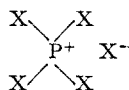


the pentachloride. The exchange proceeds through this equilibrium and if the bonds are not equivalent one might expect in an extreme case to have complete exchange of two halide atoms and none on the other three, or one might expect the two halide atoms to exchange at different rates from the other three. However, if the exchange is rapid and complete, the five halide atoms are probably equally reactive. There is still the possibility that the halide atoms are exchanging at different rates which are too fast to measure. The observation of a rapid exchange would be in harmony with Pauling's interpretation of the PX_5 structure for if there are five resonating forms where the four covalent bonds resonate among the five positions, making all bonds in the molecules equivalent in bond type



one would expect the exchange to be very rapid, in fact, too rapid to be measured by ordinary means. The present measurements indicate that the exchanges between radiochlorine and the phosphorus tri- and pentachlorides and between

radiobromine and phosphorus tribromide are rapid and complete in less than three minutes, and hence it may be concluded that in carbon tetrachloride solution when PX_3 reacts with X_2 the two new bonds formed probably do not differ in reactivity from the other three.

Acknowledgment.—The apparatus used in this research was built with the aid of a grant from the Research Corporation. One of us (W. K.) is indebted to the Charles A. Coffin Foundation of the General Electric Company for a fellowship.

Summary

Exchanges between radiobromine and phosphorus tribromide, between radiochlorine and phosphorus trichloride and between radiochlorine and phosphorus pentachloride have been studied in carbon tetrachloride solution. All of the exchanges studied were found to be rapid and complete in less than three minutes, and the conclusion was drawn that five halide atoms in phosphorus pentachloride and pentabromide are probably all equally reactive.

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Reactions Involving Oxygen, Amalgams and Hydrogen Peroxide

BY HERMAN A. LIEBHAFSKY

As in many analogous cases, hydrogen peroxide is formed from molecular oxygen when base-metal amalgams are shaken with acid solutions in contact with air. The hydrogen peroxide thus formed can be reduced to water by these amalgams; and the possibility of this reaction warrants the belief that *steady states* ought to be established, in which hydrogen peroxide disappears as rapidly as it is formed—thus remaining at constant concentration, while oxygen and the base metal are consumed. Reaction systems of this kind have been investigated briefly as a natural sequel to recent studies of the reactivities of amalgams¹; the results, though admittedly incomplete, are presented here as an invitation to further investigation.

In all oxygen experiments, approximately 25 cc. of amalgam was shaken with 40 or 50 cc. of 1

N sulfuric or perchloric acid in contact with air. Amalgam concentrations were calculated from measured electromotive forces. Hydrogen peroxide was determined spectrophotometrically as peroxytitanic acid. When necessary, the separatory funnel was opened to the air at suitable intervals to replenish the oxygen consumed.²

Stoichiometry.—A few experiments in stoichiometry were carried out by way of orientation: 0.001% amalgams were shaken to exhaustion, whereupon the hydrogen peroxide formed was determined. The ratio of the metal consumed to hydrogen peroxide produced (both expressed in equivalents) could then be calculated, for the metal initially present in the amalgam was known. When this ratio is unity, stoichiometric reduction of oxygen to hydrogen peroxide has evidently occurred; the more this ratio exceeds unity, the greater the proportion of oxygen that has been

(1) (a) Liebhafsky, *THIS JOURNAL*, **59**, 452 (1937); (b) Liebhafsky and Winslow, *ibid.*, **63**, 3137 (1941).

(2) For complete experimental details, see refs. 1a and 1b.

reduced to water. Similar experiments with 0.1% amalgams were carried to exhaustion only in the case of thallium. Thallium amalgams react so rapidly that experiments at 0.001% were not possible; copper amalgam had to be omitted from the 0.1% group because copper is not so soluble in mercury at room temperature. The results are given in Table I.

TABLE I
STOICHIOMETRY OF THE REACTIONS

1. 0.001% amalgams run to exhaustion

| Amalgam | Cu | Cd | Pb | Zn |
|---|------|-----|-----|-----|
| Metal oxidized / H ₂ O ₂ produced (equivalents) / (equivalents) | 0.95 | 7.6 | 5.0 | 5.0 |

2. Amalgams initially 0.1%

| Amalgam | Tl | Cd | Pb | Zn |
|---|-----|-------|-------|------|
| Final concentration (wt.%) | nil | 0.066 | 0.020 | 0.08 |
| Metal oxidized / H ₂ O ₂ produced (equivalents) / (equivalents) | 60 | 40 | 23 | 1000 |

The stoichiometric reduction of oxygen to hydrogen peroxide could be proved only for copper. In the other cases, the greater the amount of metal oxidized, the greater the ratio in Table I. The greater this ratio, the nearer the approach to a steady state (where the ratio would tend toward infinity). Table I shows that the tendency to approach a steady state is least for copper (the noblest) and probably greatest for zinc (the basest solute metal investigated).

