

CHAPTER 1

Introduction to the Preparation and Properties of Hydrogen Peroxide

1 Introduction

The following chapter will discuss the preparation of hydrogen peroxide, historically, the present day and future vistas for its *in situ* preparation. A brief introduction to the physical properties of hydrogen peroxide will also be made for the sake of completeness. Finally, the chapter will conclude with a practical approach to the safe handling of peroxygen species, destruction of residual peroxygens, and the toxicological and occupational health considerations required when handling hydrogen peroxide.

2 Industrial Manufacture of Hydrogen Peroxide

The industrial manufacture of hydrogen peroxide can be traced back to its isolation in 1818 by L. J. Thenard.¹ Thenard reacted barium peroxide with nitric acid to produce a low concentration of aqueous hydrogen peroxide; the process can, however, be significantly improved by the use of hydrochloric acid. The hydrogen peroxide is formed in conjunction with barium chloride, both of which are soluble in water. The barium chloride is subsequently removed by precipitation with sulfuric acid (Figure 1.1).

Hence, Thenard gave birth to the first commercial manufacture of aqueous hydrogen peroxide, although it took over sixty years before Thenard's wet chemical process was employed in a commercial capacity.² The industrial production of hydrogen peroxide using the above route was still operating until the middle of the 20th century. At the turn of the 19th century, approximately 10 000 metric tonnes per annum of barium peroxide were converted to about 2000 metric tonnes of hydrogen peroxide. Thenard's process has, however, some major drawbacks which quenched the expectant explosion of its use in an aqueous form. Firstly, only three percent *m/m* aqueous hydrogen peroxide solutions were manufactured using the barium peroxide

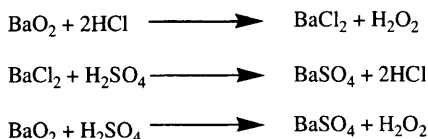


Figure 1.1 *Thenard's route to aqueous hydrogen peroxide.*

process, and hence only a limited market was afforded because production costs were prohibitively high. Further, due to the high levels of impurities present in the isolated hydrogen peroxide, subsequent stability was poor.

The disadvantages of the process discovered by Thenard were largely alleviated by the discovery in 1853 by Meidinger that hydrogen peroxide could be formed electrolytically from aqueous sulfuric acid.³ Berthelot later showed that peroxodisulfuric acid was the intermediate formed,⁴ which was subsequently hydrolysed to hydrogen peroxide, and sulfuric acid (Figure 1.2).

The first hydrogen peroxide plant to go on-stream based on the electrochemical process was in 1908 at the Österreichische Chemische Werke in Weissenstein. The Weissenstein process was adapted in 1910 to afford the Müncher process developed by Pietzsch and Adolph at the Elektrochemische Werke, Munich. In 1924, Reidel and Lowenstein used ammonium sulfate under the conditions of electrolysis instead of sulfuric acid, and the resulting ammonium peroxodisulfate (Reidel–Lowenstein process) or potassium peroxodisulfate (Pietzsch–Adolph process) was hydrolysed to hydrogen peroxide. As a result of this process, production of hydrogen peroxide as 100% *m/m* rose to approximately 35 000 metric tonnes per annum.⁵

In 1901, Manchot made a decisive breakthrough in the industrial preparation of hydrogen peroxide. Manchot observed that autoxidizable compounds like hydroquinones or hydrazobenzenes react quantitatively under alkaline conditions to form peroxides.⁶ In 1932, Walton and Filson proposed to produce hydrogen peroxide via alternating oxidation and reduction of hydrazobenzenes.⁷ Subsequently, Pfeleiderer developed a process for the alkaline autoxidation of hydrazobenzenes in which sodium peroxide was obtained, and sodium amalgam was used to reduce the azobenzene.⁸ A commercial plant based on this technology was operated by Kymmene AB in Kuisankoski, Finland.

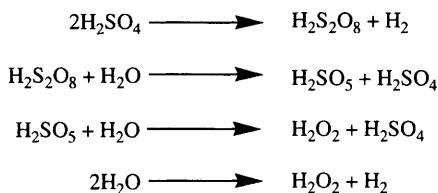


Figure 1.2 *Electrochemical manufacture of aqueous hydrogen peroxide.*

The major drawbacks associated with the azobenzene process, i.e. hydrogenation of azobenzene with sodium amalgam, and oxidation of hydrazobenzene in alkaline solution, were ultimately resolved by Riedl. Riedl employed polynuclear hydroquinones. Based on Reidl and Pfeleiderer's work, BASF developed, between 1935 and 1945, the anthroquinone process (often referred to as the AO process) in a pilot plant with a monthly production of 30 metric tonnes. Two large plants were then constructed at Heidebreck and Waldenberg, each having a capacity of 2000 metric tonnes per annum. Both plants were partially complete when construction was halted at the end of World War Two. In 1953, E.I. Dupont de Nemours commissioned the first hydrogen peroxide plant using the AO process, and consequently the production capacity of hydrogen peroxide was greatly increased. In 1996, world capacity stood at 1.3×10^6 metric tonnes as 100% *m/m* hydrogen peroxide.⁹

The underlying chemistry of the AO process is outlined in Figure 1.3 and a typical autoxidation plant schematic is summarized in Figure 1.4.

The features of all AO processes remain basically the same, and can be described as follows. A 2-alkylanthraquinone is dissolved in a suitable solvent or solvent mixture which is catalytically hydrogenated to the corresponding 2-alkylanthrahydroquinone. The 2-alkylanthraquinone solution is commonly referred to as the reaction carrier, hydrogen carrier or working material. The 2-alkylanthraquinone-solvent mixture is called the working solution. Carriers employed industrially include 2-*tert*-amylanthraquinone, 2-*iso-sec*-amylanthraquinone and 2-ethylanthraquinone. The working solution containing the carrier product alkylanthrahydroquinone is separated from the hydrogenation catalyst, and aerated with an oxygen-containing gas, nominally compressed air, to reform the alkylanthraquinone, and simultaneously forming hydrogen peroxide. The hydrogen peroxide is then extracted from the oxidized working solution using demineralized water, and the aqueous extract is then purified

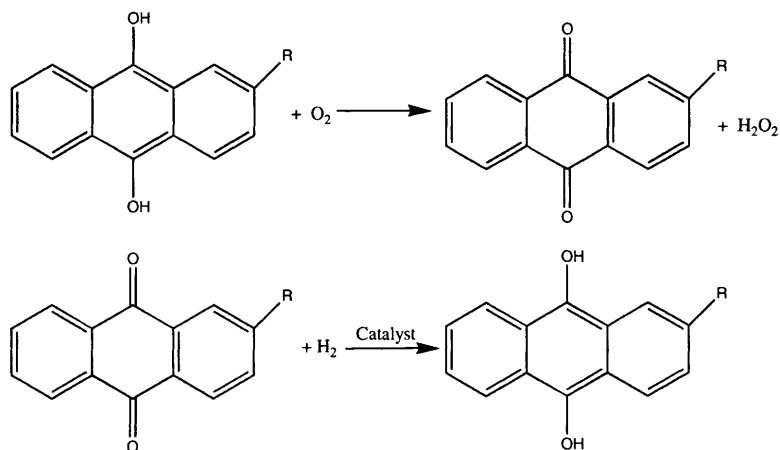


Figure 1.3 Anthrahydroquinone autoxidation process for the manufacture of aqueous hydrogen peroxide.

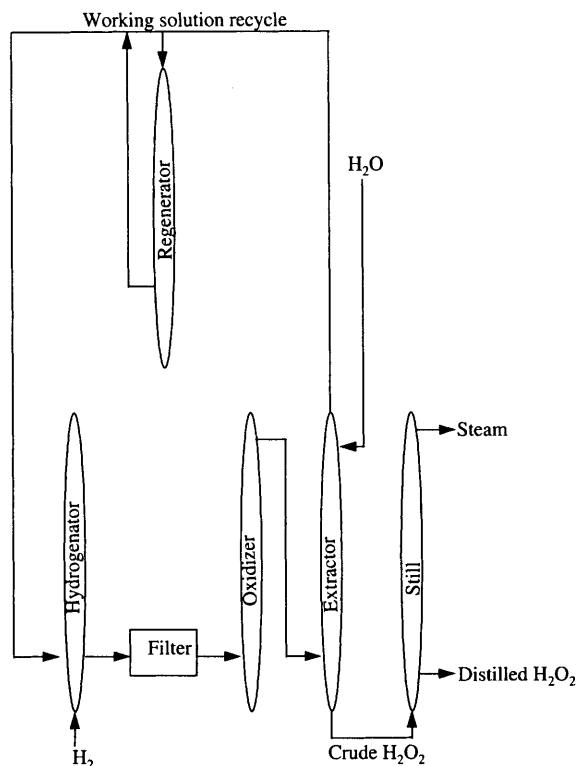


Figure 1.4 Schematic diagram of the AO process.

and concentrated by fractionation to the desired strength. The AO process, therefore, leads to the net formation of hydrogen peroxide from gaseous hydrogen and oxygen.

The choice of the quinone must be carefully made to ensure that the following criteria are optimized: good solubility of the quinone form, good solubility of the hydroquinone form, good resistance to non-specific oxidation and easy availability. The formation of degradation products, and their ability to be regenerated to active quinones also plays a rôle in the decision. A number of by-products can be formed during the hydrogenation step, and these are summarized in Figure 1.5. The process when first engaged, contains in the working solution only the 2-alkylanthraquinone species. The 2-alkylanthraquinone forms a complex with the hydrogenation catalyst, which is usually a palladium metal. The complex then reacts with hydrogen to form a species now containing the metal and the 2-alkylhydroanthraquinone. The 2-alkylhydroanthraquinone is subject to a number of secondary reactions which are continuously taking place during each process cycle.

