Decomposition of Hydrogen Peroxide in Aqueous Solutions at Elevated Temperatures

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Abstract

Decomposition of hydrogen peroxide in high-purity water has been measured at temperatures ranging 100 to 280°C in a laboratory test loop. A first-order decomposition kinetics has been observed in all cases, but the decomposition rates were found to vary widely, depending on the material used in the reaction chamber. In a 4 mm ID stainless steel tubing, the decomposition rate constant is determined to be $k = 2 \times 10^5 \exp(-14800/RT)$. This decomposition rate is approximately 100 times faster than that observed in a Teflon tubing.

The variation of decomposition rate in different reaction chambers is attributed to the heterogeneous catalytic effects. There is no evidence of reaction between H_2 and H_2O_2 in the high-purity water at temperatures up to 280°C.

Introduction

Hydrogen peroxide (H_2O_2) is one of the stable products radiolytically produced in the boiling water reactor (BWR) coolant. Understanding the chemical properties of hydrogen peroxide in the BWR coolant has become an important factor dealing with the material corrosion problems in the BWR primary system. Hydrogen peroxide is well known to decompose to form oxygen in water, and the overall reaction can be written as

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$
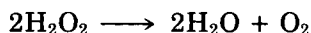
Although, hydrogen peroxide has been believed to exist in the coolant at approximately 280°C during power operation, the measurement has not been successful until recently when the water samples were taken through special arrangement. Up to ca. 124 ppb was determined in one measurement [1], and the decomposition half-time in the sample line was reported to be on the order of several seconds [2]. The actual level of hydrogen peroxide in an operating BWR is still not accurately known.

Recently, several measurements of the hydrogen peroxide decomposition rate at elevated temperatures up to ca. 280°C have been reported [3–7]. Although it is agreed that the decomposition is a first order reaction with respect to H_2O_2, the activation energy has been reported to range from ca. 5 Kcal/mol to ca. 23 Kcal/mol, and the rate constants at 280°C are significantly different from each other. More accurate data are needed in a computer radiolysis model calculation [8].

We have thoroughly investigated the decomposition of hydrogen peroxide at elevated temperatures under various conditions including the reaction in several different sizes and materials of the reaction vessel. The effects of impurities in water and the reactions between H_2O_2 and H_2, with or without a catalyst, have also been investigated. This article deals mainly with the reaction kinetics of hydrogen peroxide decomposition at elevated temperatures. The possible catalytic effects on the decomposition mechanism are also discussed.

Experimental

Test Facility

The experiments were performed in an all-purpose high temperature water loop similar to that previously used in the Co-60 deposition studies [9]. Schematic diagrams of the test loop and the test section which was used in the hydrogen peroxide studies are shown in Figures 1 and 2. The test sec-
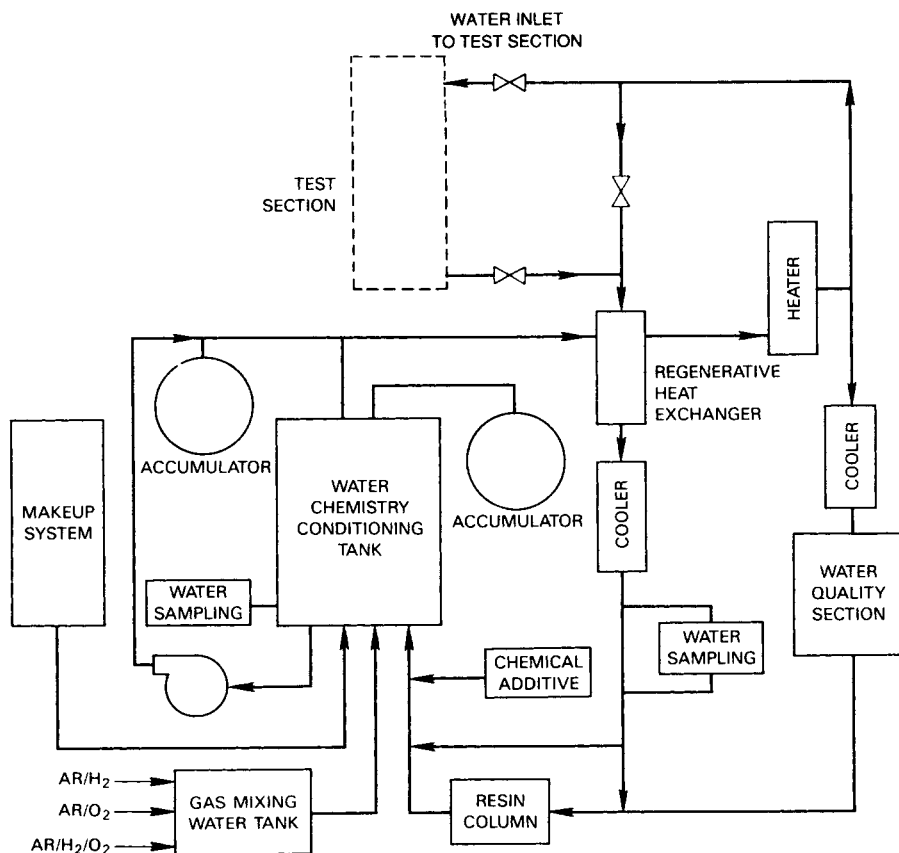
Water Temperature: 280°C
Water Flow Rate: 2.2 Kg/min

