ever, considered concentrated—8 or 10 molar. In contradiction to the behavior of all electrolytes and of sucrose, urea and mannite the apparent molal heat capacities of all these solutes except *n*-propyl alcohol *decrease* with increasing concentration. The highest value in the dilute region and the steepest slope occurs at low temperature. In other words, in almost every case when the temperature is raised, the solute shows a closer approximation to the behavior of an ideal non-electrolyte, where the apparent molal heat capacity is constant.

Acknowledgments.—It is a pleasure to express our thanks to Dr. Rossini and Dr. Bates of the Bureau of Standards for supplying us with the sucrose used in these experiments.

Summary

We have determined the specific heats of solutions of sucrose at 20 and 25° by means of a differential apparatus employing adjustable heaters.

The apparent molal heat capacity of sucrose is not constant, although it increases with concentration considerably less than a uni-univalent strong electrolyte. It is much more nearly a linear function of the first power than of the square root of the concentration. Its change with concentration decreases with rising temperature. Its limiting value at low concentration increases more rapidly with temperature than the same property of most electrolytes. The apparent molal heat capacity can be expressed satisfactorily as a second degree power series in the molality, and values of the apparent and partial molal heat capacities and the specific heats calculated by these equations are tabulated.

A review of other available specific heat data for non-electrolytes shows a general *decrease* of apparent molal heat capacity with concentration. with greater deviations at *low* temperatures.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 27, 1936

[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

The Reactivity of Zinc Amalgams

BY HERMAN A. LIEBHAFSKY

The stability of zinc amalgams, and perhaps of most amalgams, depends in a curious way upon their concentrations. The great inertness of the concentrated (say, 1%) amalgams has been observed by all investigators who have tried to make them react with hydrochloric acid: hydrogen evolution, even when fairly strong acid is employed, does not proceed rapidly with a cold amalgam although the reaction mixture is shaken; this inertness has usually been attributed, in part at least, to the overvoltage of these amalgams for hydrogen gas. On the other hand, dilute (say, 0.001%) amalgams become increasingly unstable as their concentrations decrease, so that the electromotive forces of cells containing these amalgams vary with time and cannot be measured accurately even when the amalgams are in contact with oxygen-free zinc salt solutions.[1] That these two sets of experimental facts constitute a paradox well worth investigating appears to have escaped previous notice.

Accordingly, exploratory experiments were undertaken and the following experimental method was adopted. (1) With oxidizing agents in aqueous solution, approximately 25 cc. of amalgam and 40 cc. of solution were shaken vigorously by hand at a constant rate (240 times a minute) in a 125-cc. separatory funnel. From time to time 3-cc. samples of amalgam were withdrawn into one side of a cell containing a similar portion of the original amalgam as reference electrode in the other. The electromotive force of this concentration cell was then measured, a 1 *M* zinc sulfate–0.05 *M* sulfuric acid solution serving as electrolyte. (The acid was added in order to prevent the formation of an oxidized film on the amalgam surface; concentrations as high as 0.1 *M* have been employed without sensibly disturbing the measurements except in the case of amalgams containing less than about 10^{-4} % zinc, which are so unstable anyhow that an accurate measurement is impossible.) Beyond stirring the amalgams several times during the measurements, which were made as rapidly as possible and without excluding air, no precautions were taken. The electromo-

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[1] (a) Liebhafsky, THIS JOURNAL, **57**, 2657 (1935), recently has correlated and re-interpreted the accurate electromotive force data for zinc amalgams. See also (b) Crenshaw, *J. Phys. Chem.*, **14**, 158 (1910), and the other work cited in Ref. 1a.

tive forces were read to 0.1 mv. although this accuracy was not generally necessary. For reaction times shorter than five seconds, time was estimated from the number of times the separatory funnel was shaken. (These estimates obviously become less accurate as the reaction time decreases; perhaps the maximum inaccuracy approximates ±20%.) (2) For the experiments in Fig. 1 with oxygen as the oxidizing agent, the gas was bubbled at moderate rate through a column, initially 7 cm. high, of the amalgam contained in a test-tube; samples for the electromotive force measurements were withdrawn from its bottom by means of a pipet; the original amalgam again served as reference electrode. Under these experimental conditions the measured electromotive force shows the extent to which the amalgam being oxidized has lost zinc; and the rapidity with which the electromotive force increases with the time of reaction for an amalgam of given concentration measures the reactivity of that amalgam.