The 2-alkylhydroanthraquinone (A) when in contact with the catalyst will undergo a small amount of catalytic reduction (B) on the ring, initially on the unsubstituted ring, yielding a tetrahydroalkylanthrahydroquinone. Unfortu-

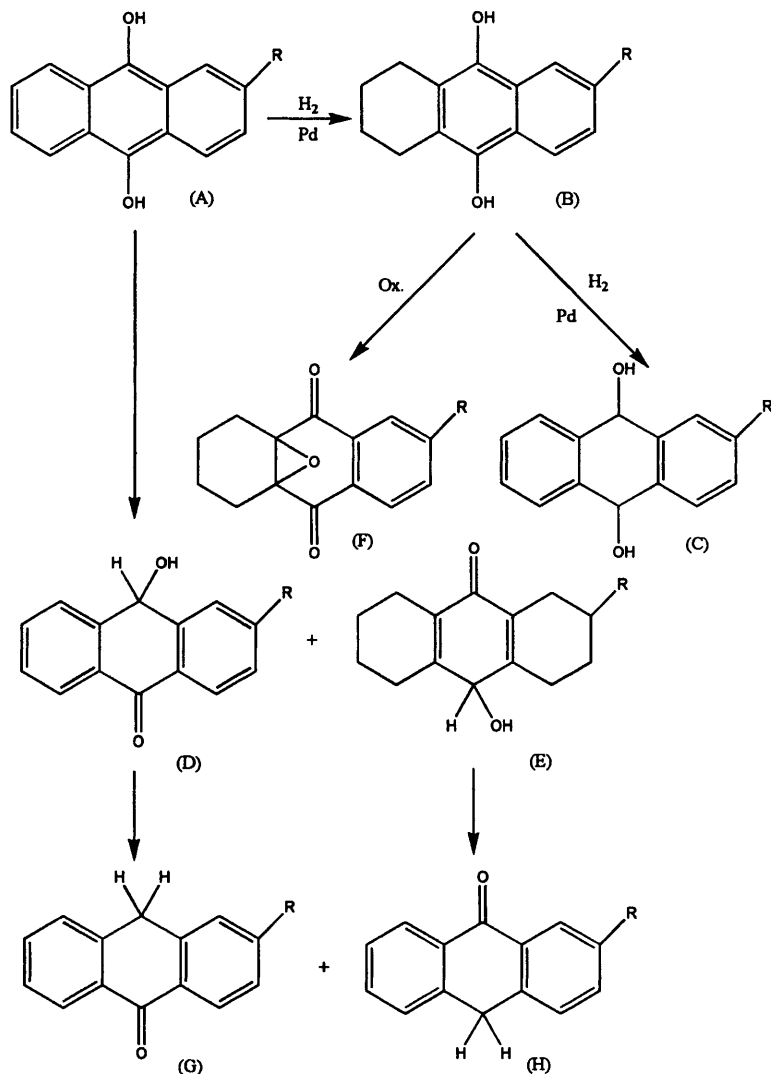
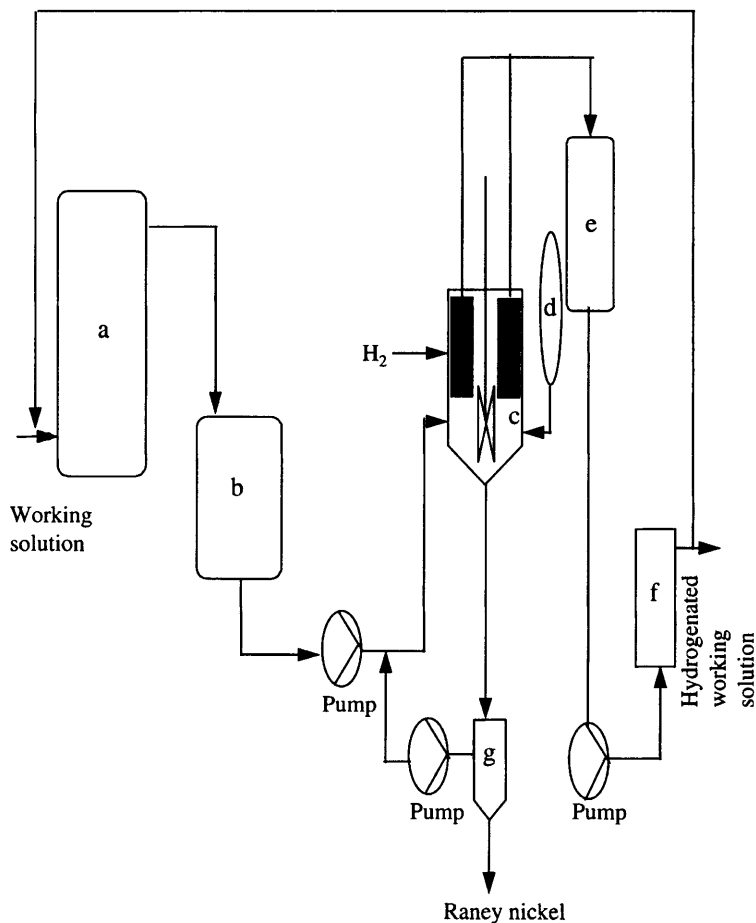


Figure 1.5 Secondary reactions taking place in the presence of 2-alkylanthrahydroquinones.

nately, once the octa-product (C) is formed, it remains until purged owing to its very low rate of oxidation. Tautomerism of the 2-alkylhydroanthraquinone yields hydroxyanthrones (D, E) which can be further reduced to the anthrones (G, H). The epoxide (F) formed from the alkylhydroanthraquinone does not participate in the formation of hydrogen peroxide, and leads to a loss of active quinone. Measures have, therefore, been suggested for regenerating the tetrahydro compound from the epoxide.¹⁰

A number of additional processes are also required to maintain the AO process. For example, in order for the hydrogenation phase to run efficiently,

part of the catalyst load is removed, regenerated and returned to the hydrogenator. The hydrogenation step is possibly the most important feature of the modern AO process. Quinone decomposition products that cannot be regenerated into active quinones are always formed during the hydrogenation phase. Therefore a tremendous amount of effort has been invested in the development of new hydrogenation catalysts and hydrogenator designs which have, in some cases, deviated dramatically from the BASF principle. The hydrogenation step in the BASF plant (Figure 1.6) employs a Raney nickel catalyst at a slight excess of pressure. However, because Raney nickel is sensitive to oxygen, the working solution from the extraction, drying and purification steps cannot be fed directly into the hydrogenator. The working solution at this stage still contains residual hydrogen peroxide, and has to be decomposed over a supported Ni–Ag catalyst



a = pre-contact column; b = feed tank to hydrogenator; c = reactor; d = catalyst feed tank; e = oxidizer feed tank; f = safety filter; g = catalyst removal tank.

Figure 1.6 BASF hydrogenator.

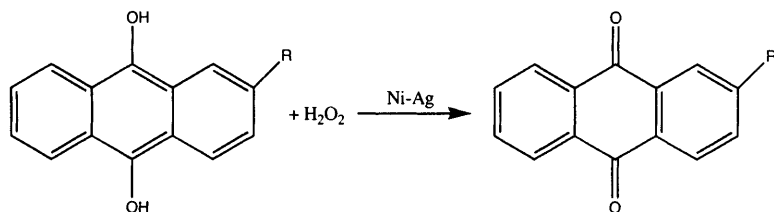


Figure 1.7 Destruction of residual hydrogen peroxide in the BASF process.

(Figure 1.7), together with a small amount of hydrogenated working solution (which also contains 2-alkylhydroanthraquinone). Such a step removes the hydrogen peroxide completely, thus extending the life of the Raney nickel catalyst.

The problem with Raney nickel as the hydrogenation catalyst is that it has a limited selectivity, i.e. the ratio of hydroquinone formation to the tetrahydro compound is low. BASF have largely alleviated this problem via pre-treatment of the catalyst with ammonium formate.¹¹ The pyrophoric properties of Raney nickel also require more stringent safety procedures when handling the material. Despite the drawbacks of Raney nickel, the catalyst is still used in some AO plants. The majority of AO plants worldwide prefer, however, to employ palladium hydrogenation catalysts because of their higher selectivity, their greater stability towards hydrogen peroxide residues and the simplified handling procedures in comparison to the Raney nickel systems. Degussa have employed palladium black as the hydrogenation catalyst in the majority of their plants.¹² The main advantages of the Degussa hydrogenation stage are: near-quantitative conversion of hydrogen, easy exchange of palladium black, the catalyst is non-pyrophoric and the palladium black is easily re-activated. Laporte chemicals made a significant breakthrough in the operation of the hydrogenation phase by employing supported palladium, which has a particle size diameter of 0.06–0.15 mm.¹³ The supported palladium catalyst allows for easier filtration, and recirculation of the catalyst back to the hydrogenator. Laporte, at the same time, also employed a new design for running the hydrogenation phase.¹⁴ Figure 1.8 illustrates the Laporte design.

The Laporte hydrogenator contains a series of tubes which dip just below the surface of the liquid. Hydrogen is then fed into the bottom of each tube, and small gas bubbles are formed. A counter current flow is set up due to the density difference between the solutions in the tube and the reactor. The palladium catalyst suspension is drawn into the tubes by a continuous movement of the working solution.

The problem with all three methods thus far discussed is the fact that the hydrogenator catalyst has to be removed prior to the formation of hydrogen peroxide. If the catalyst is not removed, then catastrophic dismutation of the hydrogen peroxide can occur. In response to the problem, FMC developed a mixed-bed hydrogenation process. The bed is impregnated with palladium, and hence the problem associated with catalyst removal is alleviated.¹⁵

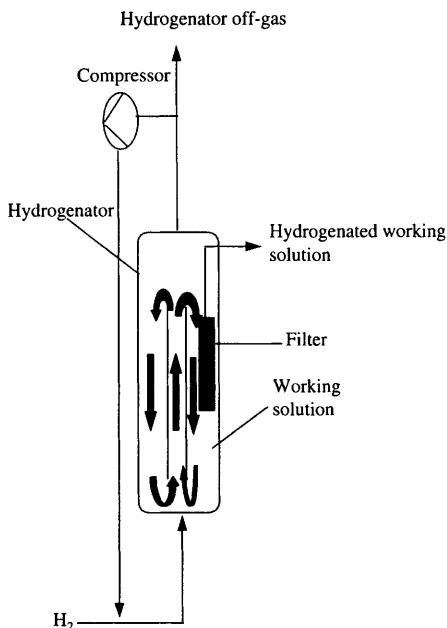


Figure 1.8 *Laporte hydrogenator.*

On an industrial scale, the catalyst-free hydrogenated working solution is generally oxidized with slight pressures of air (up to 0.5 MPa). The oxidation phase must satisfy several criteria, mainly economically driven, which include: small reactor volume to lower investment costs for equipment; efficient utilization of oxygen to reduce the volume of off-gas; and low compressor pressure to decrease energy costs. Like the hydrogenation phase, several companies have developed and used their own oxidation regimes. For example, BASF flow hydrogenated working solution through four oxidation columns arranged in series (Figure 1.9) as a cascade. The oxidized working solution then flows into an extractor tank. The nitrogen–oxygen mixture is compressed and fed into each of the four reactors.

Solvay Interlox's plant based at Warrington in the UK operates a co-current oxidation in a column.¹⁶ The whole volume of the reactor is used for air gassing (Figure 1.10). The air and hydrogenated working solution leave the top of the column and are fed into a separator. The air then reaches the two-stage activated carbon filters, which remove residual working solution and impurities. The working solution then passes to the extraction phase.

Finally, it is worth mentioning that Allied Colloids have employed a counter-flow oxidation reactor,¹⁷ which has a residence time of hydrogenated working solution of less than 2.5 min at a partial oxygen pressure of 70–100 kPa.