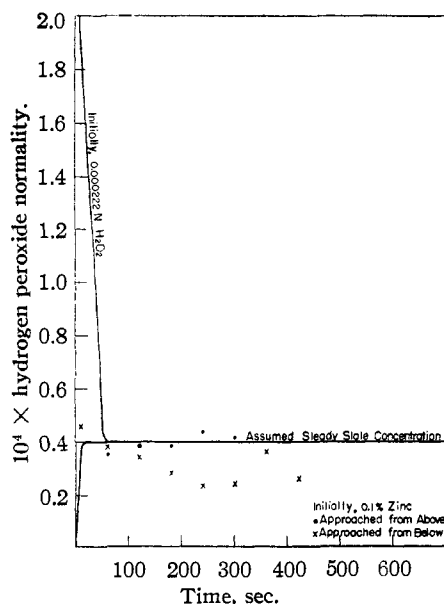


Fig. 1.—Approach to the steady state with zinc amalgam.

Approaching the Steady State.—Attempts to approach the steady state from hydrogen per-

oxide concentration zero (“from below”) and from hydrogen peroxide in excess (“from above”) were made with various amalgams, and the results are given in the first four figures. Except for zinc, the attempts to approach the steady state from below were unsuccessful owing usually to exhaustion, or virtual exhaustion, of the amalgam; the constancy to within the experimental error of the hydrogen peroxide concentration in these cases thus do not mean that a steady state has been reached.

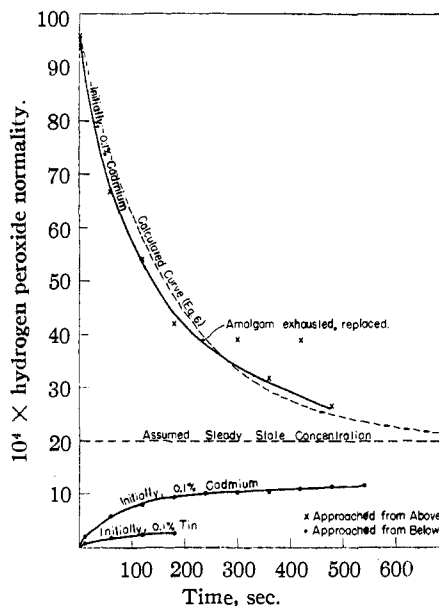


Fig. 2.—Approach to the steady state with cadmium and tin amalgams.

The tin experiment (Fig. 2) showed a decrease to zero of the hydrogen peroxide concentration beyond the last point given; since an increasing white cloudiness was observed at the same time, there is little doubt that oxidation of stannous ion by hydrogen peroxide was occurring. Duplicate experiments are shown for lead amalgam (Fig. 3), along with a third in which hydrogen peroxide was present initially and was twice added later. Only with zinc amalgam was the steady state approached from above; the steady state concentration (near $4 \times 10^{-5} N$) of hydrogen peroxide was very small and could not be accurately established.³

The first four figures give no clear indication that the rates of the reactions are affected by decreases in the amalgam concentrations, which is in accord with the results of the earlier investiga-

(3) The value $6(10^{-4})N$ given in ref. 1a on p. 456 for this steady-state concentration could not be reproduced in several attempts, all of which gave results near $4(10^{-4})N$; the higher value must be in error.

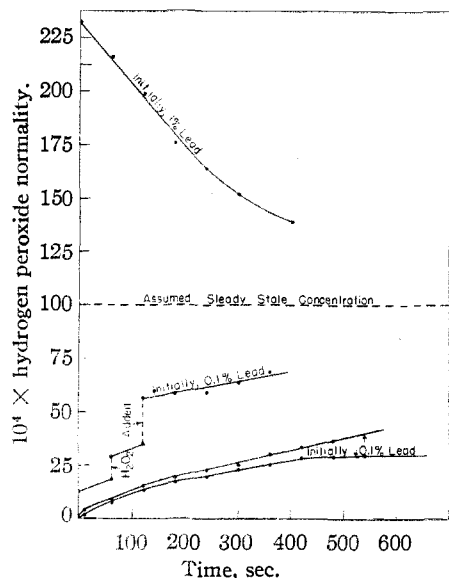


Fig. 3.—Approach to the steady state with lead amalgam. ^{1a,b} Especially is this true of Fig. 4, which shows that three lots of 0.1% thallium amalgam were exhausted in the attempt to reach the steady state from above. The decrease in peroxide concentration proceeds smoothly until the amalgam is completely exhausted, when the decrease abruptly ceases; when the exhausted amalgam is replaced by fresh, the curve does not become noticeably steeper. In other words, the rates of the reactions involved are virtually independent of the amalgam concentrations. The horizontal lines in the first four figures are assumed values,