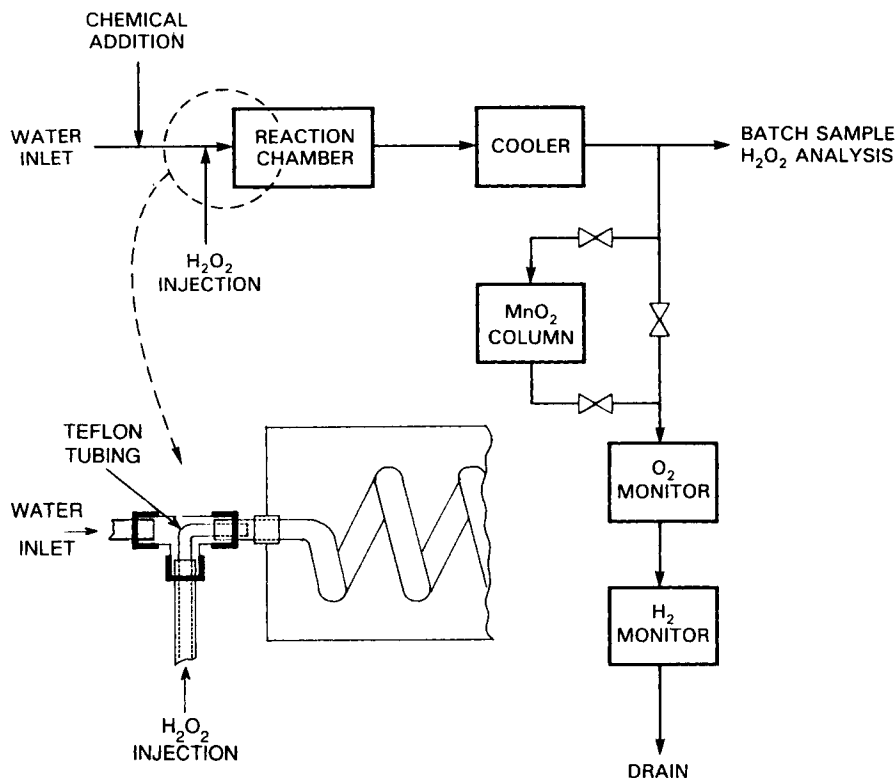Figure 1.   Schematic diagram of GE Vallecitos all-purpose test loop.

Figure 2. Schematic diagram of equipment configuration for hydrogen peroxide decomposition studies.

tion is connected to a "T" in the high temperature section of the loop. Stainless steel, titanium, and Teflon (PTFE) tubings of various sizes are used as reaction chamber. Metallic tubing was pre-conditioned by prefilming in high purity water containing ca. 200 ppb O_2 at ca. 280°C for at least 500 h. As an inert surface, Teflon tubing, which was inserted and contained in stainless steel tubing of appropriate size, was rinsed with high purity, high temperature water for several hours before the first test. Subsequently, the tubing was rinsed for ca. 1 h before each test.

The high purity water circulated in the test loop contained less than 1 ppb total metallic impurities. A typical analysis showed 0.22 ppb Ni, 0.038 ppb Zn, 0.044 ppb Fe, 0.084 ppb Mn, and 0.37 ppb Cr. The water conductivity was consistently maintained at ≤0.1 μS/cm (measured at 25°C).

During a test, the loop water which had been well adjusted to the desired water chemistry, was directed to the test chamber, and the hydrogen peroxide solution was injected at constant rates directly into the water upstream of the chamber through a 1 mm Teflon tubing. At the outlet of the reaction chamber, the water was quickly cooled to ≤35°C, and grab samples were taken from the sample point located downstream of the cooler, for H_2O_2 analysis. The effluent water containing reaction products was directed through H_2 and O_2 monitors (Orbisphere meters).

Hydrogen Peroxide Measurements

The H_2O_2 content in the reagent or stock solutions was determined by a standard procedure of permanganate titration in acidic solution. The concentration of H_2O_2 in water samples was determined by a spectrophotometric method reported in the literature [10]. In this method, phenolphthalin is oxidized by H_2O_2 to phenolphthalein in the presence of $CuSO_4$ as a catalyst. The absorbance/transmittance of the pink color of phenolphthalein in the alkaline solution at 540 nm is used for quantitative measurement of H_2O_2.

Alternatively, the H_2O_2 content in water samples was monitored continuously after H_2O_2 was catalytically converted to O_2 by MnO_2. When the sample contained both O_2 and H_2O_2, the O_2 content was first measured and then the total O_2 was measured after H_2O_2 was converted to O_2 through the MnO_2 contained in a column. Material balance was always obtained in each test, indicating H_2O_2 was completely decomposed to O_2 and there was no significant loss of either O_2 or H_2O_2 to the corrosion of the reaction chamber. The starting concentration of H_2O_2 was chosen at 1–2 ppm for convenience in measurement during the decomposition study.

Test Procedures

A traditional technique was used to determine the order of decomposition and the decomposition rate. At a preset temperature and water flow rate, diluted H_2O_2 solution was injected directly into the reaction chamber at a constant injection rate. In the effluent of the reaction chamber the dissolved O_2, H_2O_2, and total O_2 after H_2O_2 was converted to O_2 were determined. The reaction time (residence time in reaction chamber) was determined by the water flow rate (at temperature) and the volume of reaction chamber. Plug flow of water through the reaction chamber (tubing) was assumed. By changing the water flow rate ranging from ca. 50 g/s to ca. 300 g/s, a range of test data with various reaction times was obtained.

If the reaction follows a first order reaction,

$$\frac{dC}{dt} = kC$$

and, upon integration,

(1) $$C = C_0 \exp(-kt) \quad \text{or}$$

(2) $$k = -\frac{1}{t} \ln \frac{C}{C_0}$$

where
t = reaction time, s
k = first order reaction rate constant, s^{-1}
C = concentration of H_2O_2 in solution at time t, mol/L (or ppb)
C_0 = initial concentration of H_2O_2 in solution at time $t = 0$, mol/L (or ppb)
By plotting $\ln(C/C_0)$ vs. t on a semi-log paper the half-time of the reaction and the rate constant at reaction temperature can be estimated from the slope of a straight line through the data points,

$$k = \frac{0.693}{t_{1/2}}$$

Alternatively, if only the decomposition product O_2 is measured, equations (1) and (2) can be modified to