Inevitably, due to the constant circulation of working solution, by-products are formed from the working solution and the solvents. The by-products have to be purged from the system to prevent destabilization of the crude hydrogen

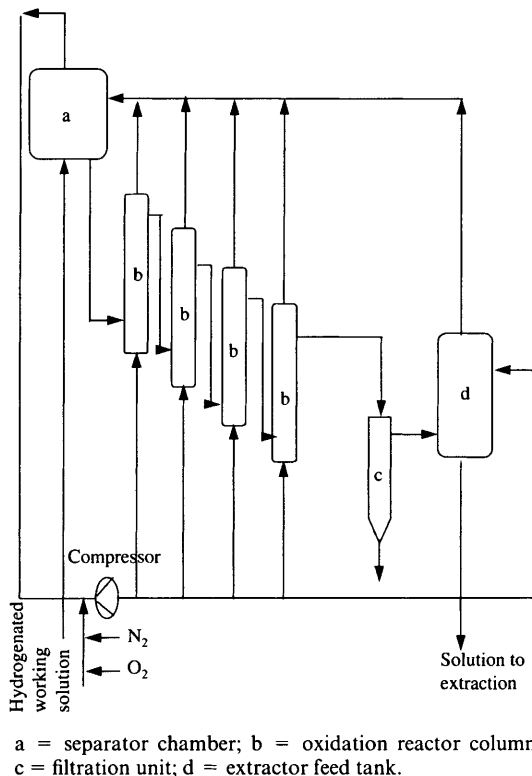


Figure 1.9 Illustration of the BASF oxidizer.

peroxide, and an increase in density and viscosity of the working solution. Further, the impurities in the working solution cause a decrease in the surface tension, and encourage the formation of an emulsion, which can be difficult to destabilize. By-product formation can also cause deactivation of the hydrogenation catalyst, hence the working solution can be purified by a range of techniques which include treatment with alkaline solution,¹⁸ treatment with active aluminium oxide or magnesium oxide at about 150 °C,¹⁹ use of alkaline hydroxide such as calcium hydroxide, ammonia or amines in the presence of oxygen or hydrogen peroxide²⁰ and treatment with sulfuric acid.²¹

The crude hydrogen peroxide exiting the extraction phase requires purification. A number of methods have been devised for the treatment of crude hydrogen peroxide including the use of polyethylene,²² ion-exchangers²³ and the use of hydrocarbon solvents.²⁴ The purified hydrogen peroxide is then fed to a distillation column where it is concentrated to the usual commercial concentration range of 35–70% *m/m*. Solvay Interlox produce 85% *m/m* hydrogen peroxide, but only use it captively for the preparation of 38% *m/m* peracetic acid used for the oxidation of cyclohexanone to ϵ -caprolactone. Higher strengths can be achieved as hydrogen peroxide does not form an azeotrope with water, but a number of technical safety requirements must be observed.

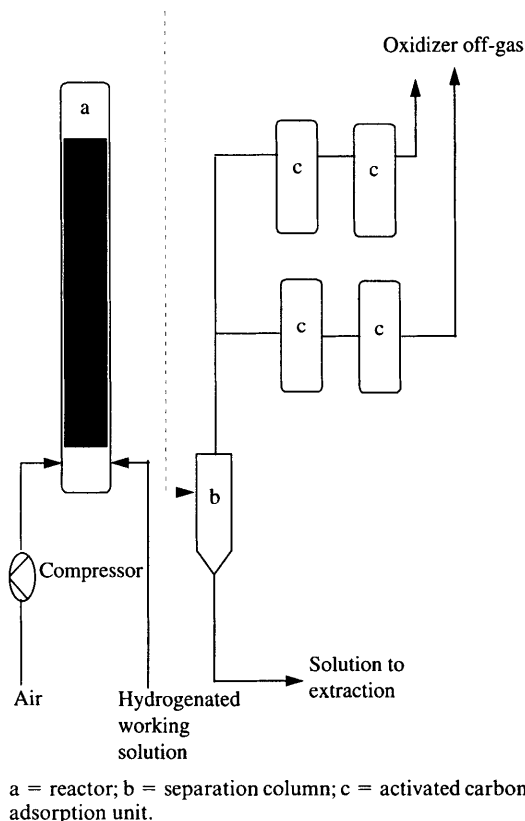


Figure 1.10 *Solvay Interlox oxidation method.*

Before we leave the discussion of industrial processes, it is worth mentioning one other autoxidation process, based on the oxidation of propan-2-ol, developed by Shell Chemicals. The process was employed by Shell in its 15 000 metric tonnes per annum facility at Norco between 1957 and 1980. The process was discovered in 1954 by Harris,²⁵ who showed that the oxidation of primary and secondary alcohols formed hydrogen peroxide, and the corresponding aldehyde or ketone (Figure 1.11).

Only propan-2-ol has had any industrial use since the aldehydes formed in the reaction with primary alcohols are easily oxidized. The oxidation of propan-2-ol in the liquid phase with oxygen does not require a special catalyst, because it is catalysed by a small amount of hydrogen peroxide, which is added to the feed-stream of the propan-2-ol in order to shorten the induction phase (Figure 1.12).

Reduction of by-products can be achieved by only partially oxidizing the propan-2-ol, and by carrying out the oxidation in several consecutive steps, at decreasing temperatures.²⁶ The hydrogen peroxide yield is typically 90–94% with respect to the propan-2-ol, and the acetone yield is 92–94%.

Over the years, there have been many other methods proposed for the

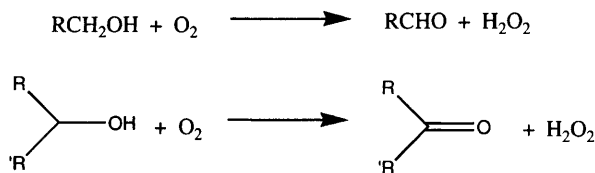


Figure 1.11 Shell process for the production of aqueous hydrogen peroxide.

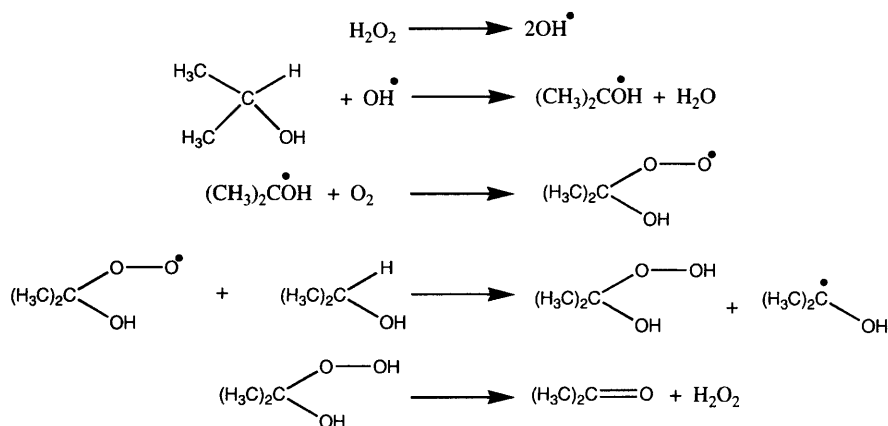


Figure 1.12 Mechanism of Shell process for the preparation of aqueous hydrogen peroxide.

preparation and subsequent purification of hydrogen peroxide. However, to date no industrial plants have been designed and commissioned based on such technologies. For example, Arco have devised a method for the preparation of hydrogen peroxide based on the autoxidation of methyl benzyl alcohol isomers with molecular oxygen.^{28,29} The process employs ethylbenzene and water to extract the hydrogen peroxide from a mixture of methyl benzyl alcohol and other oxidation by-products. For safety reasons, the water is supplied as a downward-flowing stream in the reactor, together with an upward flow of ethylbenzene. The process also contains one further feature worthy of note, which is that the crude aqueous hydrogen peroxide is passed through a cross-linked polystyrene resin which has a macro-reticular structure. This resin purification step has the advantage that subsequent concentration stages are inherently safer due to the lower organic contents. A number of novel electrochemical processes for hydrogen insertion reactions into molecules have also been applied to the preparation of hydrogen peroxide.³⁰⁻³² One process worth describing involves the electrochemical production of hydrogen peroxide together with the simultaneous production of ozone.³² The preparation of ozone is from the anode and of hydrogen peroxide from the cathode. The oxidants are generated from water and oxygen in a proton-exchange membrane (PEM) reactor. The optimum conditions for generating the oxidants were found

by the workers to be a function of applied voltage, electrode materials, catalyst loadings, reactant flow-rates and pressure. The ozone is generated at room temperature and pressure using lead dioxide powder bonded to a proton exchange membrane (Nafion[®] 117). The maximum concentration of the ozone formed is about 3 mg dm^{-3} in the aqueous phase. The cathodic reaction during the preparation of the ozone is hydrogen, which is oxidized with oxygen at 15 psi and a flow-rate of 100 ml min^{-1} . The electrocatalysts investigated were various loadings of gold, carbon and graphite powders which are bonded to the membrane or to a carbon fibre paper pressed against the membrane. Hydrogen peroxide was evolved from all the catalysts studied, with the graphite powders yielding the highest concentration (25 mg dm^{-3}). This process may have potential for the destruction of low concentrations of hazardous organic compounds in water courses.

For the conceivable future it is unlikely that there will be a radical change in the industrial production of hydrogen peroxide, i.e. the AO process will continue to dominate and the hydrogen peroxide produced bought by companies wishing to effect certain oxidation chemistries. It is, however, conceivable that in the future, progressive-thinking companies may employ an integrated process involving the manufacture and use of hydrogen peroxide for the oxidation of key intermediates. Therefore, with this in mind, the remainder of this section will be dedicated to this area of operation.