TABLE I

DETAILED RESULTS FOR 1 *N* SULFURIC ACID SOLUTIONS NEAR 25°

No.	% Zn (zero time)	Time, *t*, sec.	Millivolts	% Zn (time *t*)	Rate = $10^4 \frac{(\Delta\% \text{ Zn})^c}{\Delta t}$
1a	0.001	1	4.0	0.000735	2.7
1b	.001	2	9.5	.000480	2.6
1c	.001	3	17.7	.000255	2.3
1d	.001	4	123	.....	2.6
1e	.001	5	1183	.....	...
2	.001	1.3	6.3	.000615	3.0
3	.001	2.5	20.1	.000212	3.4
4	.001	4.2	180	.....	(1.2)[a]
5	.001	5	1180	.....	...
8	.005	5	8.0	.0027	4.6
9	.005	10	17.0	.0013	2.8
10a	.01	5	1.7	.0088	2.4
10b	.01	10	5.1	.0068	4.0
10c	.01	15	8.6	.0051	3.4
10d	.01	20	11.9	.0040	2.2
10e	.01	30	35.8	.00063	3.4
10f	.01	40	1128	.....	(0.6)[a]
11	.01	5	5.1	.0068	6.4
12	.1	10	0.2	.0984	1.6
13	.1	30	1.6	.0883	5.0
14	1.0	10	0.0	1.0	...
15	1.0	50	1.4	0.898	20[b]

[a] Exhaustion of the zinc made a higher rate impossible. [b] This high value is probably inaccurate; the least reliable rates are those calculated from the smallest electromotive forces. When 1% amalgam was shaken for 100 sec. with 1 *N* sodium hydroxide, the average rate in the above units was $6(10^{-4})$. [c] This rate is the decrease per second in the percentage of zinc in 25 cc. of amalgam, calculated independently for each "short interval," Δt.

Figure 1 shows some of the experimental results obtained with amalgams containing 1.0 and 0.001% zinc. (Because the ordinate scale for the 1% amalgams is the larger by tenfold, the difference in reactivities is correspondingly larger than the curves alone would appear to indicate.) The oxygen gas curves are not strictly comparable with the others because of the difference in experimental method, which has been mentioned above. The curves for the dilute amalgams terminate near 1100 mv., which (as Crenshaw[1b] has discovered previously) is the electromotive force of a cell like ours when the one half-cell contains pure mercury, the other a zinc amalgam of appreciable concentration. When the electromotive force has reached this value, therefore, the complete removal of zinc from the experimental amalgam has been accomplished.

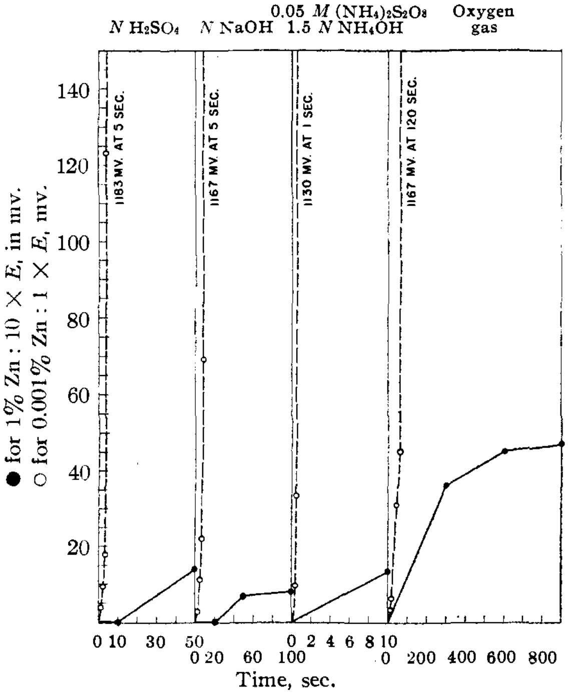

Fig. 1.

