

Industrial Process Control

Specialized equipment for industrial measurements and automatic control have been developed (18) (see PROCESS CONTROL). In general, the pH of an industrial process need not be controlled with great accuracy. Consequently, frequent standardization of the cell assembly may be unnecessary. On the other hand, the ambient conditions, eg, temperature and humidity, under which the industrial control measurements are made, may be such that the pH meter must be much more robust than those intended for laboratory use. To avoid costly downtime for repairs, pH instruments may be constructed of modular units, permitting rapid removal and replacement of a defective subassembly.

The pH meter usually is coupled to a data recording device and often to a pneumatic or electric controller. The controller governs the addition of reagent so that the pH of the process stream is maintained at the desired level.

Immersion-cell assemblies are designed for continuous pH measurement in tanks, troughs, or other vessels containing process solutions at different levels under various conditions of agitation and pressure. The electrodes are protected from mechanical damage and are sometimes provided with devices to remove surface deposits as they accumulate. Process flow chambers are designed to introduce the pH electrodes directly into piped sample streams or bypass sample loops that may be pressurized. Electrode chambers of both types usually contain a temperature-sensing element that controls the temperature-compensating circuits of the measuring instrument.

Glass electrodes for process control do not differ materially from those used for pH measurements in the laboratory, but the emphasis in industrial application is on rugged construction to withstand both mechanical stresses and high pressures. Pressurized salt bridges, which ensure slow leakage of bridge solution into the process stream even under very high pressures, have been developed. For less severe process monitoring conditions, reference electrodes are available with no-flow polymeric or gel-filled junctions that can be used without external pressurization.

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General References

Refs. 1-7 are also general references.

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HYDROGEN PEROXIDE

Hydrogen peroxide [7722-84-1], H_2O_2 , mol wt 34.016, is a strong oxidizing agent commercially available in aqueous solution over a wide range of concentrations. It is a weakly acidic, nearly colorless clear liquid that is miscible with water in all proportions. The atoms are covalently bound in a nonpolar $H-O-O-H$ structure having association (hydrogen bonding) somewhat less than that found in water. Thenard discovered hydrogen peroxide in 1818, producing it by the action of dilute acids on barium peroxide [1304-29-6], BaO_2 . Hydrogen peroxide has been an article of commerce since the mid-nineteenth century, initially as weak 3-7% solutions. Its scale of manufacture and use have increased markedly

since 1925 when electrolytic processes were introduced to the United States and industrial bleach applications were developed. Now manufactured primarily in large, strategically located anthrahydroquinone autoxidation processes, its many uses include bleaching wood pulp and textiles, preparing other peroxygen compounds, and serving as a nonpolluting oxidizing agent (see also PEROXIDES AND PEROXY COMPOUNDS, INORGANIC; PEROXIDES AND PEROXY COMPOUNDS, ORGANIC).

Physical Properties

Properties of pure hydrogen peroxide are listed in Table 1. In aqueous solution the hydrogen bonds (association) between water and H_2O_2 molecules are appreciably more stable than those between molecules of the individual species. This increase in attraction forces is evidenced from many properties such as heat of mixing, vapor pressure, viscosity, dielectric constant, etc. Physical constants have been determined or calculated for aqueous H_2O_2 solutions, the only form in which hydrogen peroxide is commercially available (Table 2). Numerous other physical property data appear in the literature, including approximation coefficients for free energy function calculations, coefficients of diffusion, partition coefficients, spectroscopic studies, thermodynamic properties, and third law entropy (1,2). Mathematical correlations for vapor pressure, surface tension, heat of vaporization, heat capacity, liquid density, thermal conductivity, and viscosity values have been established for the 0–450°C range, as well as heat and free energy of formation, vapor heat capacity, thermal conductivity, and viscosity values for the 0–1200°C range (3).

Table 1. Properties of Hydrogen Peroxide

Property	Value
mp, °C	–0.41
bp, °C	150.2
density at 25°C, g/mL	1.4425
viscosity at 20°C, mPa·s (=cP)	1.245
surface tension at 20°C, mN/m (=dyn/cm)	80.4
specific conductance at 25°C, $(\Omega \cdot \text{cm})^{-1}$	4×10^{-7}
heat of fusion, J/g ^b	367.52
specific heat at 25°C, J/(g·K) ^b	2.628
heat of vaporization at 25°C, kJ/g ^b	1.517
dissociation constant ^c at 20°C	1.78×10^{-12}
heat of dissociation, kJ/mol ^b	34.3

^aTends to supercool.

^bTo convert J to cal, divide by 4.184.