Arco have developed an integrated process for the production of industrially important epoxides via an adapted AO process (Figure 1.13).^{33,34} A sulfonic acid substituted alkylhydroanthraquinone alkylammonium salt is reacted with molecular oxygen to form the alkylanthraquinone and hydrogen peroxide. The hydrogen peroxide is then reacted with an alkene in the presence of a titanium zeolite catalyst (TS-1; see Chapter 4). The epoxide product is then separated, and the anthraquinone salt recycled to a hydrogenator for reaction with

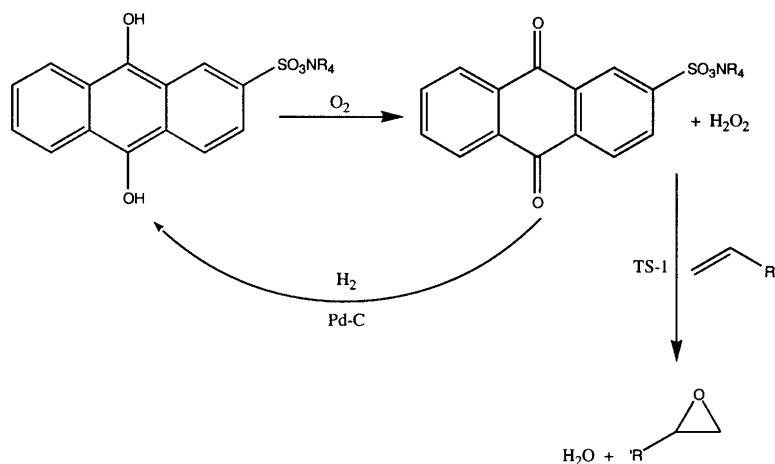


Figure 1.13 *Integrated production of epoxides via the in situ generation of hydrogen peroxide.*

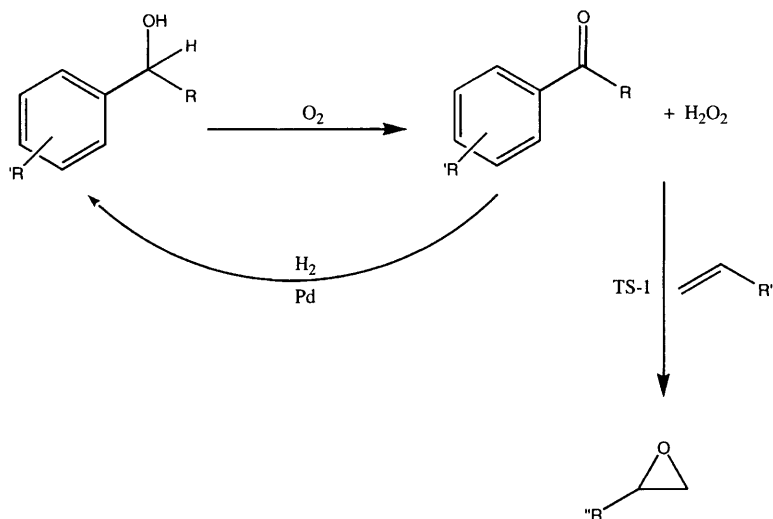


Figure 1.14 *Integrated production of epoxides via the in situ generation of hydrogen peroxide.*

hydrogen in the presence of a transition metal. The advantage of this system is the high solubility of the alkylammonium salts employed, thus allowing reactor volumes to be minimized, and higher concentrations of hydrogen peroxide to be produced. Further, no prior treatment or fractionation of the oxidation product is necessary before its use in the catalysed reaction.

Epoxides have also been prepared in a similar fashion to that described above, except an aryl-substituted alcohol is used as one-half of the redox couple (Figure 1.14).

The advantage of the above two methods are high yields of epoxides, and the titanium silicalite catalyst is not deactivated or poisoned by the contaminants in the crude oxidation mixture. Hence, the processes are commercially attractive. The *in situ* hydrogen peroxide generation based on the AO process from either the anthraquinone/anthrahydroquinone or ketone/alcohol redox couples has also been used for the following synthetic reactions:

- ammonia to hydrazine hydrate;³⁵
- ammonia and a nitrile to ketazines;³⁶
- alkanes to alcohols, aldehydes and ketones;³⁷
- phenol to hydroquinone and catechol;³⁸
- benzyl alcohols to hydroxybenzoic acids.³⁸

A number of electrochemical processes have been employed in an integrated approach for the production of hydrogen peroxide which is subsequently used to oxidize organic functional groups. The electrochemical processes have not only been employed for the preparation of fine chemical intermediates,³⁹ but also for the destruction of organic pollutants in water courses.⁴⁰

In summary, hydrogen peroxide was first prepared over 180 years ago by L. J. Thenard via the acidification of barium peroxide. The electrolysis of sulfuric acid or ammonium sulfate has also been employed industrially to prepare hydrogen peroxide. The majority of industrial processes operated today employ an anthraquinone/anthrahydroquinone couple to generate hydrogen peroxide. The Shell process based on propan-2-ol was employed industrially to prepare hydrogen peroxide between 1957 and 1980. The future is likely to see the employment of integrated approaches to organic functional group oxidation and low-level destruction of organic pollutants.

3 Physical Properties of Hydrogen Peroxide

Hydrogen peroxide is a clear, colourless liquid which is completely miscible with water. Figures 1.15–1.20 contain information on the general nature of hydrogen peroxide–water solutions, and Table 1.1 compares some of the important properties of hydrogen peroxide–water mixtures. Hydrogen peroxide and its highly concentrated aqueous solutions (> 65% *m/m*) are soluble in a range of organic solvents, such as carboxylic esters.

Hydrogen peroxide and water do not form azeotropic mixtures and can be completely separated by distillation. Most workers, however, obtain 100% *m/m* hydrogen peroxide by fractional crystallization of highly concentrated solutions. Pure 100% *m/m* hydrogen peroxide is usually only of academic interest, and is not produced on an industrial scale, although some niche uses may

Table 1.1 *Physical properties of hydrogen peroxide and water*

<i>Property</i>	<i>Hydrogen peroxide</i>	<i>Water</i>
Melting point (°C)	−0.43	0.0
Boiling point (°C)	150.2	100
Heat of melting (J/g)	368	334
Heat of vaporization (J g ^{−1} K ^{−1})		
25 °C	1519	2443
b.p.	1387	2258
Specific heat (J g ^{−1} K ^{−1})		
liquid (25 °C)	2.629	4.182
gas (25 °C)	1.352	1.865
Relative density (g cm ^{−3})		
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 (n_D^{20})	1.4084	1.3330

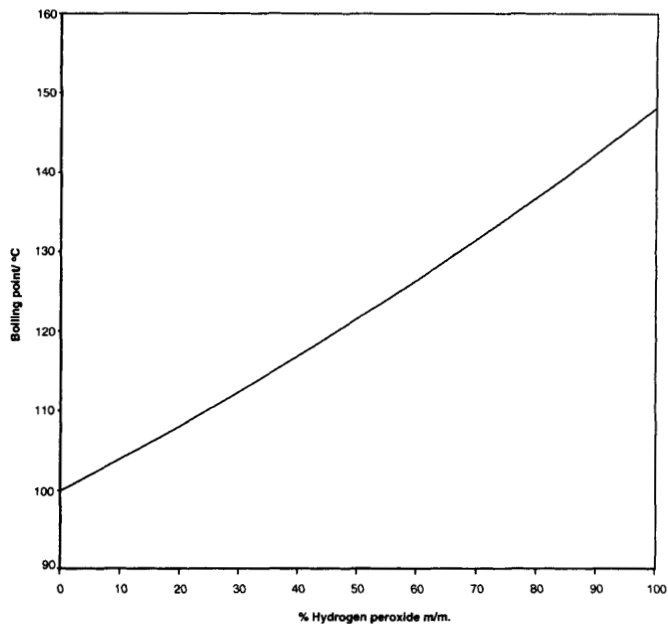


Figure 1.15 Boiling point range of hydrogen peroxide–water mixtures.

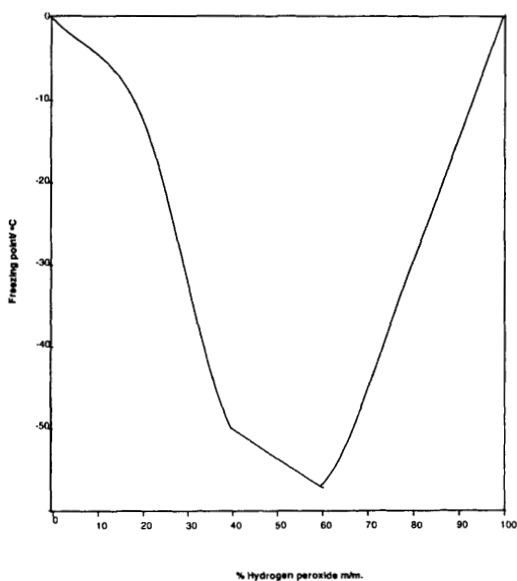


Figure 1.16 Freezing point range of hydrogen peroxide–water mixtures.

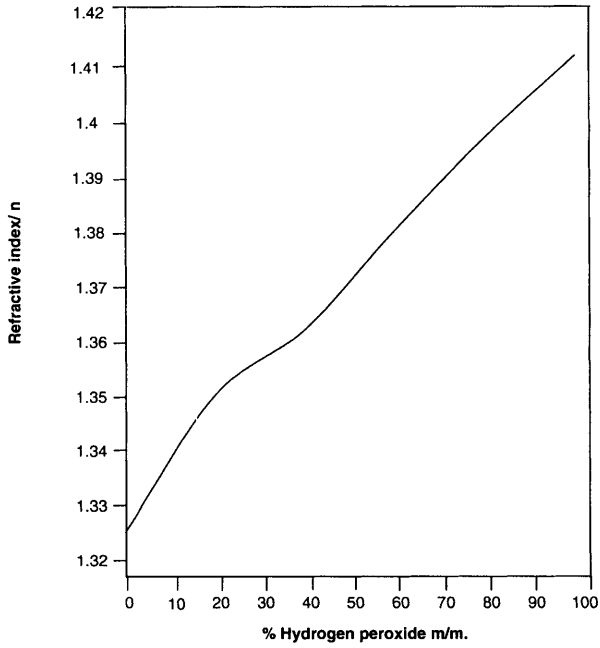


Figure 1.17 Refractive index range of hydrogen peroxide–water mixtures.

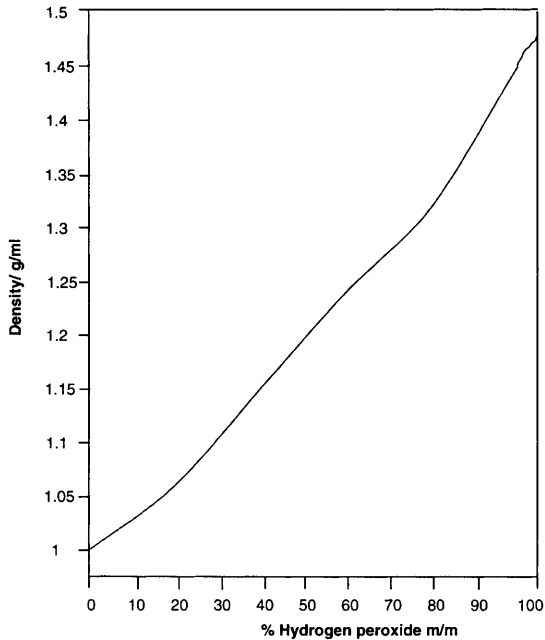


Figure 1.18 Density range of hydrogen peroxide–water mixtures.

