Table V. Gas Law Deviations of Four-Component Mixtures at 60° F. and 1 Atm.

		Mixture	
Component, Mole %		1	2
Methane		67.44	64.14
Ethane		16.37	20.68
Propane		5.30	5.02
Nitrogen		10.89	0.00
Carbon dioxide		0.00	10.16
b_m measured		0.00274	0.00331
b_m calculated[a]	(1)	0.00364	0.00444
	(2)	0.00292	0.00357
	(3)	0.00284	0.00362

[a] b_m calculated from (1) $b_m = \sum x_i b_i$. (2) $b_m = \sum x_i^2 b_i + \sum 2 x_i x_j b_{ij}$. (3) $b_m = [\sum x_i (b_i)^{1/2}]^2$, with pseudo b value 0.0041 for carbon dioxide.

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Supersaturation of Oxygen in Aqueous Hydrogen Peroxide Solutions

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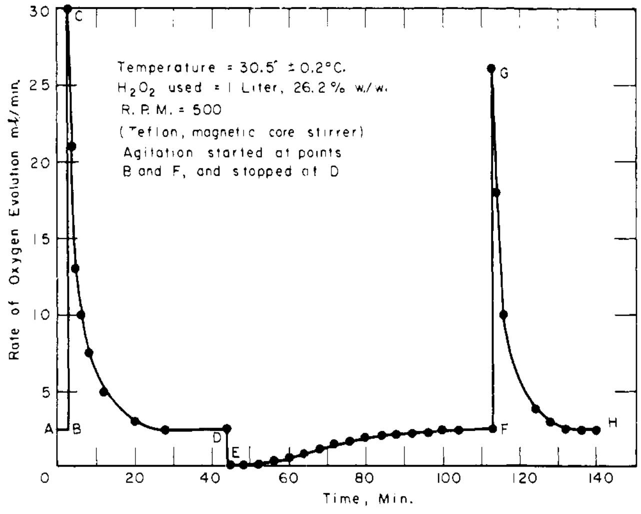
SEVERAL experimental studies on hydrogen peroxide have been misinterpreted because the researcher did not realize that the liquid can become supersaturated with oxygen. For example, recently it was claimed (2) that irradiating a hydrogen peroxide solution with ultraviolet light caused the formation of a higher hydrogen peroxide, H_2O_4, but a subsequent study (*3*) showed that the phenomenon observed was caused by oxygen supersaturation. Supersaturation can be particularly troublesome in stability or kinetic studies, where rates are most easily and commonly observed by measuring the rate of oxygen evolution. A common method of surveillance of hydrogen peroxide stored in tanks is also through the oxygen evolution rate. This report summarizes the results of a quantitative study of the phenomenon (*1, 4, 6*) and provides a guide in planning and interpreting kinetic studies with hydrogen peroxide.

METHODS AND EQUIPMENT

Hydrogen peroxide undergoes a slow decomposition to water and oxygen under all conditions, even when prepared in the highest purity and stored in the most inert containers. If one starts agitating, as with a continuous stirrer, a solution which previously has been quiescent, the rate of oxygen evolution rises suddenly and then gradually drops until it returns to the original rate which represents the true H_2O_2 decomposition rate (*BCD* or *FGH*, Figure 1). If agitation is stopped, the oxygen evolution rate drops and then slowly rises to the steady-state rate (*DEF*). The area under the curve *BCD* or *FGH* above a horizontal line through *A*, *B*, *D*, *F*, and *H* represents the amount of oxygen supersaturated in the solution. (The area *DEF* below the horizontal line is another measure of the amount of supersaturation, but since a longer time is required to reach steady state after cessation of agitation, this is a less accurate method of measurement.) In ordinary laboratory glass apparatus, agitation by conventional stirrers at rotation rates of a few hundred revolutions per minute or more completely desupersaturates a hydrogen peroxide solution. Although more vigorous agitation increases the height of the curve and its steepness, the area under the curve remains the same. The oxygen supersaturation here differs from the usual gas supersaturation phenomenon in that the amount of supersaturation is essentially independent of time, being