(1')
$$1 - \frac{B}{B_0} = \exp(-kt) \quad \text{or}$$

(2')
$$k = -\frac{1}{t} \ln\left(1 - \frac{B}{B_0}\right)$$

where
$B = O_2$ concentration in solution at time t, ppb
B_0 = total O_2 concentration (after conversion of H_2O_2 to O_2) in solution at $t = 0$.
In some cases where the test solution contained a low level O_2 background, a correction was made by subtracting the background from B or B_0. B/B_0 is the fraction of H_2O_2 decomposed and $1 - B/B_0$ equals to the fraction of H_2O_2 remaining in solution after reaction time t ($C/C_0 = 1 - B/B_0$). A typical example of the test results for the decomposition in titanium tubing is shown in Figure 3.
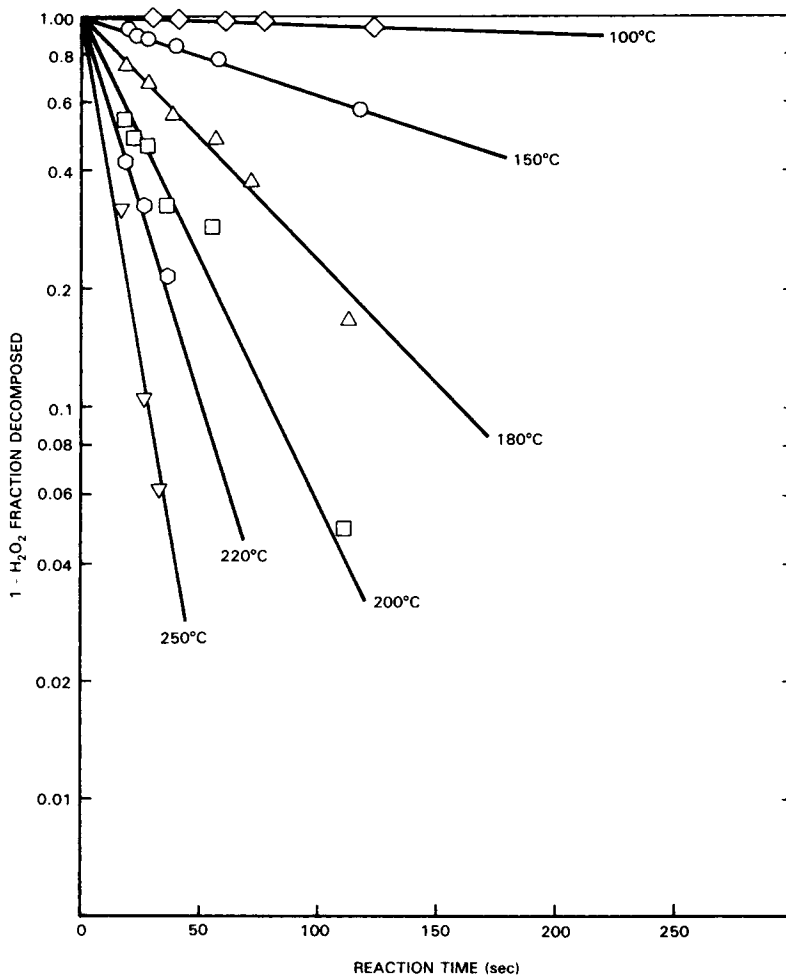

Figure 3.   Decomposition of hydrogen peroxide in Titanium tubing.

Once the reaction order had been determined to be a first order reaction, the reaction rate was more conveniently measured by varying the reaction temperature at constant flow rate in the present test apparatus. The rate constant was calculated from either equation (2) or (2') at each temperature. A correction to the water density at various temperatures was made to obtain an accurate estimate of the residence time (reaction time) in the reaction chamber. Two typical sets of data for the decomposition of H_2O_2 in Teflon and stainless steel tubing are given in Tables I and II, respectively.

The rate constants so obtained are shown on a semi-log plot in an Arrhenius form for further evaluation and comparison.

$$(3) \qquad\qquad k = A \exp\left(-\frac{E}{RT}\right)$$

where
A = reaction frequency factor, s^{-1}
E = activation energy, Kcal/mol
R = gas constant, Kcal/mol/°K
T = temperature, °K
Both A and E are estimated from the linear portion of the data in the Arrhenius plot.

TABLE I. Summary of experimental data. (1) Test No. TF7 in teflon tubing (8 mm ID).

Temperature (C°)	B_o (ppb)	B (ppb)	$\frac{B}{B_o}$	t (s)	k (s^{-1})
132	2459	8	0.003	169.4	1.92 E-5
136	2429	21	0.009	165.4	5.35 E-5
178	2429	59	0.024	161.4	1.50 E-4
200	2439	123	0.050	157.0	3.30 E-4
223	2419	248	0.103	151.8	7.13 E-4
246	2409	512	0.213	146.1	1.64 E-3
268	2379	868	0.365	140.0	3.24 E-3

TABLE II. Summary of experimental data. (2) Test No. SS7 in stainless steel tubing (4.9 mm ID).

Temperature (C°)	B_o (ppb)	B (ppb)	$\frac{B}{B_o}$	t (s)	k (s^{-1})
114	2917	85	0.029	60.9	4.86 E-4
125	2917	267	0.092	60.4	1.59 E-3
137	2917	419	0.144	59.7	2.60 E-3
148	2797	647	0.222	59.1	4.24 E-3
160	2797	927	0.331	58.3	6.91 E-3
172	2797	1307	0.467	57.6	1.71 E-2
182	2797	1737	0.621	56.9	1.71 E-2
193	2797	2097	0.750	56.1	2.47 E-2
205	2687	2187	0.814	55.2	3.05 E-2
216	2687	2357	0.877	54.3	3.86 E-2
228	2687	2487	0.926	53.3	4.87 E-2
238	2687	2697	0.967	52.5	6.49 E-2
250	2687	2677	0.996	51.4	1.09 E-1
262	2577	2567	0.996	50.1	1.11 E-1