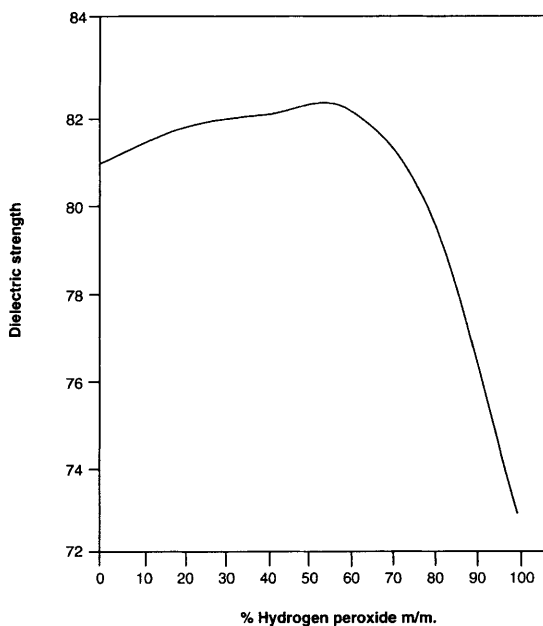


Figure 1.19 Dielectric strength range of hydrogen peroxide–water mixtures.

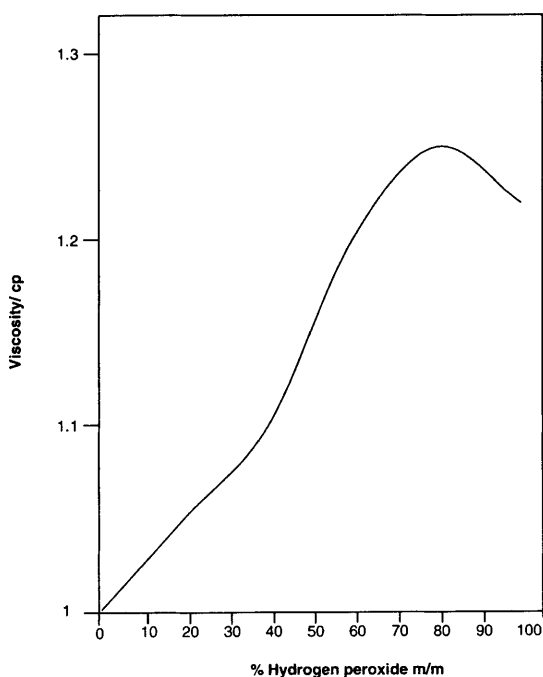


Figure 1.20 Viscosity range of hydrogen peroxide–water mixtures.

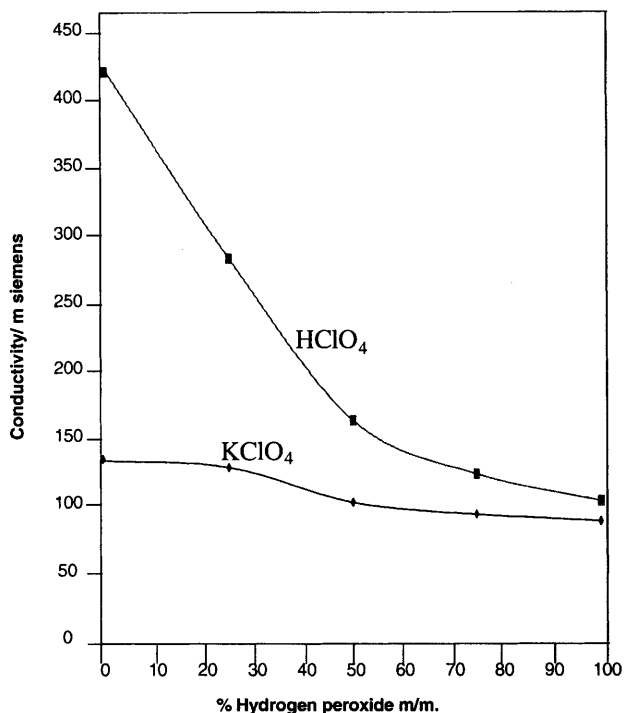


Figure 1.21 Conductance of the perchlorate anion in hydrogen peroxide–water mixtures.

become important in the future; for example, NASA are interested in the use of the pure material for the propulsion of rockets, since the handling of pure hydrogen peroxide is inherently safer than the employment of liquid oxygen. The long liquid range of hydrogen peroxide indicates a degree of association, and the very high dielectric constant indicates the presence of linear chains. On the basis of the high dielectric constant, hydrogen peroxide is a good ionizing medium. Conductance measurements have borne such observations out.⁴¹ The conductance of acids and bases is greatly reduced in hydrogen peroxide (Figure 1.21).

Generally, strong acids in hydrogen peroxide remain strong. For example, plots of equivalence conductance versus the half-power of concentration yield straight lines which are characteristic of completely dissociated electrolytes.

The behaviour of the glass electrode has also been examined.^{42–43} The glass-calomel electrode system yields stable and reproducible potentials which vary in the normal way with changes in hydrogen ion concentration. However, the EMF of the couple shifts several hundred millivolts as the solution composition changes from water to hydrogen peroxide. Table 1.2 summarizes the apparent and true pH of aqueous solutions of hydrogen peroxide.

Neutron diffraction studies on the molecular structure of solid hydrogen peroxide have also been made⁴⁴ and some of the structural data are outlined in Table 1.3.

Table 1.2 Apparent and true pH of aqueous hydrogen peroxide

Concentration of hydrogen peroxide solution (% m/m)	Equivalence point ^a	True pH	Correction factor
35	3.9	4.6	+0.7
50	2.8	4.3	+1.5
70	1.6	4.4	+2.8
90	0.2	5.1	+4.9

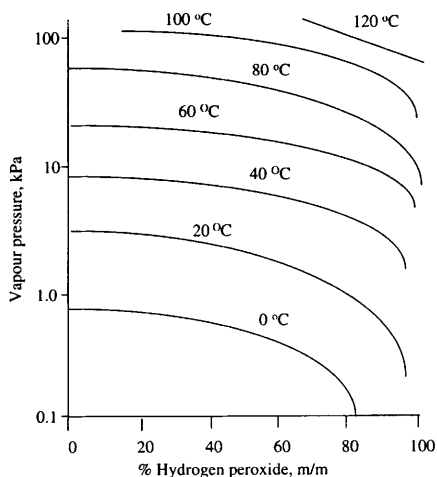
^a Measured using a calomel–glass electrode.

Table 1.3 Molecular dimensions of hydrogen peroxide in the gas phase

Characteristic	Measurement
Bond length O–O	0.1453 ± 0.0007 nm
Bond length O–H	0.0998 ± 0.0005 nm
Bond angle O–O–H	$102.7 \pm 0.3^\circ$
Azimuthal angle	$90.2 \pm 0.6^\circ$

The vapour pressure and partial pressure of aqueous hydrogen peroxide are illustrated as a function of temperature in Figures 1.22 and 1.23 respectively.

Figure 1.24 shows the vapour–liquid equilibrium curve for aqueous hydrogen peroxide.⁴⁵ The solid–liquid phase diagram shown in Figure 1.16 shows eutectic points for the mixtures ice–H₂O₂·2H₂O at 45.2% m/m hydrogen peroxide, and for solid H₂O₂–H₂O₂·2H₂O at 61.2% m/m hydrogen peroxide with a congruent meeting point for the compound H₂O₂·2H₂O between them. Numerous other

**Figure 1.22** Vapour pressure of hydrogen peroxide–water mixtures.

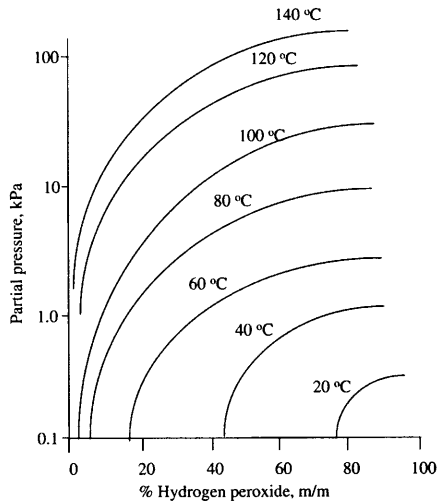


Figure 1.23 Partial pressure of hydrogen peroxide–water mixtures.

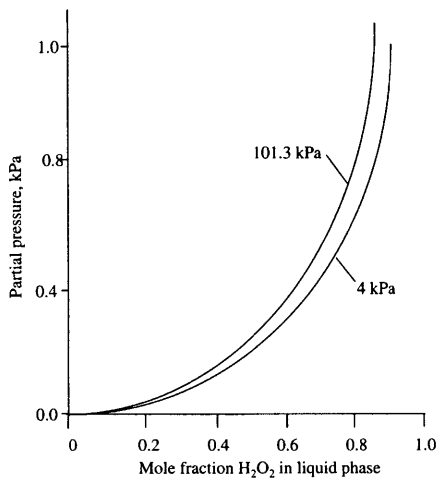


Figure 1.24 Vapour–liquid equilibrium curve for hydrogen peroxide–water mixtures.

physical data appear in the literature,⁴⁶ and such literature should be consulted for a more thorough understanding of the subject.

The heat of formation and of decomposition of hydrogen peroxide are as illustrated in Figure 1.25. The decomposition equations and heat-generated data are extremely important to know when working with hydrogen peroxide, because safety problems can occur. Decomposition is pH, temperature and impurity sensitive. The remainder of the chapter will, therefore, discuss the safe handling of hydrogen peroxide together with its destruction from process liquors.

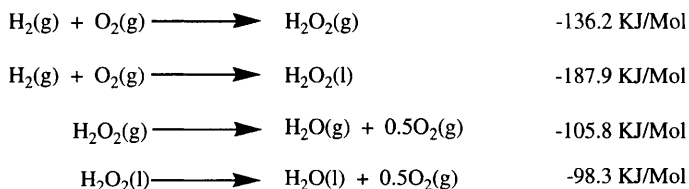


Figure 1.25 Heat of formation and decomposition of hydrogen peroxide.

4 Considerations for the Safe Use of Hydrogen Peroxide

The basic hazardous properties and causes of incidents when working with hydrogen peroxide can be attributed to the following:

- Decomposition to oxygen and water with the evolution of heat. The decomposition rate increases with temperature at about 2.3 times per 10 °C rise.
- Pressurization due to oxygen evolution. Hydrogen peroxide, in all forms, is thermodynamically unstable, and continuously dismutates to water and oxygen. Typically, commercial material loses less than 1% *m/m* of its active oxygen per year, however, 20 metric tonnes of 70% *m/m* hydrogen peroxide losing only 0.3% *m/m* of its active oxygen per year will evolve 13 dm³ of oxygen per day, enough to pressurize sealed equipment or give oxygen enrichment in the headspace of the container.
- Decomposition due to contamination or contact with active surfaces. The rate of decomposition can be increased by the presence of soluble impurities and/or contact with active surfaces. High and low pH will also destabilize hydrogen peroxide. pH affects the activity of the catalytic impurities and the stabilizers which are present.⁴⁷ Self-heating can rapidly accelerate the decomposition rate of destabilized hydrogen peroxide. Large amounts of oxygen and steam can be formed quickly (Table 1.4).
- Formation of explosive hydrogen peroxide/organic mixtures. Hydrogen peroxide is a very reactive chemical, and an extremely powerful oxidizer under certain circumstances. Hydrogen peroxide of strength higher than

Table 1.4 Decomposition data for hydrogen peroxide^a

Concentration of hydrogen peroxide solution (% <i>m/m</i>)	Isothermal volumes of hydrogen peroxide	Adiabatic volumes of oxygen and steam	Adiabatic decomposition temperature (°C)
100	512	6643	996
60	263.3	1672	100
40	163.5	932	100
10	36.6	45	89

^a Volume of oxygen evolved isothermally and volumes of total gas evolved adiabatically from unit volumes of hydrogen peroxide solutions at atmospheric pressure.