^cAt zero ionic strength.

Chemical Properties

Hydrogen peroxide is a weak acid, having a $pK_a = 11.75$.

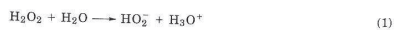


Table 2. Physical Properties of Aqueous Hydrogen Peroxide

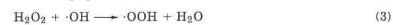
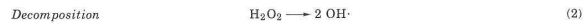
Liquid, wt % H_2O_2	Freezing point, °C	Boiling point, ^a °C	Vapor, ^a wt % H_2O_2	Density at 25°C, g/mL	ΔH_{vap} at 25°C, kJ/g ^b
10	–6.4	101.7	0.9	1.0324	2.357
20	–14.6	103.6	2.1	1.0694	2.274
30	–25.7	106.2	4.2	1.1081	2.192
40	–41.4	109.6	7.6	1.1487	2.105
50	–52.2	113.8	13.0	1.1914	2.017
60	–55.5	119.0	20.8	1.2364	1.926
70	–40.3	125.5	33.4	1.2839	1.832
80	–24.8	132.9	51.5	1.3339	1.733
90	–11.5	141.3	75.0	1.3867	1.627

^aAt 101.3 kPa (1 atm).

^bTo convert J to cal, divide by 4.184.

Dissociation of the second proton is insignificant. The pH of its aqueous solutions can be measured reproducibly with a glass electrode, but a correction dependent on the concentration must be added to obtain the true pH value. Correction values for the most common commercial solutions are listed in Table 3. The apparent pH of commercial product solutions can be affected by the type and amount of stabilizers added, and many times the pH is purposely adjusted to a grade specification range.

The reactions of hydrogen peroxide include



or



Table 3. Apparent and True pH of Aqueous Hydrogen Peroxide

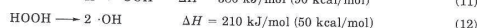
H_2O_2 conc, wt %	Equivalence point ^a	True pH	Correction factor
35	3.9	4.6	+0.7
50	2.8	4.3	+1.5
70	1.6	4.4	+2.8
90 ^b	0.2	5.1	+4.9

^aMeasured using glass electrode.

^bRoutine manufacture has been discontinued.

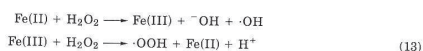
Hydrogen peroxide may react directly or after it has first ionized or dissociated into free radicals. Often, the reaction mechanism is extremely complex and may involve catalysis or be dependent on the environment. Enhancement of the relatively mild oxidizing action of hydrogen peroxide is accomplished in the presence of certain metal catalysts (4). The redox system Fe(II)—Fe(III) is the most widely used catalyst, which, in combination with hydrogen peroxide, is known as Fenton's reagent (5).

Free-Radical Formation. Hydrogen peroxide can form free radicals by homolytic cleavage of either an O—H or the O—O bond.



Equation 11 predominates in uncatalyzed vapor-phase decomposition and photochemically initiated reactions. In catalytic reactions, and especially in solution, the nature of the reactants determines which reaction is predominant.

Fenton chemistry is dependent on the formation of free radicals.



The radicals are then involved in oxidations such as formation of ketones (qv) from alcohols. Similar reactions are finding value in treatment of waste streams to reduce total oxidizable carbon and thus its chemical oxygen demand. These reactions normally are conducted in aqueous acid medium at pH 1–4 to minimize the catalytic decomposition of the hydrogen peroxide. More information on metal and metal oxide-catalyzed oxidation reactions (Milas' oxidations) is available (4–7) (see also PHOTOCHEMICAL TECHNOLOGY, PHOTOCATALYSIS).

Decomposition. The decomposition of hydrogen peroxide may be homogeneous or heterogeneous and can occur in the vapor or the condensed phase. Although there is considerable evidence that the decomposition occurs as a chain reaction involving free radicals, the products of the decomposition are water and oxygen gas. Decomposition of hydrogen peroxide must be controlled at all times, in part because of the economic impact, but more importantly because the resultant simultaneous generation of oxygen and heat may cause serious safety problems. For the decomposition of pure hydrogen peroxide at 298.16 K (eq. 5), $\Delta H = -105.26 \text{ kJ/mol (-25.26 kcal/mol)}$ of H_2O_2 when H_2O_2 is in the vapor state, and $\Delta H = -98.20 \text{ kJ/mol (-23.47 kcal/mol)}$ when H_2O_2 is a liquid.