↑ Figure 1. Desupersaturation and supersaturation phenomena in hydrogen peroxide

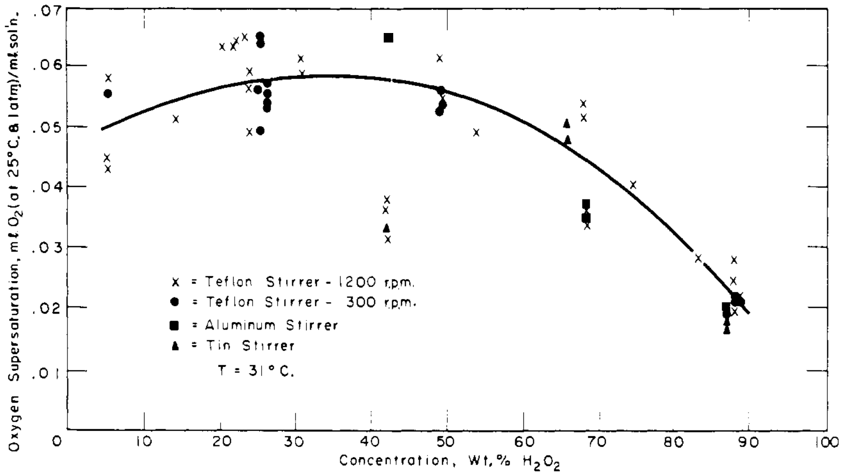


Figure 2. Oxygen supersaturation in aqueous hydrogen peroxide solution ⟶

the result of a steady-state balance between the rate of formation of oxygen by H_2O_2 decomposition and the rate of its release from solution.

Experimentally, a hydrogen peroxide solution was placed in a carefully cleaned borosilicate glass flask held in a constant temperature bath. For most studies 750 ml. of solution was used, in a 1-liter container. After the oxygen evolution rate had become constant and it was certain that the contents had reached steady state, the liquid was continuously agitated and the amount of supersaturation determined as described above. In one group of studies (*6*) the solution was agitated by rotating a 2⅛ × 0.72 inch cylinder suspended by a ¼-inch stainless steel rod coated with Teflon. A cylinder was chosen as a means of agitation in conjunction with a kinetic study that involved rotation of cylinders of catalysts in a H_2O_2 bath. In this system, a change in rotation rate between 300 and 1200 r.p.m. increased the amount of oxygen released by no more than 5%. In a second group of studies, the liquid was agitated by a Teflon-coated magnetic stirrer.

RESULTS

Figure 2 summarizes studies at 30° C. showing the amount of oxygen supersaturation as a function of H_2O_2 concentration, using the rotating cylinder method with cylinders of aluminum, Teflon, and tin (*6*). The data scatter somewhat, reflecting the fact that this is an unstable phenomenon, but show a definite decrease in the amount of oxygen supersaturation at H_2O_2 concentrations above about 50 weight %. The first preliminary set of studies, made with a magnetic Teflon-coated stirrer (*4*), showed about the same results, but with more scattered points and slightly higher degree of supersaturation at concentrations below 30 weight %.

For a H_2O_2 concentration of 35 weight % the amount of supersaturation increases with temperature, over the range of 0° to 30° C. and then seems to level off at temperatures up to 50° C. Typical data on a 35 weight % H_2O_2 solution using a Teflon-coated magnetic stirrer at 500 r.p.m. for agitation are (*1*):

Temp., ° C.	O_2 Supersatn.[a]	Estd. Supersatn. Ratio
0	0.030	1.5
15	0.037	2.0
30	0.058	3.1
50	0.055	3.4

[a] Mean values, ml. O_2 at 25° C. and 1 atm. per ml. soln.