Reactivity and Concentration.—All the detailed results for amalgams of intermediate concentrations need not be reported since the curves for these concentrations fall at regular intervals between those of Fig. 1. The most important results for 1 *N* sulfuric acid are given in Table I; the rates are "short interval" values.

The conclusion to be drawn from the last column of Table I is that the rate at which zinc disappears from an amalgam shaken in air with 1 *N* sulfuric acid is virtually independent of the concentration of zinc. This conclusion is supported most strongly by the data for dilute amalgams, where the relative concentration changes are most pronounced; it shows that concentrated zinc amalgams appear to be "inert" because their absolute rate of reaction is proportionately so small as to escape detection. The results with 1 N sodium hydroxide closely parallel those given in Table I, and those with oxygen gas do not differ greatly. The persulfate results are the most unreproducible, because the reaction is so extremely rapid and attended by complications (temperature rise in the reaction mixture, cloudiness, scum formation); but here also the rate increases relatively little with increasing concentration of zinc; 0.001 (representing complete removal), 0.009, 0.006, 0.012%/sec./25 cc. were obtained for 0.001, 0.01 and 1% amalgams, respectively. These exploratory experiments lead to the conclusion that the absolute rate of oxidation of zinc amalgams increases only slightly with the concentration of zinc.

Air as the Oxidizing Agent.—The close parallelism of the results with 1 N sulfuric acid and 1 N sodium hydroxide suggested the investigation of intermediate acid concentrations. This investigation was restricted to the 0.001% amalgams, which were studied by the shaking method already described. The estimated times required at room temperature for the electromotive forces to reach 100 mv. (which represents almost complete removal of the zinc) in these experiments were

Solution	1 N NaOH	1.5 N NH_4OH	0.001 N H_2SO_4
Time, sec.	4[a]	4	6[a]
Solution	0.01 N H_2SO_4	0.1 N H_2SO_4	1 N H_2SO_4
Time, sec.	7	8	4 and 5

[a] Zinc hydroxide precipitated in these experiments.

These data suggest that the principal oxidizing agent for the experiments is neither hydrogen nor hydroxide ion, and probably not water. That this oxidizing agent is the oxygen of the air appears from the following results

Solution	1 N NaOH	H_2O	1 N H_2SO_4
Atmosphere	Hydrogen	Hydrogen	Hydrogen
Time, sec.	60	60	60
E. m. f., mv.	2.5	1.2	0.9
Solution	1 N H_2SO_4	1 N H_2SO_4	None (Dry)
Atmosphere	Air	Oxygen	Oxygen
Time, sec.	4	1	10
E. m. f., mv.	123	108	39

Within the accuracy of the experiments, the rate of oxidation is proportional to the partial pressure of oxygen,[2] and the reaction is less rapid when no solution is present.