The mechanism and rate of hydrogen peroxide decomposition depend on many factors, including temperature, pH, presence or absence of a catalyst (7–10), such as metal ions, oxides, and hydroxides, etc. Some common metal ions that actively support homogeneous catalysis of the decomposition include ferrous, ferric, cuprous, cupric, chromate, dichromate, molybdate, tungstate, and vanadate. For combinations, such as iron and copper together, the decomposition rate is greater than for the individual components. A key factor is that copper reduces iron and thus assures a greater concentration of the more active ferrous ions. Other combinations yield similar results. Catalase enzyme and the

halide ions except for fluoride also can be active. Active common catalytic surfaces include copper, mild steel, iron, silver, palladium, platinum, and oxides of iron, lead, nickel, manganese, and mercury.

The stability of pure hydrogen peroxide solutions increases with increasing concentration and is maximum between pH 3.5–4.5. The decomposition rate of ultrapure hydrogen peroxide increases 2.2–2.3-fold for each 10°C rise in temperature from ambient to about 100°C. This approximates an Arrhenius-type response with activation energy of about 58 kJ/mol (13.9 kcal/mol). However, decomposition increases as low as 1.6-fold for each 10°C rise have been noted for impure, unstabilized solutions.

The decomposition of aqueous hydrogen peroxide is minimized by various purification steps during manufacture, use of clean passive equipment, control of contaminants, and the addition of stabilizers. The decomposition is zero-order with respect to hydrogen peroxide concentration.

Stabilization. Pure hydrogen peroxide solutions are relatively stable and can be stored for extended periods in clean passive containers. Commercial solutions, however, invariably contain or may be exposed to varying amounts of catalytic impurities and must therefore contain reagents which deactivate these impurities, either by adsorption (qv) or through formation of complexes (see CHELATING AGENTS). For example, sodium pyrophosphate [7758-16-9], $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$, added to acidic hydrogen peroxide solutions, acts as a complexing agent, whereas sodium stannate trihydrate [12058-66-1], $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, forms protective colloids (qv). Alkaline solutions of hydrogen peroxide are inherently less stable than acidic solutions, and often magnesium or silicate ions are added to alkaline solutions to form soluble or colloidal compounds which deactivate tramp metal ions. Additionally, the use of amine-substituted organophosphonic acids or their alkali metal salts for stabilizing weak hydrogen peroxide solutions (0.01–5.0%) in the pH range of 7–12.5 has been patented (11).

Many stabilizer systems have been tailored to a particular industry need or for particular areas where dilution water quality is poor. These grades are heavily stabilized and may contain organic sequestering agents, ie, stannate, phosphates, and nitrate ions, so that the weak solutions produced by dilution from hard water retain acceptable stability. The nitrate is not a stabilizer, but it inhibits corrosion of aluminum storage tanks by chloride ion.

Several patents (12–14) claim that adding small amounts of organic sequestering agents to aqueous hydrogen peroxide solutions, that contain normal stabilizers such as stannates and phosphates, improves the resistance against polyvalent metal cation-induced decomposition. Other patented stabilizer packages include combinations of organic compounds and organometallic salts with or without stannates and phosphates (15–21).

Special hydrogen peroxide stabilizer packages have been tailored for uses such as cleaning high capacity semiconductor chips and other critical electronic components for the computer industry (see SEMICONDUCTORS). These grades require extremely low metal ion content and, in some cases, the use of all-organic stabilizers (22–28) is cited. Some very pure, unstabilized 30% hydrogen peroxide containing <1 ppb of total metal ions has reportedly been used in this market. Because container corrosion would be a source of metal ion contamination, the containers are either special glass or are lined.

Molecular Addition. Oxyacid salts, metal peroxides, nitrogen compounds, and others form crystalline peroxyhydrates in the presence of hydrogen peroxide. When dissolved in water, the peroxyhydrates react as solutions of their components. The peroxyhydrates formed from sodium carbonate and urea are commercially available. Examples of peroxyhydrates can be found in the literature (29,30).

Sodium perborate tetrahydrate [10486-00-7] is formed from hydrogen peroxide and sodium borate [1303-96-4] and, although cited often as an example of a peroxyhydrate, has been shown to be a true peroxy compound, sodium peroxyborate trihydrate (31). The peroxyborate is a key bleaching ingredient in laundry detergent formulations (see BLEACHING AGENTS). Most recently, sodium perborate monohydrate [10338-33-9] has been used. This pure compound has no water of hydration and properly should merely be called sodium peroxyborate.