Results and Discussion

Surface Effects on Decomposition Rate

The first order rate constant as a function of temperature for the hydrogen peroxide decomposition in Teflon tubing is shown in Figure 4. Although the data obtained in several runs are somewhat scattered, the decomposition rates are very low compared to the reaction rates in other reaction chambers (see later). It is well known that the hydrogen peroxide decomposition is extremely sensitive to catalysis, homogeneous and heterogeneous [11,12]. It seems obvious that the decomposition in Teflon tubing was affected by the trace impurities in water or of impurities on the Teflon sur-
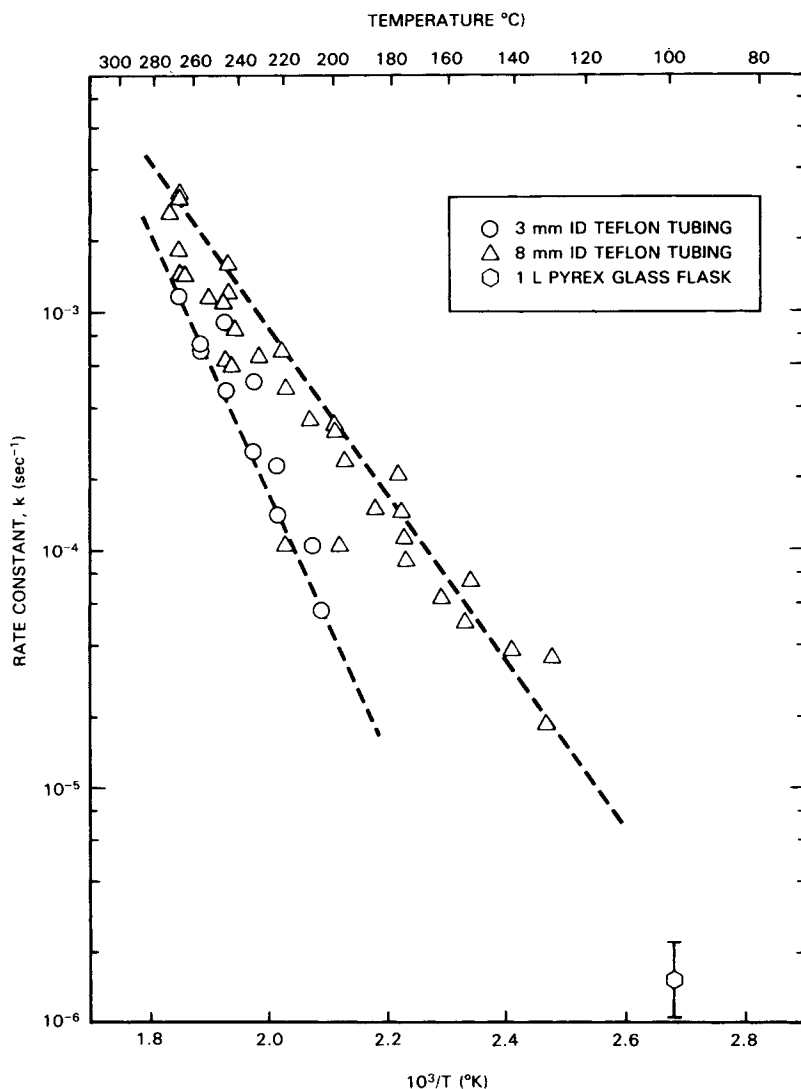

Figure 4. Dependence of hydrogen peroxide decomposition rate constant on temperature. Decomposition in Teflon tubing.

faces. It should be mentioned that the two different sizes of Teflon tubing used in the present study came from different vendors. In a number of earlier test runs in the 8 mm I.D. tubing, the decomposition rate was 3.5 times higher, and it eventually decreased to a reproducible level shown in Figure 4.

A comparison of the test results with the literature data obtained with either glass or Teflon reaction vessels is shown in Figure 5. It is of particular
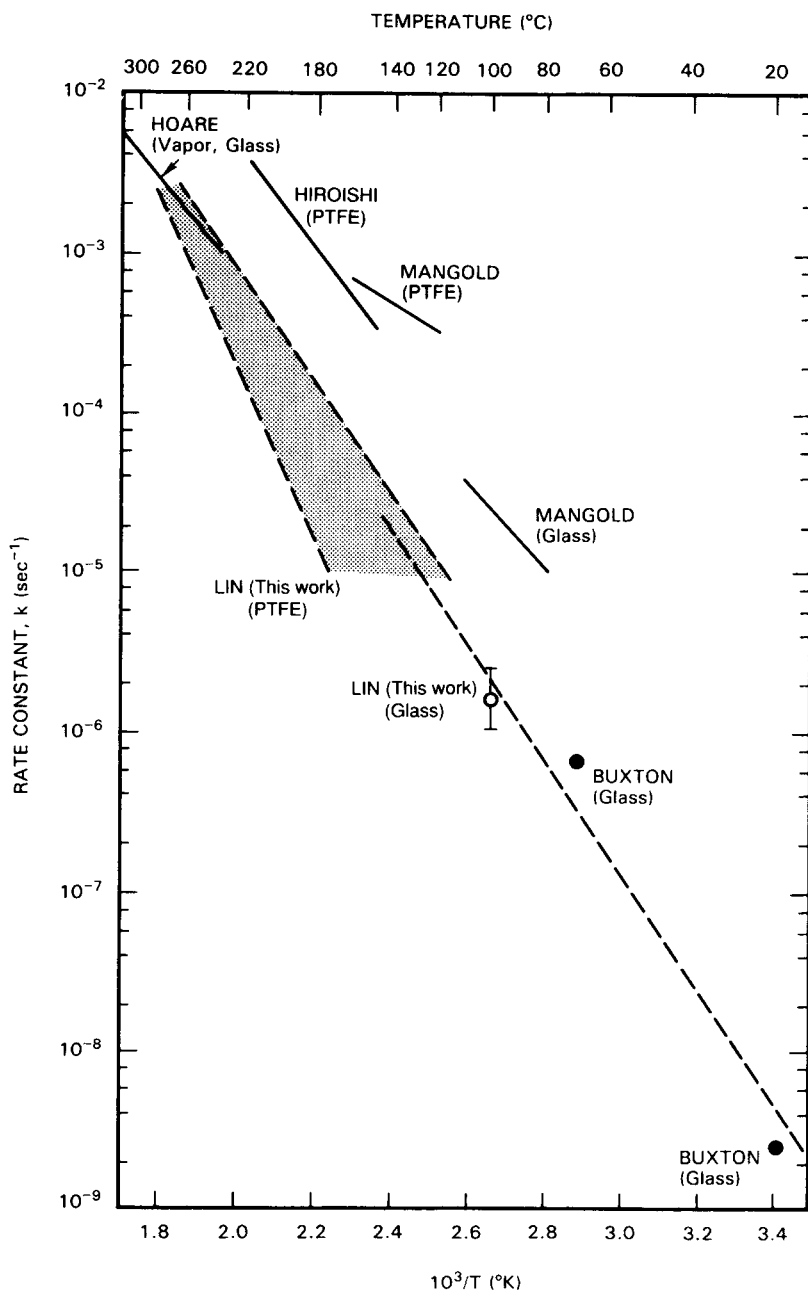