Table 1.5 Explosive power and sensitivity of various substances

Substance	Explosive power	Sensitivity (kg cm)
Nitroglycerine	52	2–5
85% m/m hydrogen peroxide/glycerol	46	10–15
70% m/m hydrogen peroxide/polyethylene	30	22
Picric acid	32	75
Trinitrotoluene	30	150
97% m/m hydrogen peroxide	17	Insensitive

about 40% m/m can also form explosive mixtures with organic compounds. Such mixtures can equate to conventional high explosives in power, but may be much more sensitive in terms of detonation (Table 1.5).

- Spontaneous reaction of hydrogen peroxide/sulfuric acid/water/organic mixtures. These reactions can accelerate rapidly and terminate violently, and can be outside the predicted explosive area.
- Vapour phase hydrogen peroxide explosions. Hydrogen peroxide vapour of concentration above 39% m/m at atmospheric pressure is explosive (Figure 1.26).⁴⁸

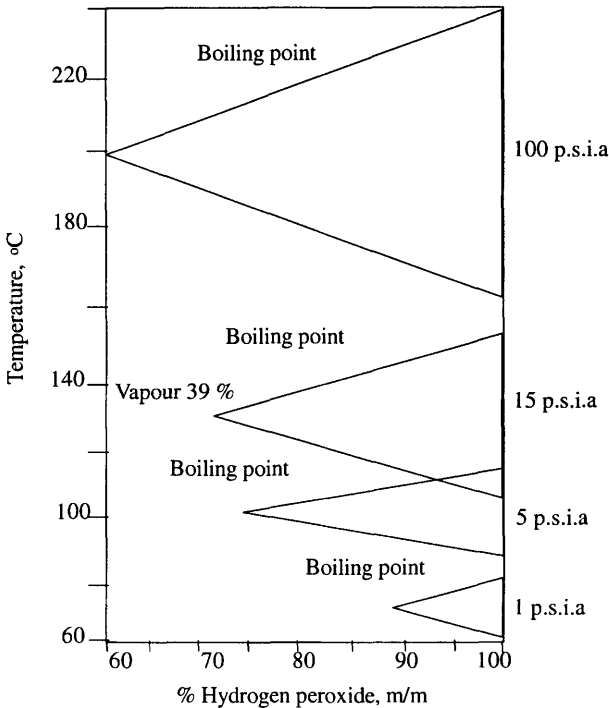


Figure 1.26 Compositions of liquid hydrogen peroxide which form ignitable vapour.

Table 1.6 Minimum ignition energies (mJ) in air and oxygen

Substance	In air	In oxygen
Methane	0.3	0.003
Acetone	1.15	0.0024
Diethyl ether	0.20	0.0013

- Oxygen enrichment. Oxygen evolved by decomposition may give rise to atmospheres with a high oxygen content. Oxygen-rich flammable atmospheres have low ignition energies (Table 1.6). The rate of burning is also increased. Flame arrestors and other flame-proofing provisions may be ineffective. Explosive limits are widened, but there are no significant changes to the lower explosive limit and flash point. Some vapours and gases which are not flammable in air are flammable in oxygen, for example, some chlorinated solvents.⁴⁹

The above discussion is not meant to deter any interested parties from employing hydrogen peroxide during their work, but it is intended to allow one to embark on studies using peroxygen compounds via an understanding of the main hazards and how to avoid them. The remainder of the section will discuss the practicalities of employing hydrogen peroxide, and peroxy-carboxylic acids (RCO_3H).

Hydrogen peroxide and peroxy-carboxylic acids (RCO_3H) are normally relatively stable, but as mentioned above they can be rendered unstable by a wide variety of contaminants, particularly at excessively high temperatures. Cleanliness, good housekeeping and proper storage are therefore essential. The major contaminants that cause decomposition are combustible organic materials (e.g. cotton, wool, paper) or metals, particularly transition metals and their salts (Table 1.7).⁵⁰ Alcohol thermometers or stainless steel thermocouples

Table 1.7 Effect of added metal ions on the decomposition rate of hydrogen peroxide

Metal ion	Amount added (ppm)	Active oxygen lost in 24 h at 100 °C ^a (%)
None	—	2
Al(III)	10	2
Sn(IV)	10	2
Zn(II)	10	10
Fe(III)	1.0	15
Cu(II)	0.01	24
Cr(II)	0.1	96

^a Hydrogen peroxide not stabilized.

should be used for determining temperature and stainless steel ball hydrometers used for density measurements.

Copious supplies of water should always be at hand for washing spillages including contact with skin. The latter should be avoided by wearing adequate protection, particularly for the hands and eyes. Before commencing experiments, glass equipment should be thoroughly washed with water (and a little detergent) and rinsed. Washing with dilute nitric acid (< 5% *m/m*) followed by distilled water will remove acid-soluble impurities (*e.g.* metals). Hydrogen peroxide and peroxy-carboxylic acids should be stored in vented polyethylene bottles and kept cool. Peroxy-carboxylic acids should not be kept for longer than six months.

Prior to using active oxygen compounds, the selection of solvents for experiments and for cleaning purposes should be considered carefully. A number of incidents have occurred in the past due to the use of acetone, a result of the formation of acetone peroxides, some of which are highly explosive and crystallize readily. For this reason, acetone or other low molecular weight ketones should never be employed as solvents for extraction or as cleaning agents. Chlorinated solvents, esters and alcohols can, however, be safely employed.

The importance of planning reactions of peroxygen compounds with a pre-knowledge of potential hazards and their control is self evident. In a new field or with a new reaction, the user should conduct initial experiments on a small scale and pay adequate regard to the reaction conditions employed. Standard practical techniques should be used to observe and understand the reaction as it is occurring.

To prevent incidents caused by the rapid decomposition or explosion of active oxygen compounds in reactions with organic substances, a set of safety rules should be followed. These rules have been derived logically and quantitatively. The approach may be illustrated by reference to a three-component mixture of hydrogen peroxide, organic substance and water. The three-component mixture for typical organic compounds is represented in the triangular diagram in Figure 1.27. The diagram was obtained by the deliberate detonation of different mixtures using the blasting cap test. Outside the heaviest shaded area of detonable composition, mixtures could not be exploded. The results above refer to tests with glycerol,⁵¹ however, an extensive range of other organic compounds, for example, acetic acid, ethanol, aniline and quinoline, have been shown to behave similarly.

When working with active oxygen compounds, steps should be taken to ensure that mixtures do not occur in the detonable area during the reaction or processing phases. It should be noted that when using 35% *m/m* or less hydrogen peroxide then it is unlikely that detonable compositions will be formed. Therefore, use of 35% *m/m* or less hydrogen peroxide should be employed wherever possible and higher strengths discouraged. Peroxy-carboxylic acids can be broken down to their organic acid and hydrogen peroxide components for comparison with the diagram. It is recommended that reactions are carried out in such a way as to prevent the hydrogen peroxide content (or

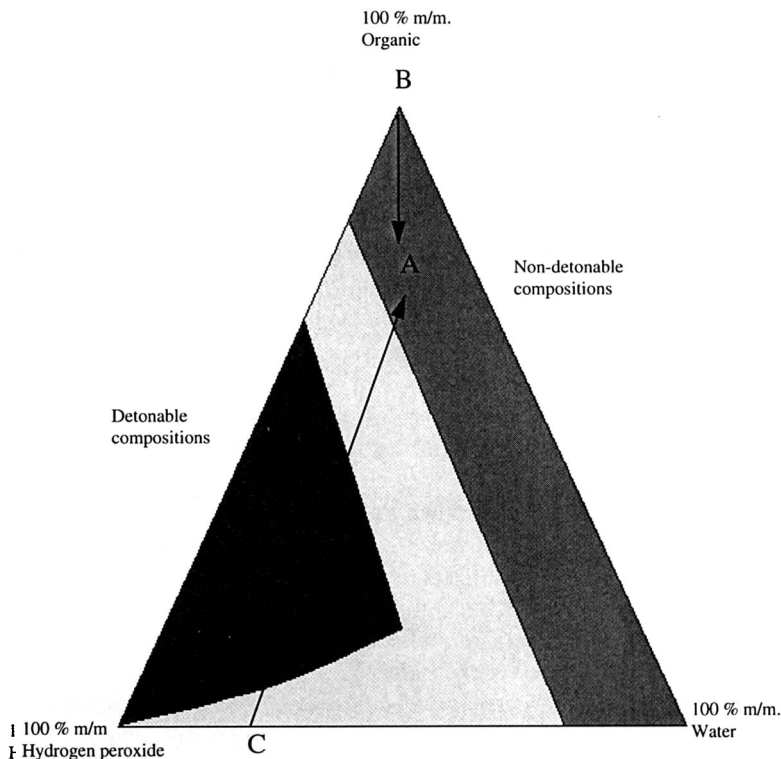


Figure 1.27 Preferred operating region for peroxygen processes.

equivalent) exceeding 20% *m/m*. If the reaction has two or more phases, this recommendation should be applied to each phase. Proper attention should be paid to ensure adequate mixing of all phases takes place.

There are, however, systems where the general triangular diagram represented in Figure 1.27 does not hold. Replacement of the inert diluent, water, with significant quantities of sulfuric acid will alter the position and area of the explosive region, bringing it closer to the 20% *m/m* hydrogen peroxide zone. This and other similar situations occur during certain procedures for preparing peroxycarboxylic acids, and not normally when using percompounds as oxidizing agents in reactions. Further information can be obtained from Solvay Interlox.⁵²

The importance of the order of addition is also illustrated in the triangular diagram. For example, assume an experiment is being conducted with 70% *m/m* hydrogen peroxide and an organic compound. The final composition of the final mixture is represented by point A if no reaction occurs. Addition of organic compound to hydrogen peroxide would result in a reaction mixture with an initial composition at point C. As the organic mixture is added, the reaction mixture composition will pass through the detonable region before reaching A. By adding hydrogen peroxide to the organic compound, the composition would

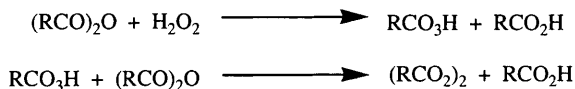


Figure 1.28 Formation of diacyl peroxides in systems containing an excess of acid anhydride compared to hydrogen peroxide.

change from point B to A, without the composition passing through the detonable area. It is therefore always advisable to carry out reactions in this way even when using low concentration hydrogen peroxide. There is, however, one specific circumstance where the rule of adding hydrogen peroxide last is changed. This is where acid anhydrides are present, when the hydrogen peroxide must be in molar excess to avoid the formation of diacyl peroxides (Figure 1.28).