Substitution. A variety of peroxygen compounds can be formed through substitution reactions of hydrogen peroxide with organic reagents. These compounds are commercially useful as catalysts for polymerizations and oxidizing agents for a number of specialized reactions. The reactant and principal product of such reactions include alkylating agents, ie, alkylhydroperoxides; carboxylic and peroxy acids; acid anhydrides or chlorides, ie, diacyl peroxides; and ketones and ketone peroxides. These derivatives are considerably more hazardous than hydrogen peroxide and should be handled with extreme care, per manufacturer instructions.

Inorganic peroxygen compounds can be prepared through similar reactions with inorganic reagents. Alkaline-earth metal peroxides are prepared from hydrogen peroxide and the corresponding hydroxide, and monoperoxydisulfuric acid by reacting hydrogen peroxide and sulfur trioxide or sulfuric acid.

Oxidation. Hydrogen peroxide is a strong oxidant. Most of its uses and those of its derivatives depend on this property. Hydrogen peroxide oxidizes a wide variety of organic and inorganic compounds, ranging from iodide ions to the various color bodies of unknown structure in cellulosic fibers. The rate of these reactions may be quite slow or so fast that the reaction occurs on a reactive shock wave. The mechanisms of these reactions are varied and dependent on the reductive substrate, the reaction environment, and catalysis. Specific reactions are discussed in a number of general and other references (4,5,32-35).

Reduction. Hydrogen peroxide reduces stronger oxidizing agents such as chlorine, sodium hypochlorite, potassium permanganate, and ceric sulfate. The last two are used for the volumetric determination of hydrogen peroxide. The ability of hydrogen peroxide to reduce chlorine and hypochlorite leads to the use of H_2O_2 as a pollution abatement treatment for industrial waste streams (see WASTES, INDUSTRIAL).

Manufacture

Hydrogen peroxide is composed of equal molar amounts of hydrogen and oxygen and can be formed directly by catalytically combining the gaseous elements. It can also be formed from compounds that contain the peroxy group; from water and oxygen by thermal, photochemical, electrochemical or similar processes; and by the uncatalyzed reaction of molecular oxygen with appropriate

hydrogen-containing species. It has been manufactured commercially by processes based on the reaction of barium peroxide or sodium peroxide with an acid, the electrolysis of sulfuric acid and related compounds, the autoxidation of 2-alkylanthrahydroquinones, isopropyl alcohol, and hydrazobenzene, and more recently by the Huron-Dow (36-38) process through the cathodic reduction of oxygen in an electrolytic cell using dilute sodium hydroxide as the electrolyte. By far, the majority of hydrogen peroxide produced since 1957 has been based on the autoxidation of 2-alkylanthrahydroquinones.

AUTOXIDATION METHODS

Anthrahydroquinone Autoxidation. It was discovered in 1901 that hydroquinone [123-31-9] and hydrazobenzene [122-66-7] would each react with O_2 , forming H_2O_2 quantitatively. Then in 1935 it was found that 2-alkylanthraquinones (2-alkyl-9,10-anthracenediones) were well suited for use as the reaction hydrogen carrier in a cyclic process (39). The first semiworks-scale anthrahydroquinone autoxidation process plant, producing H_2O_2 at a rate of 30 t/mo, was operated as a production unit by I. G. Farbenindustrie in Germany during World War II (40). All subsequent anthrahydroquinone autoxidation processes retain the basic features of this, the Riedl-Pfleiderer process, shown in Figure 1.

A 2-alkylanthraquinone (RAQ) (1) dissolved in a suitable solvent or solvent mixture is catalytically hydrogenated to the corresponding 2-alkylanthrahydroquinone (RAHQ) (2), ie, 2-alkyl-9,10-anthracenediol or 2-alkylanthraquinol (eq. 15). The 2-alkylanthraquinone is commonly called the reaction carrier, hydrogen carrier, or working material; the 2-alkylanthraquinone-solvent mixture is called the working solution. Carriers in industrial use include 2-tert-amylan-

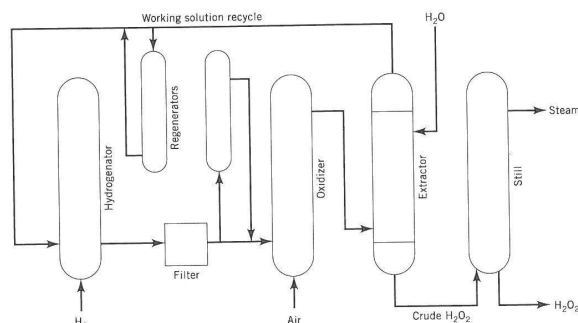
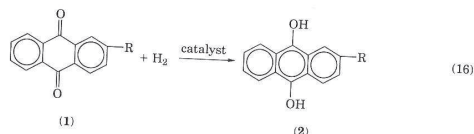
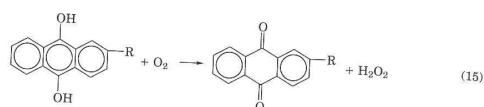


Fig. 1. Anthrahydroquinone autoxidation, Riedl-Pfleiderer process.

thraquinone [32588-54-8], 2-iso-sec-amylnthraquinone [68892-24-4], 2-tert-butylanthraquinone [84-47-9], and 2-ethylanthraquinone [84-51-5].