Hydrogen Peroxide Formation.—Although the status of hydrogen peroxide as an intermediate step in the reduction of oxygen is so well established as to make specific reference unnecessary, the interesting work of Furman and Murray[3] deserves mention, because the reducing agent in their case was metallic mercury. To prove that hydrogen peroxide was formed also when zinc amalgam was the reducing agent, several experiments were performed with 0.01% zinc amalgam, air and 1 N sulfuric acid; hydrogen peroxide was identified by the formation of peroxytitanic acid and determined iodimetrically. The number of moles of hydrogen peroxide formed in these experiments was about $^1/_{15}$ to $^1/_{20}$ of the number of moles of zinc initially present, pointing either to catalytic decomposition or, more plausibly, to reduction of hydrogen peroxide by zinc. That the latter reaction occurred was proved by shaking 25 cc. of 0.01% amalgam for twenty seconds with 40 cc. of 1 N sulfuric acid containing 0.01 M hydrogen peroxide: here the zinc was completely removed, as compared with half-removal under similar conditions with the peroxide absent. $4.5(10^{-4})$ mole of zinc was oxidized, but only $3.1(10^{-4})$ of $4.0(10^{-4})$ mole of the peroxide was reduced, indicating that oxygen oxidizes some of the zinc even when hydrogen peroxide is present. These results agree with the fact that hydrogen peroxide was found at relatively low concentration when none had been added initially; in other words, hydrogen peroxide is an intermediate step in the reduction of oxygen by zinc amalgams and, under our experimental conditions, is comparable in reactivity with oxygen itself. Comparison with the work of Furman and Murray shows that

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(2) There is a chance that the results in Table I for the 1% amalgam are somewhat low because of a decrease in the partial pressure of oxygen, although the separatory funnel was opened each time a sample was withdrawn. The results with the more dilute amalgams escape this criticism since only 0.13 cc. of oxygen is required to lower the concentration of 25 cc. of amalgam by 0.001% if the oxygen is reduced to hydrogen peroxide, and nearly one hundred times that much oxygen was normally present.

Whether or not significant amounts of hydrogen gas were evolved when oxygen was reduced in the experiments with aqueous solutions is not certain. There is always the remote possibility that the reaction producing hydrogen is accelerated by the reaction between zinc amalgam and oxygen; but in the absence of concrete evidence this possibility will not be considered further. Zinc amalgams that had stood overnight in contact with the 0.05 M sulfuric acid electrolyte solution often showed a bubble of gas (presumably hydrogen) the next morning.

(3) Furman and Murray, THIS JOURNAL, **58**, 429 (1936).

hydrogen peroxide is far more inert than oxygen when mercury alone is the reducing agent. A complete investigation of the kinetics of these reactions must include a measurement of the concentration of hydrogen peroxide under various experimental conditions—at different temperatures, for example.

Temperature Coefficient.—For 0.1% amalgams, the following results were obtained after shaking for 120 sec.

Temperature	Near 0°	Near 30°	Near 55°
E. m. f., mv.	2.0[a]	2.1	2.1

[a] Estimated; actual results: 0.2 mv. at 80 sec.; 2.3 mv. at 160 sec.; 2.6 mv. at 240 sec.

For 0.001% amalgams, the times required at these temperatures to reach an e. m. f. of 100 mv. were estimated from the data for amalgam samples withdrawn after different times of shaking. The results were

Temperature	Near 0°	Near 30°	Near 55°
Time, sec.	6 and 7	5	5

In these measurements, the temperature was not controlled accurately; during the 0° work it rose, and during the 55° work it fell, several degrees. Nevertheless, these data show that the temperature coefficient of the reaction is near unity, and the energy barrier involved must consequently be small—perhaps three or four thousand calories.[4]

Other Oxidizing Agents.—It has been mentioned above that 40 cc. of ammoniacal 0.05 M (or 0.1 N) ammonium persulfate solution oxidized 25 cc. of zinc amalgam at a rate near 0.01%/sec.; Table I shows that the average rate for 40 cc. of 1 N sulfuric acid saturated with air is $3(10^{-4})$%/sec. To a first approximation, both rates are independent of the zinc concentration; with oxygen, the rate was roughly proportional to its partial pressure, hence to its concentration in solution. The concentration of oxygen in 1 N sulfuric acid in equilibrium with air near room temperature is about $2.2(10^{-4})M$,[5] or $9(10^{-4})N$, if the oxygen is reduced to water. The specific rate, assuming this equilibrium to be maintained under our experimental conditions, for the oxidation of zinc amalgams by dissolved oxygen will be taken as $k = 3(10^{-4})\%/\text{sec.}/25 \text{ cc. amalgam}/9(10^{-4}) = 0.3$. The corresponding specific rate for ammoniacal persulfate is $0.01/0.1 = 0.1$. That two such dissimilar oxidizing agents should have virtually identical specific rates, leads to the conclusion that the reaction under investigation is essentially simple.