Figure 5. Comparison of hydrogen peroxide decomposition rate constants measured in inert (glass and Teflon) reaction vessels.

interest to compare the present test results with the data obtained in the vapor phase reported by Hoare et al. [13]. Only the lower temperature ($\leq 420°C$) portion of the data are reproduced. They reported a decomposition activation energy of 48 Kcal/mol in the pure H_2O_2 vapor phase at higher temperatures ($\geq 420°C$) while the activation energy is much lower at ca. 15 Kcal/mol for the decomposition at lower temperatures due to catalysis effect. The higher value of activation energy is consistent with the accepted value of $O-O$ bond dissociation energy (48 Kcal/mol) in H_2O_2 [14–16]. It is a well known fact that the catalysis effects would reduce the activation energy in the rate determining step of the reaction [17]. The results reported by Hoare et al. are in agreement with the present data obtained in Teflon tubings.

Other interesting data shown in Figure 5 are two unpublished lower temperature data provided by Buxton [18]. The lowest data point at 20°C is about six orders of magnitude lower than the highest one at 260°C. The half-time of decomposition at 20°C is about 3 years, which is long enough to be considered "stable" in most chemical reactions. The best estimate first order rate constant for this group of data is

$$k = 4 \times 10^3 \exp(-16000/RT).$$

However, if one assumes that the lowest decomposition rate with highest activation energy represents the closest to the catalysis free decomposition rate in the test environment, the first order rate law for the H_2O_2 decomposition in an "inert" reaction vessel can be described by

$$-d[H_2O_2]/dt = k[H_2O_2]$$

$$k = 2.3 \times 10^7 \exp(-25400/RT)$$

The decomposition rates measured in stainless steel and titanium tubings are practically identical and much higher than that measured in Teflon tubing. The Arrehenius plots (Fig. 6) indicate that the data at higher temperatures ($\geq 200°C$) deviate from a straight line drawn through the data points at lower temperatures. Similar results have been reported by Rebensdorff and Wikmark [19]. The exact reasons for such deviation are not known, but it is not uncommon to observe this phenomenon in radiation chemistry involving free radical reactions [20]. It is hypothesized that the decomposition process takes place on a catalysis surface following a mass transfer process (diffusion) from the balk water to the surface. At lower temperatures, the rate determining step is the decomposition process at the surface, whereas the mass transfer process became the rate determining step at higher temperatures as the rate of decomposition process on the surface increases rapidly. Further discussion and calculations of mass transfer coefficients and mass transfer-controlled reaction rates are given in Appendix A.

The best estimated first order rate constant for the H_2O_2 decomposition in a 4 mm stainless steel tubing is

$$k = 2.0 \times 10^5 \exp(-14800/RT).$$

A comparison of the test results with the literature data obtained in a 4 mm I.D. stainless steel tubing is shown in Figure 7. The shaded area covers all the data obtained in this work. The decomposition rate was slightly lower in
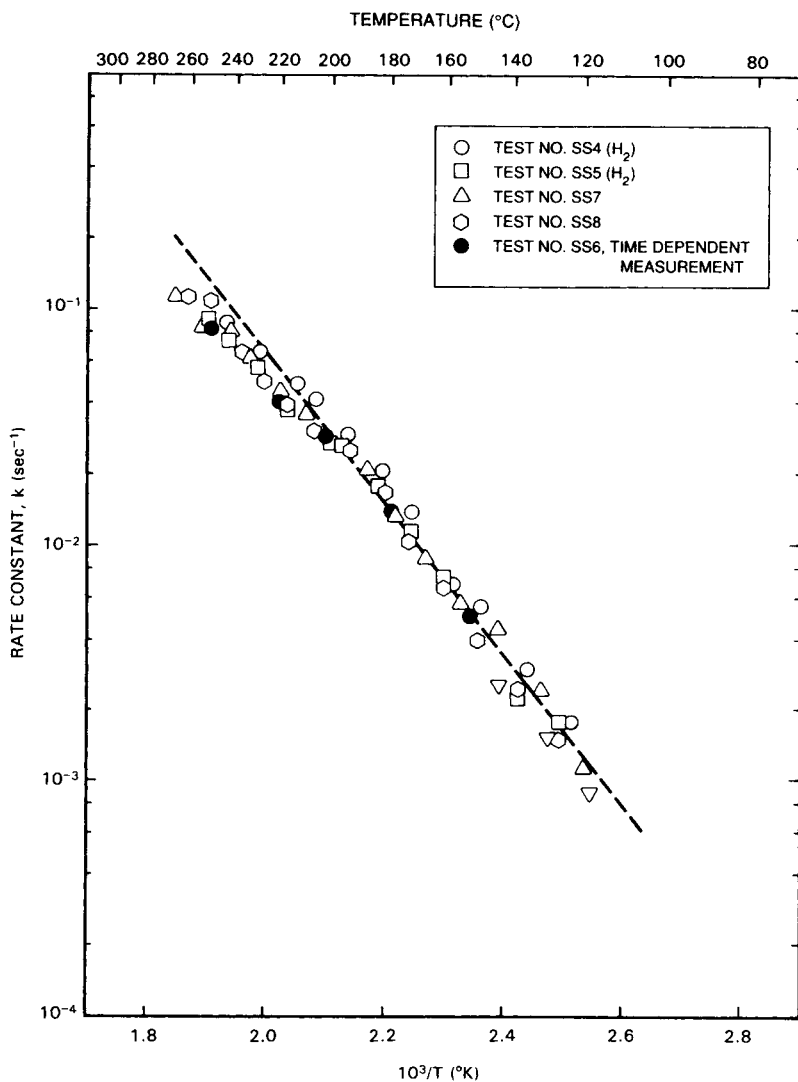
Figure 6.   Dependence of hydrogen peroxide decomposition rate constant on temperature. Decomposition in stainless steel tubing.

earlier tests, in the same tubing. This result may be attributed to a change in the surface condition as the oxide film stabilized in later measurements. With the exception of Uchida's data, all literature data are in good agreement, considering the difficulty of measurement.