It is equally important to prevent the hydrogen peroxide (or equivalent) concentration exceeding 20% *m/m*. Diacyl peroxides, and many other organic peroxides, are hazardous in their own right. It is important that the active oxygen is reacting in the intended way, and is not being converted into organic peroxides or other hazardous material; this can be prevented by understanding the chemistry of the system and by routine analysis of the reaction mixture. For example, *in situ* chlorine generation may oxidize nitrogenous materials to the potentially detonable nitrogen trichloride.

Reactions with hydrogen peroxide and peroxycarboxylic acids are exothermic. When hydrogen peroxide decomposes to oxygen and water, the heat generated is approx. 98 kJ mol⁻¹. In comparison, the oxidation of most organic compounds liberates 3–4 times as much heat. As a consequence, even when compositions are not in the detonable zone, appreciable temperature rises can occur. To obtain high yields, it is desirable to carry out reactions in a controlled manner and maintain peroxygen content as low as possible to prevent by-product formation. Temperature control on its own should be adequate but care should be taken to ensure over-cooling does not occur, as a slight exotherm is often required to ensure reaction is taking place. It is also advisable to pre-heat the reactor contents to about 5°C below the proposed operating temperature before adding the peroxygen species. This will minimize percompound build-up at low temperatures before the reaction is initiated, thus limiting possible run-away reactions. Until a reaction is familiar, the reaction mixture should be analysed for peroxygen content during addition. Incidents have been caused by increasing reaction temperatures, which occur once all the percompound has been added, particularly if no reaction has taken place. In such circumstances, the reaction must be abandoned and a further experiment carried out at a higher operating temperature. It is advisable to have fast methods of cooling available to prevent any incidents occurring due to run-away reactions.

Reactions using active oxygen compounds must always be provided with adequate venting so that decomposition does not result in a pressure build-up. Release of oxygen can lead to oxygen enrichment of the atmosphere above the normal 21% oxygen in air, and can consequently greatly increase the suscept-

ibility to ignition of flammable materials and vapours, and the intensity of any fire or explosion that results from it. Adequate precautions should be taken during work-up, particularly in the case of distillation or evaporative crystallization, to prevent concentration of peroxidic species. If formation of an additional phase occurs, whether liquid or precipitate, it must be investigated with appropriate precautions, as it may contain active oxygen. The absence of percompounds should be confirmed before commencing any purification operations. Destruction of residual peroxides will be discussed later.

In summary, the following check-list should be referred to when employing percompounds with organic materials:

- (1) Wear adequate personal protection.
- (2) Clean all glassware and the working area.
- (3) Protect vessels from sources of contamination.
- (4) Store active oxygen compounds away from sunlight and heat in ventilated containers.
- (5) Vent all reactors adequately to ensure pressure relief if decomposition occurs.
- (6) Carry out new reactions on a small scale, *i.e.* ca. 10 g.
- (7) Use alcohol thermometers, stainless steel thermocouples and stainless steel ball hydrometers.
- (8) Always plan reactions.
- (9) Always add the percompound to the organic material (except with acid anhydrides).
- (10) Control addition carefully, observing the reaction.
- (11) Provide efficient agitation. Stop the peroxygen feed if the agitator fails.
- (12) Ensure the content of hydrogen peroxide (or equivalent) does not exceed 20% *m/m* during the reaction.
- (13) Pre-select the reaction temperature. Do not increase the temperature after addition if no reaction takes place.
- (14) Supply adequate cooling to the reaction.
- (15) Analyse the reaction mixture and remove or destroy any percompound present before distillation or crystallization.
- (16) Never use acetone or other lower aliphatic ketones as a solvent for extraction or cleaning.
- (17) Use nitrogen to render inert flammable atmospheres.

In the vast majority of cases the precautions quoted above will ensure no incidents occur.

Product solutions or effluents of peroxygen reactions may contain variable amounts of unreacted peroxide, usually in the form of hydrogen peroxide, percarboxylic acids, and/or organic peroxide. For reasons related to safety, waste treatment or product stability, it is usually necessary to destroy unreacted peroxide species in the product solution or effluent prior to discharge or work-up, and certainly before any product concentration process. The remainder of

this chapter summarizes methods for removing residual peroxides which can be applied to commercial processes.

Most oxidation with peroxygen compounds requires a slight excess of oxidant to facilitate efficient conversion of the substrate. Frequently, the excess of peroxide is decomposed under the conditions of the reaction, *e.g.* at elevated temperatures, particularly in strongly basic or acidic conditions and/or in the presence of metal catalysts. However, in many cases, unreacted peroxide persists when the reaction is terminated. In two-phase systems consisting of an aqueous and an organic layer, it is often sufficient to separate the aqueous phase and water-wash the organic phase until no residual peroxide is present. Alternative removal methods will be required where the peroxide is difficult to remove by washing, where recovery of material from the aqueous phase is required (*e.g.* solvent reclamation) or where safe disposal of the aqueous phase cannot be provided. Similarly, in a water-miscible medium where physical separation is not possible, a method for peroxide removal by chemical reduction or physical decomposition must be employed. A final level of <0.1% *m/m* available oxygen will normally allow solutions containing volatile solvents to be concentrated to at least 10% of their initial volume before having to re-check the solution. If necessary, the solution can be retreated to complete the peroxygen decomposition. It is clear that it can be extremely difficult to remove the last few ppm residual peroxide from a solution. And finally, where no material recovery from aqueous solutions is required, consideration may be given to blending the solution with other process waste streams to effect a reduction in toxicity, biodegradability or oxygen demand of the other waste streams whilst simultaneously removing the peroxide.

Several methods of decomposing peroxide are employed commercially. Reactions with chemical reductants have the advantage of transferring oxygen from the peroxide to the reductant molecule, thereby avoiding enrichment of the atmosphere oxygen level. The most commonly used reducing agents for treatment of either water miscible or immiscible waste is solutions of sulfite or bisulfite. Where contact with water must be avoided, treatment with a non-aqueous reducing system may be required. Sulfur dioxide, hydrazine, tertiary phosphines and thioacids have all been employed in this capacity on a laboratory scale, whereas sulfite, and sulfur dioxide are more easily handled on a production scale. It is worth noting that the presence of excess of reducing agent in the treated solution may render subsequent testing negative, and it is therefore essential to ensure that peroxide is indeed removed by the reductive treatment. This is best achieved by adding the product solution to an agitated solution of excess reductant above ambient temperature. Although this mode of treatment is not always necessary (*e.g.* where the excess peroxide is in the form of hydrogen peroxide or alkylhydroperoxide under neutral conditions), it is required where organic peroxy acids are likely to be present. For example, it has been shown that the reaction of excess peracid with sulfite can lead to the formation of diacyl peroxide. The diacyl peroxide is an explosive species and is stable to reduction under normal conditions, but it is not detected under normal

wet analytical techniques. Its formation can only be prevented by reducing the peracid with excess reductant. Where it is undesirable to introduce a reducing agent into a product solution, it is normally possible to use a peroxide decomposition agent in the form of a homogeneous or heterogeneous catalyst. These agents may be high surface area substances (*e.g.* active carbon or a transition/heavy metal or oxide). The main function of such a system is to transfer electrons to the peroxide molecule. The decomposition process, therefore, liberates oxygen. When employing catalytic decomposition systems, it is important to ensure the oxygen evolved is not allowed to mix with volatile organics. This problem is best avoided by working in an open system purged with nitrogen to prevent oxygen enrichment. In practice, this danger can be eliminated by operating below the flash point of the product mixture, and maintaining the atmospheric oxygen content below 10% v/v (by nitrogen dilution).

Homogeneous decomposition processes are best suited to aqueous solutions which are to be discarded. Frequently used catalytic agents include iron salts [iron(II) sulfate], copper salts [copper(II) sulfate] and catalase (limited to small-scale operations). The efficiency of such systems may show extreme pH dependence. For example, the metal salts are less effective in acid systems, whereas the enzyme methods are restricted to near-neutral pH. However, an enzyme called *Aspergillus niger* shows activity at a pH of 2–3. When the aqueous phase is to be recovered (*e.g.* by distillative or extractive processes), a solid decomposition catalyst is often preferable, since it may be readily removed by filtration. In this way, subsequent contamination of columns or stills involved in the product work-up is prevented. Further, rarely do heterogeneous decomposition processes affect the integrity of the product. Examples of catalysts known to be particularly effective in this area include platinum, platinum black, silver, cobalt or reduced palladium (either as gauzes or on supports), and the active manganese ore, pyrolusite. These systems are particularly unique in their high activity in acidic solutions. The major drawback with heterogeneous decomposition catalysts is their propensity to lose activity in the presence of oils, inorganic phosphates, colloidal tin and silica complexes, *etc.* Similarly, highly acidic liquors or those containing strong chelating agents tend to leach the catalysts from their supports.