The results with other oxidizing agents confirm this conclusion. The experiments in Table II were carried out by the experimental method previously described, but 50, not 40, cc. of aqueous solution was usually employed. The specific rates were calculated as in the case of dissolved oxygen; an arithmetical average of the normality of the oxidizing agent was substituted for the normality of the dissolved oxygen. The results indicate that persulfate in acid solution reacts somewhat more rapidly than in ammoniacal; no great significance can be attached to this difference, however, because experimental conditions were not identical. The concentration of zinc ion in the latter solution is presumably much the lower because of the formation of the zinc–ammonia complex ion; perhaps this indicates that the rate of removing zinc ions from the amalgam, like the zinc concentration itself, has no influence on the rate of reaction. In the peroxide and permanganate experiments, a decrease in hydrogen ion concentration accompanies the oxidation of zinc; this circumstance probably complicates the permanganate results, but permanganate reactions are generally so complex anyhow that the point was not investigated further. The small and nearly constant rate observed in the experiments where persulfate and peroxide were completely consumed may be the rate at which hydrogen ion oxidizes zinc amalgam; this oxidizing agent is certainly far less reactive than the others in this group. The copper ion results are complicated by the formation of copper amalgam (the solubility of copper in mercury is about 0.002% at these temperatures).[6] The behavior of zinc amalgams toward these oxidizing agents under our experimental conditions may be summarized as follows. (1) Dissolved oxygen, hydrogen peroxide, persulfate ion, permanganate ion and copper ion oxidize zinc amalgams at about the

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(4) Since the solubility of oxygen in water decreases about 2.5-fold between 0 and 55°, there should be a corresponding decrease of rate with temperature if the heat of activation were zero. No decrease was observed, and the results of the above experiments indicate that the heat of activation is approximately large enough to counteract the decrease in solubility as the temperature is changed. On this basis, the heat of activation is about 3600 cal.

(5) Bohr, *Z. physik. Chem.*, **71**, 47 (1910). His data correspond to $10^3\alpha = 25$ for oxygen in equilibrium with sulfuric acid near 25°. The manner in which these data are cited (under "Air") in "I. C. T.," Vol. III, p. 272 ("Values of cm.^{3} of N_2 and O_2 at S. T. P. dissolved by 1 liter of soln. in equilibrium with the normal dry atmosphere") makes them liable to misinterpretation.

(6) Unpublished results from this Laboratory have confirmed published values of this datum.

same rate. (No great accuracy is claimed although the measurements are fairly reproducible.) (2) Hydrogen ion is comparatively inert, perhaps because of the difficulty of forming monatomic hydrogen.

TABLE II

ZINC AMALGAMS AND VARIOUS OXIDIZING AGENTS NEAR 25°

Time, sec.	% Zn	$10^4 \frac{(\Delta\% \text{ Zn})}{\Delta t}$	(Ox)[a]	k
1. Ammonium Persulfate in 0.1 *N* Sulfuric Acid				
0	0.0135	26	0.020	0.19
2.5	.0071	12	.007	.27
5.0	.0040	8	.002	
7.5	.0021	4	"nil"	
10.0	.0010	3	"nil"	
12.5	.0030	(1)[b]	"nil"	
15.0	"nil"		"nil"	
0	.0135	74	.040	.24
1.25	.0042	33	.021	.20
2.5	.0001	(1)	.012	
3.75	"nil"		.012	
2. Hydrogen Peroxide in Sulfuric Acid Initially 0.1 *N*				
0	0.0135	22	0.020	0.15
2.5	.0080	14	.009	.28
5.0	.0044	8	.001	
7.5	.0025	5	"nil"	
10.0	.0013	4	"nil"	
12.5	.0004	(2)	"nil"	
15.0	"nil"		"nil"	
0	.0135	55	.040	.17
1.25	.0066	38	.026	.18
2.5	.0019	(15)	.016	(.14)
3.75	"nil"		.012	
3. Potassium Permanganate in Sulfuric Acid				
0	0.0135	40	0.020[c]	0.2
2.5	.0036		"nil"	
0	.0135	93	.040[d]	.3
1.25	.0019		.016[e]	
2.5	"nil"			
4. Copper Sulfate in 0.1 *N* Sulfuric Acid				
0	0.0108	140	0.078	0.2
0.25	.0073[f]		.067	