Recently, both Rebensdorff and Wikmark [21] and Hiroishi and Ishigure [7] have suggested that the apparent decomposition rate constant measured in stainless steel tubing consists of two terms,

$$k = k_b + k_s(S/V)$$

where k_b and k_s are the decomposition rates in the balk water and at the surface, respectively. S/V is the ratio of surface area in contact with water to the volume of water contained in the reaction vessel. In the present study,
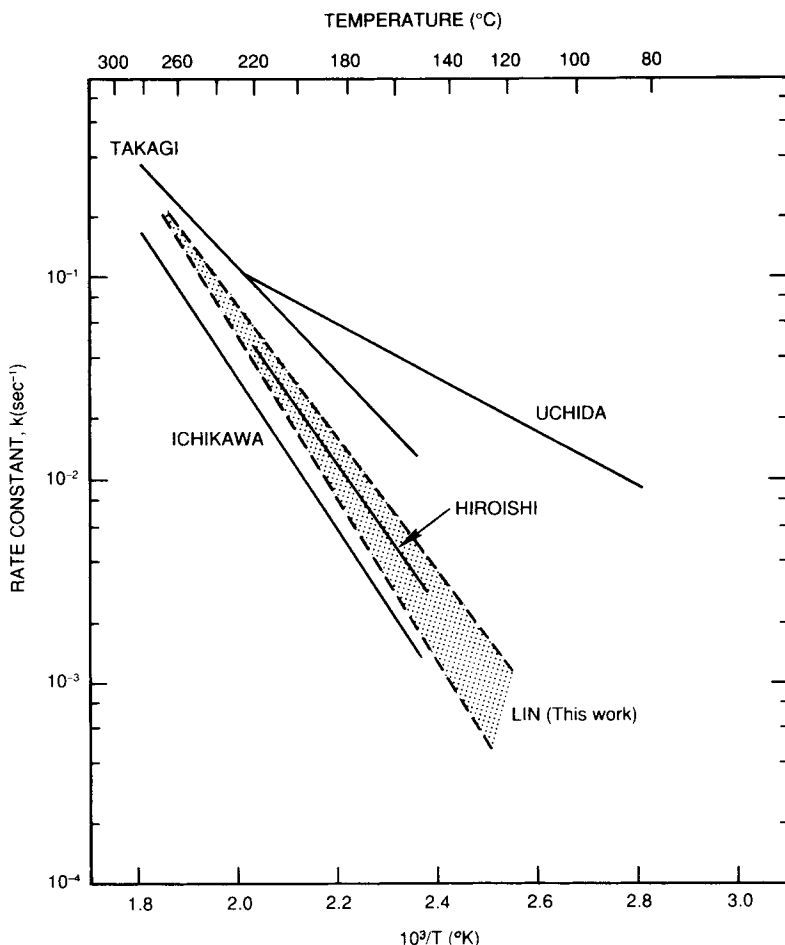
TEMPERATURE (°C)

Figure 7. Comparison of hydrogen peroxide decomposition rate constants measured in 4 mm ID stainless steel tubing.

the decomposition rate in the balk water as measured in Teflon tubing is very small compared to the surface catalysis decomposition rates measured in either stainless steel or titanium tubing, e.g., $k_b \ll k_s$ (S/V). This was also confirmed in one measurement with 9 mm I.D. stainless steel tubing, in which the decomposition rate was found to be approximately proportional to the S/V ratio.

In summary, the best estimated kinetics parameters for the decomposition of H_2O_2 in high purity water in three different reaction vessels are given in Table III.

Decomposition Mechanisms

It is not the primary objective of this work to investigate the mechanisms of hydrogen peroxide decomposition. However, it is appropriate to prevent some important findings which may lead to a better understanding in future investigations on the reactions of hydrogen peroxide at elevated temperatures.

TABLE III. Summary of best estimated first order H_2O_2 decomposition rate constants.

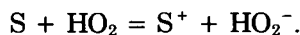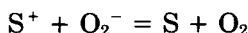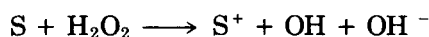| Reaction Vessel	Rate Constant
"Inert"[a]	$k = 2/3 \times 10^7 \exp(-25400/RT)$
Teflon and Glass[b]	$k = 4.0 \times 10^3 \exp(-16000/RT)$
Stainless Steel Tubing[c]	$k = 2.5 \times 10^5 \exp(-14800/RT)$
Titanium Tubing[c]	$k = 7.2 \times 10^5 \exp(-16300/RT)$

[a] Lower limit of all measurements in Teflon tubing.
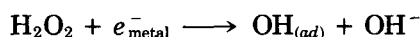[b] Average of all measurements in Teflon and glass reaction vessels.
[c] 4.9 mm I.D.

The higher decomposition rates in metallic tubing are attributed to surface catalytic effects which are most likely due to a charge transfer process involving radicals. It has been hypothesized [21] that the catalytic decomposition rate of hydrogen peroxide is related to the oxidation potential of metal or metallic oxide catalysts. A few catalytic decomposition mechanisms have been reported in the literatures [13,22,23], but none has been clearly proven.