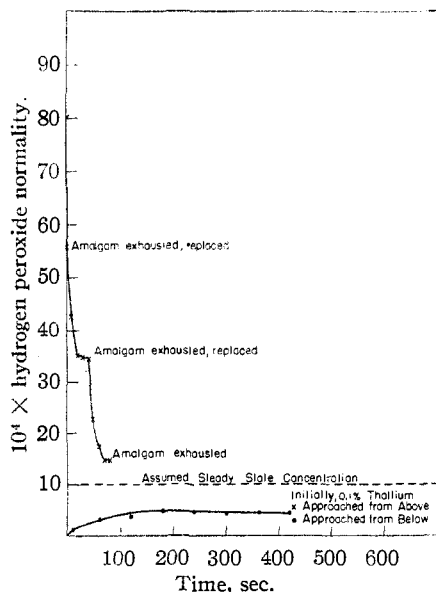


Fig. 4.—Approach to the steady state with thallium amalgam.

which should be approximately correct, for the steady state hydrogen peroxide concentrations.

Hydrogen Peroxide Experiments.—In the work so far reported, the reaction mixtures were always in contact with air so that dissolved oxygen at some concentration near $9 \times 10^{-4} N$ was always present. But a complete understanding of these reaction systems presupposes a knowledge of the reduction of hydrogen peroxide by the amalgams—reactions simplest to investigate when hydrogen peroxide is the only oxidizing agent present. Oxygen was accordingly removed from solutions of hydrogen peroxide in N sulfuric or perchloric acid by bubbling hydrogen through them; and 50 cc. of such a solution was shaken in the standard way with 25 cc. of amalgam, a hydrogen atmosphere being maintained. Peroxide determinations on small samples withdrawn at suitable intervals gave the data for the semi-logarithmic plots conventional for first-order reactions (Fig. 5). The reactions are evidently first order with respect to the hydrogen peroxide concentration, and virtually independent of the concentration of the amalgam. As in Fig. 4, reaction ceased without previous warning when thallium amalgam was exhausted; the lead in a 0.1% amalgam was completely consumed without causing a noticeable departure from linearity. The values of the specific rates (k_s 's) calculated from the slopes of the lines are given in Fig. 5.

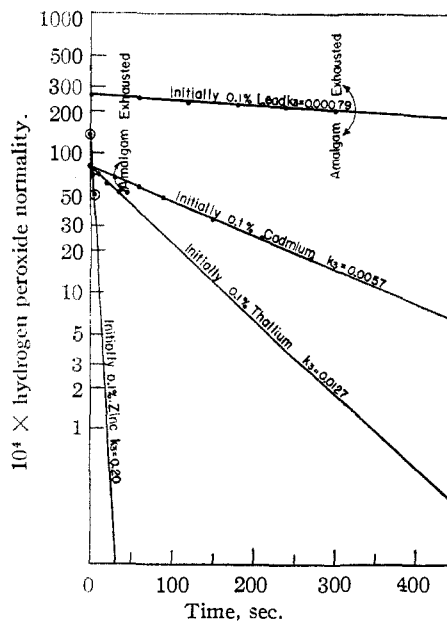
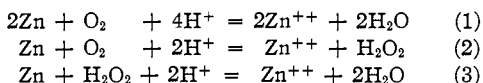


Fig. 5.—Rate of reduction of hydrogen peroxide by various amalgams.

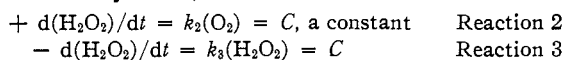
0.05 k_3 gives the rate in equivalents/sec. at which hydrogen peroxide is consumed when N peroxide (50 cc.) is used in the standard experiment; equivalents of metal are removed at the same rate from the 25 cc. of amalgam. The k_3 's are thus analogous to the equivalent rates of Fig. 1, Ref. 1b, to which Fig. 6 is analogous in turn. It appears that a relationship between rate and electrode potential of the type deduced for oxygen is valid also for hydrogen peroxide; but the rate changes much more rapidly with the potential for the latter oxidizing agent.