The previously mentioned list of solid catalysts is not meant to exclude other transition/heavy metals or their oxides, most of which are known to be good decomposition catalysts for peroxygens. Notable exceptions include tantalum and tin compounds, the latter being used as stabilizers in certain grades of hydrogen peroxide. Non-metallic agents which provide high surface areas and contain Lewis acid sites have also been used as heterogeneous peroxide decomposition agents. These include activated carbons, calcined alumina, zeolites and aluminosilicates. Although such agents are less effective in acid solution compared with their metal counterparts for removing peroxides from alkali solution, they are generally preferred from a cost perspective. As is generally the case with solid decomposition catalysts, increasing the temperature substantially improves their catalytic activity. Figure 1.29 illustrates a

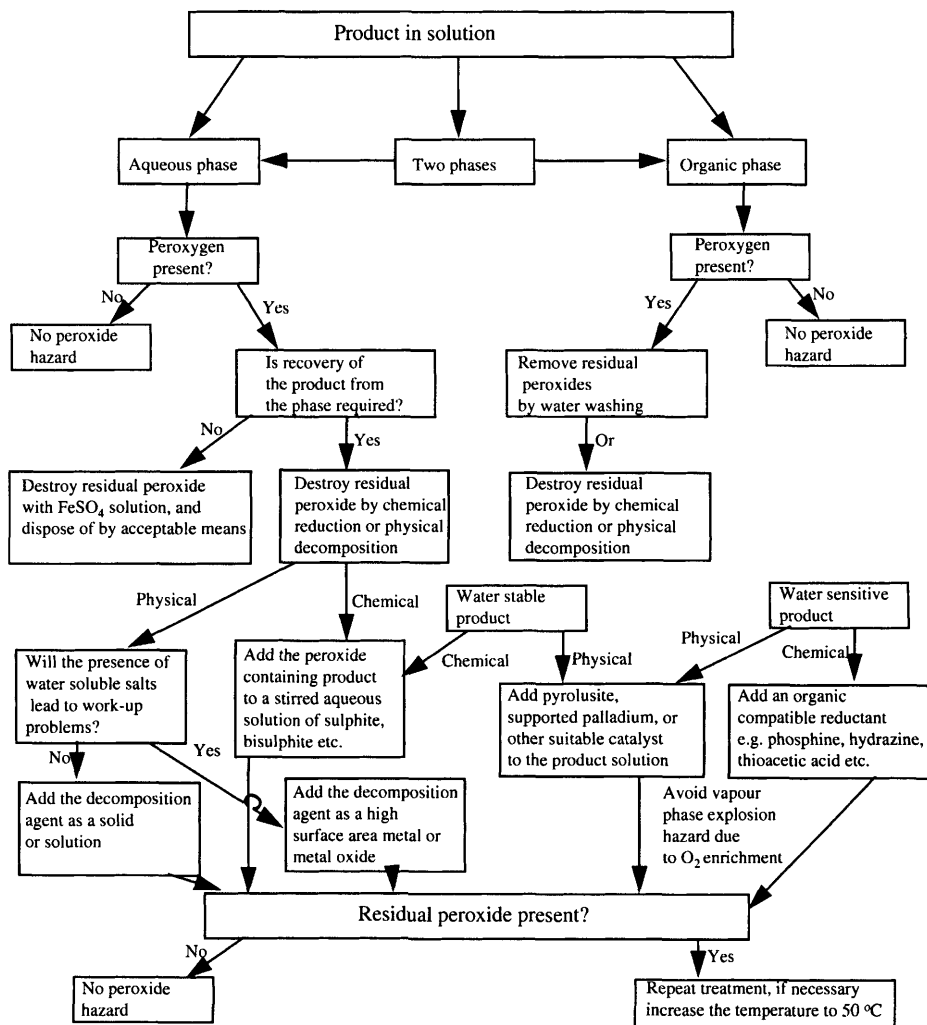


Figure 1.29 *Residual peroxides: removal and destruction.*

flowsheet which can be employed for choosing the best decomposition method for removal of residual peroxides from process liquors.

In general, peroxides are more difficult to remove from acidic solution. This trend arises due to two factors: the loss of activity of many catalytic agents (particularly homogeneous catalysts) and the inherently greater stability of peroxides in slightly acidic solution (this phenomenon relates to the so-called equivalence point of hydrogen peroxide solutions, which corresponds to a pH value of *ca.* 4.5). In fact, hydrogen peroxide can be considered a mild reducing agent at pH < 2–3. These factors are illustrated in Table 1.8, which surveys the performance of various decomposition agents for removal of residual peroxide (hydrogen peroxide and peracetic acid) from a simulated acidic process liquor.

Table 1.8 Removal of residual peroxide in acidic pH^a (simulated liquor: 10% glacial acetic acid; 3% hydrogen peroxide; 87% water)

Reagent	Amount added (% m/m)	AvOx removed at 25 °C (%)	Reaction time (h)	AvOx removed at 60 °C (%)	Reaction time (h)
Blank	—	0.0	3.00	0.5	3.00
HCl	2.2	6.0	3.00	91.0	3.00
HCl	6.0	37.0	3.00	98.0	1.50
Reduced Pd ^b	0.02 as Pd	100	0.25	100	0.25
Oxidized Pd ^b	0.02 as Pd	38	3.00	96.0	3.00
Activated charcoal ^c	1.0	39	3.00	98.0	3.00
Montmorillonite	1.0	19.0	3.00	91.0	3.00
FeSO ₄	2.5	46.0	3.00	98.0	3.00
MnO ₂	1.0	21.0	3.00	64.0	3.00
Catalase ^d pH = 2	0.04	22.0	3.00	—	—
Catalase ^d pH = 4	0.04	35.0	3.00	—	—

^a pH = 2 unless otherwise stated; ^b 2% on aluminosilicate (<200 mesh); ^c Darco 6-60 (100-325 mesh); ^d Bovine liver catalase containing 11 000 units/mg (1 unit = 1 μmol hydrogen peroxide per min at pH = 7 and 25 °C).

As discussed earlier, heterogeneous catalysts using a supported metal such as palladium are most effective. It should be mentioned, however, that after six recycles, the supported palladium catalyst has lost 35% of the active palladium metal, due to leaching into the solution. Decomposition processes become considerably more effective as pH of the solution increases. In the near-neutral region, this is thought to be attributed to increased activity of many of the catalytic agents. As an example, Table 1.9 illustrates the relative performance of several decomposition agents in a simulated liquor containing hydrogen

Table 1.9 Removal of residual peroxide in neutral pH^a (simulated liquor: 10% methanol; 3% hydrogen peroxide; 87% water)

Reagent	Amount added (% m/m)	AvOx removed at 25 °C (%)	Reaction time (h)	AvOx removed at 60 °C (%)	Reaction time (h)
Blank pH = 7	—	2.8	3.00	7.1	3.00
Reduced Pd ^b	0.02 as Pd	100	0.25	100	0.25
Oxidized Pd ^b	0.02 as Pd	100	1.00	100	0.50
Activated charcoal ^c	1.0	83	3.00	90.7	3.00
Montmorillonite	1.0	10.6	3.00	55.6	3.00
FeSO ₄	2.5	70.4	3.00	99.1	1.00
MnO ₂	1.0	97.3	1.50	98.9	1.00
Catalase ^d pH = 2	0.001	99.0	0.25	—	—

^a pH = 7 adjusted by NaOH; ^b 2% on aluminosilicate (<200 mesh); ^c Darco 6-60 (100-325 mesh); ^d Bovine liver catalase containing 11 000 units/mg (1 unit = 1 μmol hydrogen peroxide per min at pH = 7 and 25 °C).

Table 1.10 Removal of residual peroxide in basic pH^a (simulated liquor: 10% methanol; 3% hydrogen peroxide; 87% water)

Reagent	Amount added (% m/m)	AvOx removed at 25 °C (%)	Reaction time (h)	AvOx removed at 60 °C (%)	Reaction time (h)
Blank pH = 12	—	41.5	3.00	93.7	3.00
Reduced Pd ^b	0.02 as Pd	100	0.25	100	0.25
Oxidized Pd ^b	0.02 as Pd	99.7	0.50	99.0	0.50
Activated charcoal ^c	1.0	98.9	1.00	99.6	1.00
Montmorillonite	1.0	98.0	3.00	99.8	1.00
FeSO ₄	2.5	99.8	1.00	99.8	1.00
MnO ₂	1.0	99.7	0.50	99.7	0.50
Catalase ^d pH = 12	0.001	61.9	3.00	—	—

^a pH = 12 adjusted by NaOH; ^b 2% on aluminosilicate (< 200 mesh); ^c Darco 6–60 (100–325 mesh); ^d Bovine liver catalase containing 11 000 units/mg (1 unit = 1 μmol hydrogen peroxide per min at pH = 7 and 25 °C).

peroxide, methanol and trace of orthophosphoric acid. In contrast to acidic solutions, higher pH environments are much less aggressive towards leaching metals from their supports.

Continuing with the pH trend, peroxide solutions are readily decomposed in alkaline solution, whereas near-neutral decomposition processes rely heavily on catalytic activity of the decomposition agent, alkaline processes relying more on the inherent instability of the perhydroxyl anion under high pH conditions.

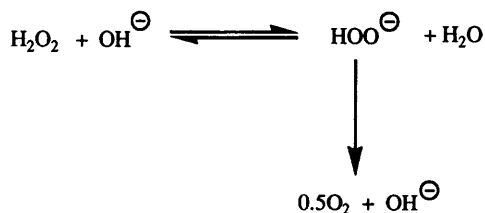


Table 1.10 surveys several catalytic agents for removing residual peroxides from a liquor containing hydrogen peroxide, anionic surfactant and ethanol. Whilst general recommendations have been offered, these should serve only as a guideline.

5 Toxicology and Occupational Health Aspects of Hydrogen Peroxide

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

Table 1.11 *Acute toxicities of hydrogen peroxide in animals*

<i>Test</i>	<i>Animal</i>	<i>Area</i>	<i>Concentration</i>
LD ₅₀	Mouse	Oral	2538 mg/kg
LD ₅₀	Mouse	Oral	2000 mg/kg
LD ₅₀	Rat	Oral	4060 mg/kg
LD ₅₀	Mouse	Dermal	1.2 × 10 ⁴ mg/kg
LC ₅₀	Rat	Inhalation	2000 mg/m ³

injury. Hydrogen peroxide aerosol or vapour causes irritation and in severe cases damage to the upper respiratory tract and lungs.^{53,54} The human reaction to the irritating effect of hydrogen peroxide on the mucous membrane 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⁻³ in rats, but only 10 mg m⁻³ in humans; the corresponding values for skin are 110 mg m⁻³ for rats and 20 mg m⁻³ for humans.⁵⁵ 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 for hydrogen peroxide are 1.4 mg m⁻³. Acute toxicities in animals are shown in Table 1.11.⁵⁶

Acute dermal toxicity depends on hydrogen peroxide concentration. With 90% *m/m* hydrogen peroxide, the dermal LD₅₀ in rabbit is 650 mg kg⁻¹ and in rat 4800 mg kg⁻¹.⁵⁷ So far, no problems associated with reproduction in animals have been found.⁵⁸ Hydrogen peroxide has a mutagenic effect on fungi and bacteria (*e.g.* Ames test), but not on insects or mammalian cells *in vitro*.⁵⁹ Oral administration of hydrogen peroxide produced tumours in the small intestine of mice.⁵⁹ However, when hydrogen peroxide was given orally to rats, no significant differences occurred between the two test groups and the control group.⁶⁰ No evidence of tumour formation was found one year after exposure of mouse skin to 5% *m/m* hydrogen peroxide.⁶¹

6 Conclusion

It is hoped that this chapter has given the reader an understanding of the production of hydrogen peroxide over the last two centuries and why its application in the early years was limited strictly to bleaching. The major breakthrough was made when the autoxidation of hydroquinones (AO process) was discovered. The AO process allows for the production of more stable and higher concentrations of aqueous hydrogen peroxide, thus extending the range of applications for the reagent, particularly in the field of fine organic synthesis.

This chapter also illustrates that by observing some simple guidelines, aqueous hydrogen peroxide can be used commercially in a safe manner. It is hoped that the reader will now contemplate the use of such a versatile reagent within their particular area of expertise.

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