Weiss [22] has proposed the following surface catalysis reactions:

$$S + H_2O_2 \longrightarrow S^+ + OH + OH^-$$

$$H_2O_2 + OH \longrightarrow H_2O + HO_2$$

$$HO_2 = H^+ + O_2^-$$

$$S^+ + O_2^- = S + O_2$$
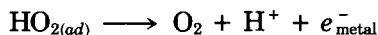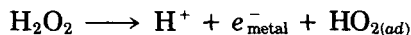
$$S + HO_2 = S^+ + HO_2^-.$$

In an electrochemical study, Gerischer and Gerischer [23] suggested that the metallic surface is polarized and radicals are not "free" from the metallic surface. They proposed the following reactions:
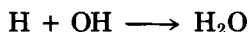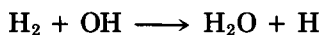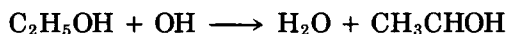
Cathodic Reaction:

$$H_2O_2 + e^-_{metal} \longrightarrow OH_{(ad)} + OH^-$$

$$OH_{(ad)} + e^-_{metal} \longrightarrow OH^-$$

Anodic Reaction:

$$H_2O_2 \longrightarrow H^+ + e^-_{metal} + HO_{2(ad)}$$

$$HO_{2(ad)} \longrightarrow O_2 + H^+ + e^-_{metal}$$

The short-lived $OH_{(ad)}$ and $HO_{2(ad)}$ radicals remain adsorbed on the catalyst surface which would affect their reactivity towards species in bulk solution.

In some experiments conducted in either stainless steel or titanium tubing, about 200 ppb of dissolved H_2 was maintained in the loop water to test the effect of dissolved H_2 on the H_2O_2 decomposition. The results indicated the addition of H_2 in water did not change the decomposition rate, and it was also observed that neither H_2 nor O_2 (from H_2O_2 decomposition) concentrations decreased in the process. Similar results were obtained with C_2H_5OH addition instead of H_2. Since H_2 and C_2H_5OH are excellent OH

radical scavengers [24], the reactions

$$H_2 + OH \longrightarrow H_2O + H$$

$$H + OH \longrightarrow H_2O$$

and

$$C_2H_5OH + OH \longrightarrow H_2O + CH_3CHOH$$

$$CH_3CHOH + OH \longrightarrow CH_3CHO + H_2O$$

would have occurred and both O_2 and H_2 (or C_2H_5OH) would have been consumed, if "free" OH radicals were available in solution for reaction. Thus, it can be certain that without any ionic catalyst in water (see later), the initial step of H_2O_2 decomposition in high purity water was not a simple bond-breaking process

$$H_2O_2 \longrightarrow 2 \, OH$$
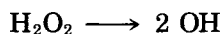
as those observed in photo decomposition [25,26] or decomposition in the vapor phase [13,14]. This conclusion is supported by the fact that the activation energy (15 kcal/mol) is much lower than the bond dissociation energy (48 kcal/mol). The charge transfer mechanism on the surface is more likely and also consistent with the fact that H_2O_2 enhances the electrochemical potentials (ECP) of stainless steel [27].

Effects of Chemical Impurities

To assure the kinetic data obtained in the present study was not influenced by trace impurities in the system, a number of common laboratory chemicals, NaCl, Na_2SO_4, NaOH, H_2SO_4, and $CuSO_4$ were tested as additives in H_2O_2 decomposition measurements in Teflon tubing. The concentrations of additives were not measured, but their concentrations were monitored in the loop water by controlling the water conductivity at 0.5 $\mu S/cm$ in each case. The rate constants determined in those measurements are within the range that observed in high purity water (conductivity ≤ 0.1 $\mu S/cm$). There was no apparent effect on the H_2O_2 decomposition in water by the nonmetallic ions at a level which is comparable to that generally observed near the maximum impurity level in the BWR coolant.

It has been reported by Rebensdorff and Wikmark [19] that the effects of Fe and Cr ions in water (at 10 ppb level) on the H_2O_2 decomposition were insignificant compared to the heterogeneous catalytic effect on the reaction vessel wall. In the present study the metallic ion concentrations in water were maintained at <1 ppb, thus no homogeneous catalytic effect by metallic impurities in water can be assured.

The effect of Cu^{+2} ions on the H_2O_2 decomposition was found to be more profound. Preliminary results obtained with 5–30 ppb Cu^{+2} ions indicate that the rate constant is approximately proportional to the copper ion concentration in water and the activation energy is approximately 16 kcal/mol in all cases, independent of the copper concentration. Furthermore, the copper ions may be involved in homogeneous catalytic effect on the mechanisms of H_2O_2 decomposition. With 30 ppb Cu ions in water containing

100 ppb H_2, there was clear evidence of O_2 reduction from the decomposition of H_2O_2 and consumption of H_2 in the test. This suggests that portion of H_2O_2 was catalytically decomposed through the OH radicals, and some of these radicals have reacted with H_2 to form water. The experimental data have been documented elsewhere [28], and more details will be published later.

Conclusions

A significant heterogeneous surface catalytic effect of H_2O_2 decomposition in water has been observed. H_2O_2 decomposes about 100 times faster in either stainless steel or titanium tubing than in Teflon tubing. The decomposition of hydrogen peroxide appears to be a first order reaction in all cases. The activation energies were found to vary from ca. 14 to ca. 26 Kcal/mol, compared to the lowest chemical bond dissociation energy of 48 Kcal/mol in H_2O_2.

In addition to the low activation energy, the results of the tests with H_2 and C_2H_5OH suggest that the mechanisms of decomposition do not involve "free" OH radicals, and the charge transfer process on the surface may be the primary step in the decomposition mechanism.

Acknowledgments

Appendix A

Calculations of Mass Transfer Coefficients and Reaction Rate Constants

The rate of a heterogeneous catalyzed reaction is dependent upon both mass transfer and chemical activation processes. The observed rate constant (k_{obs}) is related to the individual rate constants by the equation [29,30]

$$\frac{1}{k_{obs}} = \frac{1}{k_{dif}} + \frac{1}{k_{act}}$$

or

$$k_{obs} = \frac{k_{act} k_{dif}}{k_{act} + k_{dif}}$$

where k_{act} is the rate constant attributed to chemical activation process that would be observed if there were no diffusion restriction on the reaction rate, and k_{dif} is the rate constant for complete diffusion (mass transfer) control. If k_{dif} and k_{act} relate to processes having significantly different activation energies, then there will be a mostly diffusion-controlled reaction ($k_{obs} \approx k_{dif}$) at one end and a mostly activation-controlled reaction ($k_{obs} \approx k_{act}$) at the other end of a wide range of temperature. In the present study of hydrogen peroxide decomposition, it is apparent the mass transfer process is slower and therefore rate-determining at higher temperatures.