All have the alkyl group in the 2-position; thus the terms alkylanthrahydroquinone and alkylanthraquinone are taken to mean C-2 substitution herein. The working solution containing the carrier product alkylanthrahydroquinone is separated from the hydrogenation catalyst and aerated with an oxygen-containing gas, usually compressed air, to reform the alkylanthraquinone carrier while simultaneously producing hydrogen peroxide (eq. 16). The hydrogen peroxide is then extracted from the oxidized working solution using demineralized water, and the aqueous extract is purified and concentrated by fractionation to the desired strength. The extracted working solution is dried and recycled back to hydrogenation.

When the process is first started, the working solution contains only the alkylanthraquinone specie. The alkylanthraquinone (RAQ) acts in close concert with the catalyst, which is usually palladium metal, and can be envisioned as Pd:RAQ. The complex reacts with hydrogen, yielding Pd:RAHQ. The alkylanthrahydroquinone is subject to many other secondary reactions that occur continuously during each process cycle. During the short time that the alkylanthrahydroquinone is in contact with the catalyst, a minor amount of catalytic reduction of the unsubstituted aromatic ring occurs at the 5, 6, 7, and 8 positions, yielding the tetrahydroalkylanthrahydroquinone (3) shown in Figure 2. Further ring reduction may occur in the 1, 2, 3, and 4 positions of the substituted ring yielding octahydroalkylanthrahydroquinone (4). Once this compound is formed, it remains until purged owing to its essentially nonexistent oxidation rate. Transannular tautomerization of the alkylanthrahydroquinone also yields the hydroxyanthrones (oxanthrones) (5) and (6) which can be reduced to the anthrones (7) and (8). Another possible chemical route to the oxanthrone is via the formation and subsequent breakup of a quinhydrone-type charge-transfer complex. Although the formation of tetrahydroalkylanthrahydroquinones (3) is slow, these oxidize yielding H_2O_2 and the corresponding tetrahydroalkylanthraquinones which are the apparent precursors to the tetrahydroalkylanthraquinone epoxide (9). This series of reactions repeats with

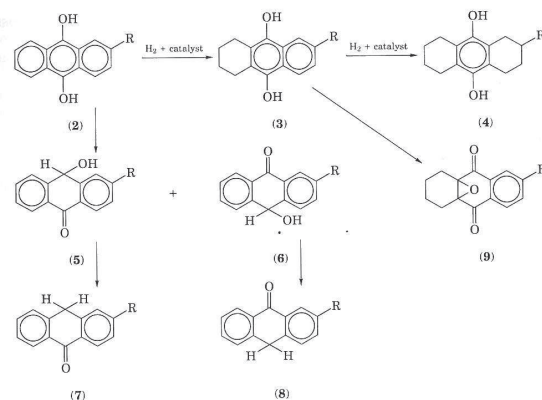
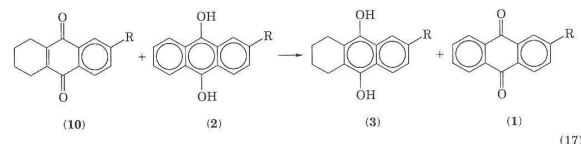


Fig. 2. Possible secondary reactions of 2-alkylanthrahydroquinones.

each subsequent cycle of equations 15 and 16, resulting in a continuing buildup of the tetrahydroalkylanthraquinones, until these secondary products could become the dominant anthraquinone species if not reverted. These compounds react directly with alkylanthrahydroquinone accepting its hydrogen to form the tetrahydroalkylanthrahydroquinone (THRAQ) (10) and thus freeing the alkylanthraquinone (eq. 17) to continue the hydrogenation cycle.



Although considered an active participant in the process cycle, the tetrahydroalkylanthraquinone (10) may not be a significant part of the catalytic hydrogenation because, dependent on the concentration in the working solution, these could all be converted to the hydroquinone by the labile shift per equation 17 and not be available to participate. None of the other first- or second-generation anthraquinone derivatives produce hydrogen peroxide, but most are susceptible to further reaction by oxidative or reductive mechanisms.