqueous hydrogen peroxide.

Results are summarized below, but the literature must be consulted for details. In specific cases, especially when hydrogen peroxide is used with organic compounds, the intended work area must be checked for hazards if it has not already been certified as safe by a safety examination.

**Pure Hydrogen Peroxide—Vapor Phase** [5], [116]–[119]. Explosive vapor mixtures are formed at atmospheric pressure when the hydrogen peroxide concentration in the vapor phase exceeds 26 mol%. Figure 16 shows the explosive



**Figure 16.** Dependence of the explosive range of the vapor phase (> 26 mol% H<sub>2</sub>O<sub>2</sub>) on the temperature and the hydrogen peroxide concentration of liquid phase (at atmospheric pressure)



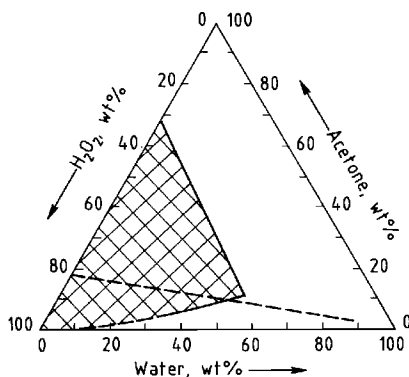
**Figure 17.** Dependence of the explosive range of vapor phase on pressure

range as a function of temperature and hydrogen peroxide concentration.

For the industrial concentration of hydrogen peroxide solutions, it is important to note that at reduced pressure the critical hydrogen peroxide concentration of the vapor phase may exceed 26 mol% (Fig. 17).

**Pure Hydrogen Peroxide—Liquid (Aqueous) Phase** [120], [121]. The explosive risk of pure, highly concentrated hydrogen peroxide solutions has been examined by various methods, but the sometimes contradictory findings are difficult to interpret consistently.

Results are influenced primarily by test conditions and not by hydrogen peroxide concentration. For example, 90.7 wt% hydrogen peroxide in a tube with an internal diameter of 2.67 cm (1.05 inches) could not be exploded by the detonation shock of a tetryl booster, whereas explosion occurred in a tube with an internal diameter of 4.09 cm (1.61 inches). Similarly, 86% hydrogen peroxide in a tube of 4.09 cm internal diameter was exploded by raising the



**Figure 18.** Explosive range (hatched area) of hydrogen peroxide-acetone-water mixtures  
Dashed line, indicates the stoichiometry  
 $8 \text{H}_2\text{O}_2 + \text{CH}_3\text{COCH}_3 \rightarrow 3 \text{CO}_2 + 11 \text{H}_2\text{O}$

temperature above 50 °C [120], [121]. The decisive factors for explosion of pure aqueous hydrogen peroxide seem to be the degree of occlusion, the insulation, and the energy of detonation.

**Mixtures or Solutions of Aqueous Hydrogen Peroxide with Organic Compounds** [122]–[124]. The hazards associated with mixtures of hydrogen peroxide and organic chemicals are important for its industrial production and, especially, for its uses. As an example, Figure 18 shows results obtained with the hydrogen peroxide-acetone-water system [122]. Many other organic compounds give similar results. The size of the explosive region depends on the organic compound and the test conditions.

For practical use, safety tests of the intended working area are very important. When systems such as hydrogen peroxide-formic acid-water are used, other products may be formed (in this case performic acid), that are more dangerous than the original mixture [123].

## 7. Uses

Development of the AO process permitted large-scale production of hydrogen peroxide, which is now used widely in almost all industrial areas. Its main use is in bleaching (→ Bleaching, A4, p. 194). Uses in the chemical industry and in environmental protection are increasing because its great advantage is that the degradation product is water.

Hydrogen peroxide is used in the textile industry for bleaching cotton, linen, bast fibers, wool, silk, polyester fiber, and polyurethane fiber. In the pulp and paper industry, it is used to bleach sulfate and sulfite cellulose, wood pulp, and wastepaper, and to brighten wood veneers and wooden structures.