The lowered oxygen supersaturation at low temperatures is readily demonstrated by allowing, for example, a 35 weight % H_2O_2 solution to come to quiescent steady state at room temperature. A temporary increased rate of bubble evolution is noticed as the bath temperature is lowered. For a given degree of agitation, the rate of desupersaturation increases with temperature. A solution at 0° C., while holding less oxygen, requires more time to desupersaturate than one at 50° C.

Since the rate of evolution of oxygen from solution centers around a nucleation phenomenon, one might expect the amount of oxygen supersaturation to be profoundly affected by the nature and amount of surface present. In fact, the amount of oxygen supersaturation was not significantly different in vessels equipped with aluminum, tin, and Teflon cylinders as stirrers. However, any difference might have been obscured by the fact that the stirrer area was a small fraction of that of the borosilicate glass vessel. Nevertheless, the aluminum stirrer desupersaturated the solution in about ⅒ of the time required by the Teflon stirrer and the tin stirrer in about half the time required with the Teflon surface. Moderate differences were also observed between two borosilicate glass flasks. In the studies on effect of temperature, hydrogen peroxide contained in one borosilicate glass flask consistently showed oxygen supersaturation about 20% higher than that in a second flask of the same geometry. The effect was caused by the flask surface and not the H_2O_2, as shown by studies with different batches of H_2O_2.

DISCUSSION

The usual case of gas supersaturation in a liquid comes about by a sudden or rapid decrease of pressure and the focus of attention is particularly on the subsequent rate of change of gas evolution with time and the effects of various nucleating agents upon the rate process. Here we are dealing instead with a steady-state phenomenon; the amount of oxygen supersaturation is essentially constant with time and is determined by a balance between the rate of release of oxygen into solution by H_2O_2 decomposition and the rate of oxygen evolution by bubble formation and growth.

The behavior of nucleating agents is more complex than in the usual case, in that most of them accelerate not only bubble formation but also oxygen formation by hydrogen peroxide decomposition. This decomposition occurs on the walls of the containing vessel, on finely dispersed catalytic impurities suspended in the liquid, and by homogeneous catalytic processes. (Homogeneous uncatalyzed thermal decomposition of the pure liquid appears to be negligible.) The first two sources of oxygen formation by decomposition also can be nucleating agents for oxygen bubble evolution. Moreover, the amount of supersaturation is presumably also affected by the rate at which supersaturated oxygen can diffuse into gas bubbles, which are always present. The rate of this mass transfer process is a function of the degree of agitation and the extent of oxygen-liquid interphase. The latter in turn is dependent upon rate of decomposition and vessel geometry. It is apparent that the steady-state level of oxygen supersaturation here reflects the complex interaction of a substantial number and variety of rate processes.

The formation of a bubble involves overcoming the secondary valence forces holding the molecules of liquid together or those holding the liquid to a surface. The free energy of cohesion of a highly polar liquid is greater than that of adhesion to most solid surfaces, but, more important, the usual solid is not completely uniform at the molecular scale, and a bubble will commence to form at those points at which adherence is particularly weak. The ease of formation of a gas bubble at a solid-liquid interface depends upon the interfacial tension. Gases supersaturated in water are released most rapidly in the presence of oily or other solid surfaces which are relatively nonwetted by water. Hydrogen peroxide readily supersaturates because, first, it must be manufactured in extremely high purity in order to minimize subsequent decomposition in storage and, secondly, because of the oxidizing and reactive characteristics of hydrogen peroxide itself. Organic impurities will be readily oxidized and removed. Small amounts of inorganic impurities on vessel walls tend to become leached out into the H_2O_2 solution, frequently being converted into a soluble and less active form.