The mass transfer coefficient (K) in well-defined flow conditions can be estimated from the following mass transfer correlation [31–33]

$$\text{Sh} = 0.023 \ \text{Re}^{0.8}\text{Sc}^{0.33}$$

where Sh, Re, and Sc are the Sherwood, Reynolds, and Schmidt numbers, respectively, and

$$\text{Sh} = \frac{Kd}{D}$$

$$\text{Re} = \frac{dU}{\nu}$$

$$\text{Sc} = \frac{\nu}{D}$$

where
d = diameter of tubing (reaction chamber)
D = diffusivity of H_2O_2
U = water flow velocity
ν = kinematic viscosity
Thus, the mass transfer coefficient and the mass transfer-controlled reaction rate constant can be calculated by:

$$K = 0.023 \ \text{Re}^{0.8}\text{Sc}^{0.33}\frac{D}{d}$$

and

$$k_{\text{dif}} = K\left(\frac{S}{V}\right)$$

where S/V is the surface to volume ratio in the reaction chamber as defined earlier.

Using the data available in the literature [29,31,33–35] (Table A–1) mass transfer-controlled rate constants are calculated and compared with the rate constants measured in a titanium tubing in Figure A-1. Recognizing the large uncertainties in the data used in calculation, the rate constant calculated at 280°C is in good agreement with the data observed at higher temperatures. It is obvious that at temperatures lower than ca. 200°C the decomposition reaction is mostly activation-controlled, and above ca. 200°C mass transfer process becomes an important factor in determining the overall reaction rate.

TABLE A-1. Data used in mass transfer coefficient calculation.

Parameter	25°C	50°C	100°C	280°C
d (cm)	0.49	0.49	0.49	0.49
U (cm/s)	8.7	8.8	9.0	11.6
S/V (cm^{-1})	8.16	8.16	8.16	8.16
D (cm^2/s)[a,b]	2.5×10^{-5}	3.5×10^{-5}	8.0×10^{-5}	3.5×10^{-4}
ν (cm^2/s)[a]	9×10^{-2}	5.5×10^{-3}	3.0×10^{-3}	1.4×10^{-3}

[a] Data obtained from ref. [29], [31], [33], [34], and [35].
[b] Since no data is available for H_2O_2 diffusivity of O_2 is adopted.
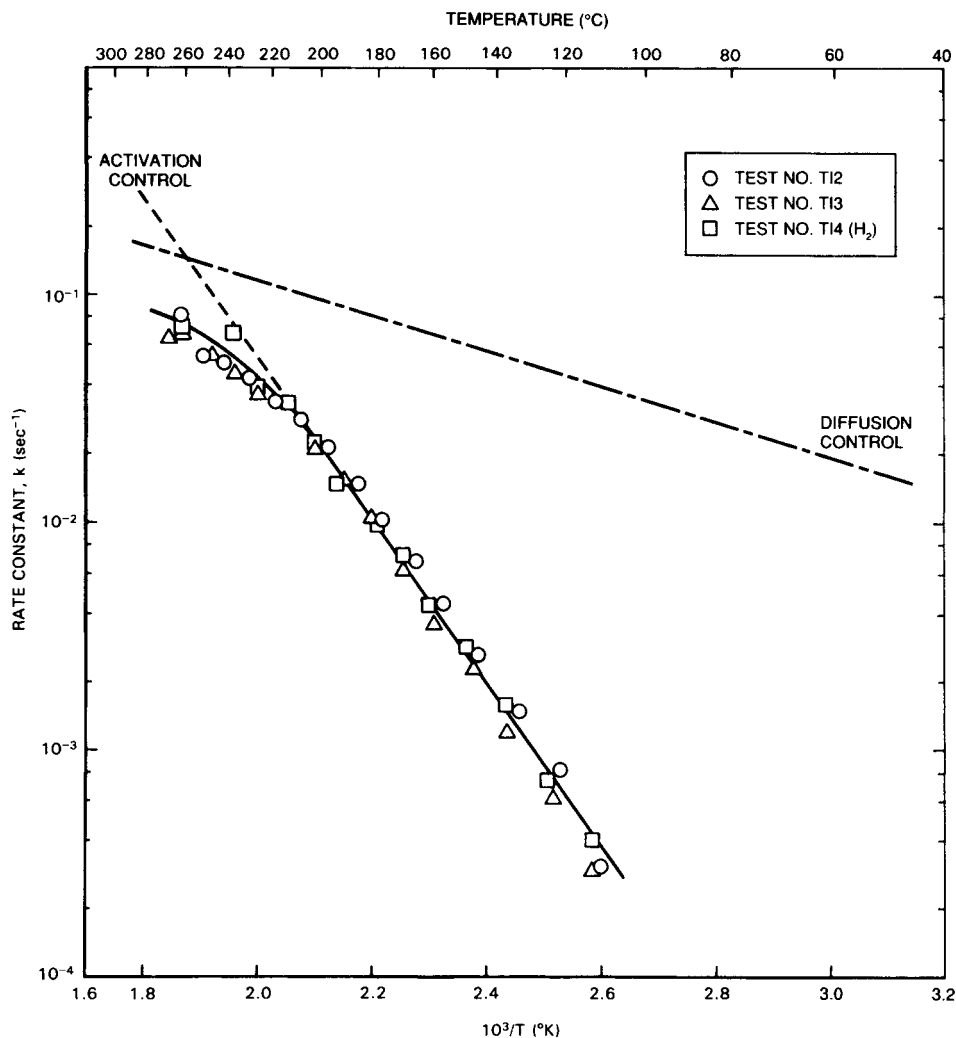
Figure A-1. Comparison of activation-controlled and diffusion-controlled decomposition rate constants as function of temperature.

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