The chemical industry employs hydrogen peroxide for the production of peroxy compounds such as sodium perborate, sodium percarbonate, metallic peroxides, or percarboxylic acids. Hydrogen peroxide is very important in organic chemistry for epoxidation and hydroxylation (manufacture of plasticizers and stabilizers for the plastics industry), oxidation (manufacture of amine oxides as washing-up liquids), oxo-halogenation, and initiation of polymerization.

Sulfuric acid solutions of hydrogen peroxide are used for the pickling and chemical polishing of copper, brass, and other copper alloys, as well as for etching and cleaning printed circuit boards. Highly purified hydrogen peroxide is used in the manufacture of silicon semiconductor chips to clean silicon disks and to remove photoresist layers. It is also used for in situ leaching in underground uranium mining.

Hydrogen peroxide is increasingly used in environmental protection to detoxify effluents containing formaldehyde, phenols, or cyanide (e.g., wastewater from mines and tempering works, galvanizer concentrate, photochemical effluents), and to deodorize sulfur-containing effluents. Smoke and exhaust gases containing sulfur dioxide can be completely detoxified with hydrogen peroxide.

Hydrogen peroxide is a highly efficient disinfectant (especially for packaging materials); it is also used as a bleaching agent in hair preparations and as a propellant in space technology.

## 8. Toxicology and Occupational Health

**Toxicity in Humans.** In humans, brief contact of hydrogen peroxide with the skin leads to irritation and whitening (cutaneous emphysema), the severity of which depends on concentration. Longer contact or higher concentration can lead to burns.

Contact with the eyes also leads to serious injury. Hydrogen peroxide vapor or aerosol causes irritation or damage of the upper respira-

tory tract and serious lung injuries [125], [126]. The human reaction to the irritating effect of hydrogen peroxide on the mucous membranes and skin is far more sensitive than that of the rat. The threshold concentration for acute irritative effects of gaseous hydrogen peroxide on the respiratory tract is 60 mg/m<sup>3</sup> in rats but only 10 mg/m<sup>3</sup> in humans; the corresponding values for skin are 110 mg/m<sup>3</sup> for rats and 20 mg/m<sup>3</sup> for humans [127].

Accidental ingestion of hydrogen peroxide (33 wt% solution) in five cases led to stomach and chest pain, respiratory depression, foaming at the mouth, and loss of consciousness. Muscle and nerve disturbances and fever were observed as added complications. However, all affected persons recovered after several weeks [128].

Hydrogen peroxide has not been found to produce teratogenic or carcinogenic effects in humans; mutagenic or chromosomal effects have not been observed. The MAK and TLV-TWA values (1987) are 1 ppm (1.4 mg/m<sup>3</sup>).

**Toxicity in Animals.** Acute toxicities of hydrogen peroxide in animals follow [128]:

LD <sub>50</sub> (mouse, oral)	2538 mg/kg
LD <sub>50</sub> (mouse, oral)	2000 mg/kg
LD <sub>50</sub> (rat, oral)	4060 mg/kg
LD <sub>50</sub> (mouse, dermal)	1.2 × 10 <sup>4</sup> mg/kg
LC <sub>50</sub> (rat, inhalation, 4 h)	2000 mg/m <sup>3</sup>

Acute dermal toxicity depends on hydrogen peroxide concentration. With 90 wt% hydrogen peroxide, the dermal LD<sub>50</sub> in rabbit is 630 mg/kg and in rat 4800 mg/kg [129]. So far no indication of a toxic effect on reproduction in animals has been found [130].

Hydrogen peroxide has a mutagenic effect on fungi and bacteria (e.g., Ames test), but not on insects or mammalian cells in vitro [130].

Oral administration of hydrogen peroxide produced tumors in the small intestine of mice [131], [132]. According to the criteria of the International Agency for Research on Cancer (IARC), however, only "limited evidence of the carcinogenicity of hydrogen peroxide to experimental animals" exists [130]. When hydrogen peroxide was given orally to rats, no significant differences occurred between the two test groups and the control group [133]. No evidence of tumor formation was found one year after exposure of mouse skin to 5% hydrogen peroxide [134].

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#### Hydrogen Selenide → Selenium and Selenium Compounds

#### Hydrogen Storage Alloys → Hydrides