Mechanism.—Any discussion of mechanism is necessarily preliminary and should in consequence be brief. Three types of reactions that must be considered will be written for zinc amalgam



(With copper amalgam, reaction 3 has not been demonstrated. With tin amalgam, reactions enter that involve stannous ion; thallium, cadmium and lead are like zinc in that only the three foregoing reactions are important. Reaction 1 is evidently the sum of the other two.)

The rate laws that should govern reactions 2 and 3 at a steady state will now be written. The rate of reaction 2 is known^{1a,b} to be virtually independent of amalgam concentration and of acidity, and first order with respect to the pressure of oxygen, which is constant in the present experiments. The rate of reaction 3 is also virtually independent of amalgam concentration, is first order with respect to the concentration of hydrogen peroxide (Fig. 5), and presumably independent of the acidity. (Since we are concerned only with 1 N acid solution, the latter point is unimportant.) At the steady state, we should have



Let a represent the steady state concentration of hydrogen peroxide, and x its concentration at a distance from the steady state. When the steady state is approached from below

$$\begin{aligned} dx/dt &= C - k_3x = k_3(a - x) & \text{(Differential form)} & (4) \\ \ln[a/(a - x)] &= k_3t & \text{(Integral form)} & (5) \end{aligned}$$

These equations are formally identical with those governing the rates of first-order reactions. The reasonableness of the proposed mechanism will now be tested by comparing x as calculated from the integral equation for ten and sixty seconds with the corresponding experimental values; this

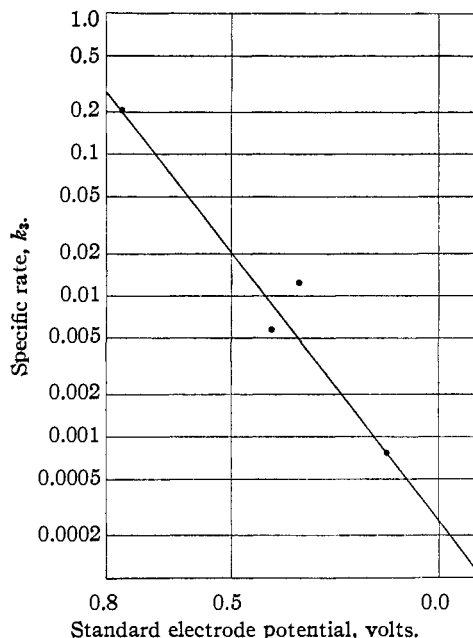


Fig. 6.—Correlation between k_3 and the standard electrode potential.

comparison (Table II) constitutes a real test of mechanism since it replaces $k_2(\text{O}_2)$, the rate at which hydrogen peroxide is produced beginning at $t = 0$, by k_3a , the rate at which it is consumed at the steady state.

TABLE II
THE APPROACH TO THE STEADY STATE

| Amalgam | Zinc | Thal- lium | Cad- mium | Lead |
|--------------------------------------|-------------------|---------------|--------------|------------------|
| $(10^4)k_3$ (Fig. 5) | 2000 | 127 | 57 | 7.9 |
| $(10^4)a$ (Figs. 1-4) | 0.4 ^a | 10 | 20 | 100 |
| $(10^4) x_{\text{calcd.}}$ (10 sec.) | 0.35 ^a | 1.2 | 1.1 | 0.8 |
| $(10^4) x_{\text{measd.}}$ (10 sec.) | 0.40 ^a | 1.2 | 1.7 | 2.0 ^b |
| $(10^4) x_{\text{calcd.}}$ (60 sec.) | 0.4 ^a | 5.3 | 5.8 | 4.6 |
| $(10^4) x_{\text{measd.}}$ (60 sec.) | 0.4 ^a | 3.1 | 3.2 | 8.0 ^b |

^a All hydrogen peroxide concentrations are normalities.
^b Value from lower curve, Fig. 3.

The comparison of calculated with measured x values shows that the proposed mechanism is reasonable, but much more precise measurement will be required to prove it.

A similar test of mechanism, which has already been applied in Fig. 2 for the approach to the steady state from above, leads to about the same conclusion. With an initial hydrogen peroxide concentration b , the integration of Eq. 4 between the limits $x = b$ at $t = 0$, and $x = x$ at $t = t$ gives

$$\ln [(b - a)/(x - a)] = k_3t \quad (6)$$

The broken curve in Fig. 2 was calculated from Eq. 6 and the values $b = 96(10^{-4})N$ (Fig. 2), $a = 20(10^{-4})N$ (Fig. 2), and $k_3 = 5.7(10^{-3})$ (Fig. 5).