Several studies were made of the net effects of surfaces on the amount of oxygen supersaturation. Any colloidal suspension in the H_2O_2 apparently substantially reduces the amount of oxygen supersaturation, whether it is catalytically active or inert. For example, addition of 112 p.p.m. of Sn^{+2} as $SnCl_2 \cdot 2H_2O$ to a 26 weight % solution formed a flocculent white precipitate, presumably of a hydrated stannous oxide or oxychloride. Although such a precipitate is innocuous in causing H_2O_2 decomposition and even acts as a stabilizer by adsorption of traces of heavy metals, this addition lowered the oxygen supersaturation to about one half of its normal value. Addition of iron, as $FeSO_4$, which forms a ferric hydroxide that is an active catalyst, caused a drop in oxygen supersaturation from 0.055 ml. per ml. of solution initially to 0.042 with 0.23 p.p.m. of Fe^{+3}, 0.030 with 2.1 p.p.m., 0.018 with 10.4 p.p.m., and 0.017 with 13 p.p.m. Here the increase in oxygen-liquid interphase from the increased rate of decomposition presumably eases the rate of mass transport of oxygen from the liquid. To obtain consistent data in such studies, it is necessary to allow solutions to stand for several hours after addition of the iron salt, to allow time for oxidation of the iron and formation of the colloidal dispersion.

When the H_2O_2 solution at 30° C. was irradiated with ultraviolet light (375-watt G.E. photolamp) under conditions to cause a 20- to 30-fold increase in decomposition rate, the amount of oxygen supersaturation increased from 50 to 100% over the entire concentration range above that observed under thermal decomposition conditions alone. This is consistent with the above view of the supersaturation mechanism, since the increase in rate of formation of oxygen by ultraviolet radiation does not provide any increase in nucleating sites for oxygen evolution.

The extent to which a solution is supersaturated is logically represented by the supersaturation ratio, which here would be the activity of oxygen in solution divided by the activity in a saturated solution. No information has been published on the solubility of oxygen in hydrogen peroxide solutions, but one can make an approximation by assuming it equals that in water. The ratios thus calculated are shown in the table for the effect of temperature at 35 weight % concentration. The data in Figure 2 correspond to ratios varying between 2 and 3.5. These ratios are relatively low compared to those that can be maintained in quiescent liquids for substantial periods of time when supersaturation is produced by a sudden decrease in pressure.

The cause of the substantial decrease in oxygen supersaturation at high H_2O_2 concentrations is speculative. The rate of decomposition expressed as milliliters of oxygen per milliliter of solution drops with increased concentration, but not this markedly. Some unpublished studies of a preliminary nature by Shanley (5) indicated a lowering in oxygen solubility as H_2O_2 concentration increased, so it is possible that the supersaturation ratio may not vary significantly with concentration.

Some indication of the significance of oxygen supersaturation in H_2O_2 stability and surveillance tests may be made by calculating the time required for normal H_2O_2 decomposition to form the quantity of oxygen which is supersaturated in the solution under steady-state conditions. This sets a minimum limit on the time required for a steady-state rate of oxygen evolution to be reached after the H_2O_2 has been agitated, as in transfer between vessels.

Consider a relatively stable solution of 90 weight % H_2O_2 at 50° C. with a decomposition rate of 0.001 % per hour. If the supersaturation level is that from Figure 2, this corresponds to the oxygen released in about 5 hours. Thus the custom in 50° C. stability tests of allowing the sample to stand overnight in the constant temperature bath before measuring the gas evolution rate ensures that true steady-state conditions have been achieved. On the other hand, a typically stable 50 weight % solution at 30° C. might show a decomposition rate of about 0.0001 % per hour or less. If its supersaturation level is again that from Figure 2, this corresponds to the oxygen released over about a 10-day period. In the case of commercial operations, the amount of oxygen supersaturation may be somewhat reduced below the values of Figure 2, because metal surfaces are probably better nucleating sources than borosilicate glass and also because colloidal suspensions of stabilizers are frequently present, which have been shown to reduce supersaturation. Nevertheless, at normal room temperatures or less, several days may be required for a steady-state oxygen evolution rate to become established after agitation. Any surveillance methods or stability or other kinetic studies based on oxygen evolution should be interpreted with full consideration of oxygen supersaturation phenomena.

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