The agreement in Fig. 2 between the curve and the experimental points is moderately satisfactory. No independent value of k_3 for 1% lead amalgam is available for the calculation of a similar curve for Fig. 3. Instead, the upper experimental points in this figure have been used to calculate k_3 , giving $k_3 = 1.4(10^{-3})$, which is almost double the Fig. 5 value for 0.1% lead amalgam. In the case of zinc amalgams also,^{1a} it was observed that the rate of oxidation increased slightly with the concentration of the amalgam.

An important question, which the foregoing experimental evidence helps to answer, is whether hydrogen peroxide necessarily is intermediate in the oxidation of metals by molecular oxygen—whether, in other words, a hydrogen peroxide molecule escapes into the solution for each oxygen molecule entering into reactions like Eq. 1. In such event, k_1/k_2 will be unity provided moles of oxygen consumed in unit time are being considered; but if some oxygen molecules capture four electrons each so that water is formed, the ratio will be greater than unity. Table III gives calculated values of these ratios; k_1 is obtained from data in ref. 1b in the manner shown beneath the table, and k_2 is the quotient of $C = k_3a$ (a being expressed in moles/liter) by $2.3(10^{-4})M$, the concentration (in the same units) of oxygen in 1 *N* acid in equilibrium with air.

TABLE III
CALCULATED SPECIFIC RATES

| Amalgam | Zinc | Thallium | Cadmium | Lead |
|--------------|-----------------|----------|---------|------|
| $(10^6)k_3a$ | 4 | 6.4 | 5.7 | 4.0 |
| $(10^2)k_2$ | 1.7 | 2.8 | 2.5 | 1.7 |
| $(10^2)k_1$ | 72 ^a | 48 | 35 | 24 |
| k_1/k_2 | 42 | 17 | 14 | 14 |

^a Detailed calculation of k_1 for zinc: from Table I, ref. 1b, on the average in a standard experiment, $3.2(10^{-4})\%$ of zinc disappears per second from 25 cc. (340 g.) of amalgam into 0.05 l. of solution from which an equivalent amount (Reaction 1) of oxygen is removed. This rate corresponds to the removal of $3.2(10^{-4}) \times 3.4/32.7 \times 4 \times 0.05 = 1.66(10^{-4})$ moles/liter/second of dissolved oxygen, 32.7 being the equivalent weight of zinc. $k_1 = 1.66(10^{-4})/2.3(10^{-4}) = 0.72$. The k_1 's are obviously not identical with the "specific rates" of ref. 1b, footnote 9.

Table III indicates that the reduction of oxygen to water occurs more frequently with each of these metals than does the reduction by way of hydrogen peroxide as an intermediate product that leaves the amalgam surface. Furthermore, the values of k_1/k_2 point to the existence for reaction 2 of a relationship between rate and electrode potential like that given in Fig. 1, ref. 1b

for reaction 1. Table I has already shown that the reduction of oxygen to water does not occur with copper amalgam. Since k_1/k_2 thus has its highest value with zinc and its lowest with copper, it may be that the reduction of oxygen to water is the more probable, the baser the metal.

I am grateful to Mr. W. O. Bachli, Schenectady Works Laboratory, General Electric Company, for helping with much of the experimental work reported here.

Conclusion and Summary

The recent work on reactions involving oxygen, amalgams, and hydrogen peroxide is exploratory—not definitive. Before the conclusions reached so far may be considered proved, many and more precise experiments will have to be done. For these experiments, mechanical shaking and more elaborate means of maintaining constant a known concentration of dissolved oxygen are highly desirable. (Variations in this concentration may well be responsible for the scattering in the experimental results of Fig. 1 and the divergence between the two attempts, recorded in Fig. 3, to approach the steady state from below.)

The work done so far may be summarized as follows:

1. Reaction systems composed of oxygen, amalgams and hydrogen peroxide have been explored to discover whether they reach steady states in which oxygen and base metal are consumed while hydrogen peroxide is maintained at a constant concentration.

2. Although such a steady state was actually attained only with zinc amalgam, evidence has been presented that the reaction systems of other base-metal amalgams are essentially similar to that of zinc amalgam.

3. The reduction of hydrogen peroxide by each of four base-metal amalgams has been investigated briefly.

4. Laws have been formulated for the steady state and for the approaches thereto.

5. Experimental evidence indicates that the reduction of molecular oxygen by the baser metals need not involve hydrogen peroxide as an isolable intermediate product; in fact, this reduction to hydrogen peroxide appears to be less probable than the reduction to water. With copper amalgam, however, stoichiometric reduction of oxygen to hydrogen peroxide occurs.