[a] (Ox) denotes the normality of the oxidizing agent. [b] Values in parentheses may be low because of exhaustion of zinc. [c] Sulfuric acid initially 0.1 *N*. [d] Sulfuric acid initially 0.2 *N*. [e] Concentration uncertain because of oxidation of appreciable mercury. [f] This percentage was computed from the decrease, determined colorimetrically, of the copper ion concentration in the 45 cc. of solution employed. It was found that the formation of a zinc–copper amalgam made e. m. f. values unreliable for the computation of the remaining % Zn. The e. m. f. in experiments like these never reached 1100 mv., which is characteristic of pure mercury, but seemed to approach a limit near 70 mv. For the experiment above, the e. m. f. corresponded to 0.0011% zinc at 0.25 sec.

In the experiments with air as oxidizing agent, the final concentration of hydrogen peroxide was near $6(10^{-4})N$. The normality of dissolved oxygen in equilibrium with air is about $9(10^{-4})N$. The specific rate for dissolved oxygen is about 0.3; that for peroxide, about 0.2. These data agree well enough to indicate that the peroxide exists at a steady-state concentration near $6(10^{-4})N$.

The experimental data, crude though they are, permit an interesting calculation bearing on the collision number in aqueous solution. The usual calculation, in which it is assumed that the Arrhenius constant A is identical with or simply related to the collision number Z, applies to collisions within aqueous solutions; one of the underlying assumptions, which is by no means always valid, is that $k = Ae^{-Q/RT}$, where Q is the empirically determined heat of activation. We shall make a similar assumption and attempt to identify A with the number of collisions between the oxidizing agent and the amalgam surface. The calculation will be carried out for dissolved oxygen; since all the oxidizing agents investigated show comparable specific rates, the conclusions presumably are of general application. The concentration of dissolved oxygen is about $2.2(10^{-4})$ M, corresponding to a pressure of $5.5(10^3)$ dynes/sq. cm. How large will be the amalgam surface struck per second by $2.5(10^{-4})$ g. of oxygen (assumed to be unhydrated), which corresponds to removing zinc at the average rate of $3(10^{-4})$%/sec. from 25 cc. of amalgam?

The calculation was carried out according to one equation given by Langmuir[7] and according to another given by Hinshelwood[8] with the identical result: area = 0.0032 sq. cm. The area of contact between the amalgam and aqueous solution at rest was near 15 sq. cm.; during the shaking, it was of course larger—say, 40 sq. cm. The ratio of the actual rate to the kinetic theory rate is therefore 1/12,500; if this factor is equal to $e^{-Q/RT}$, $Q = 5600$ cal., approximately. The agreement between this result and the estimate[4] $Q = 3600$ cal. is good enough to encourage confidence in the calculation; if the assumption $k = Ae^{-Q/RT}$ is valid, the sign of the discrepancy indicates either that the number of collisions is smaller than kinetic theory calls for or that the requirement of minimum energy is not alone mandatory

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(7) Langmuir, *Phys. Rev.*, **2**, 329 (1913).

(8) Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press, Oxford, 1933, p. 4.

for the occurrence of reaction on collision. The agreement indicates further (as do the facts that all oxidizing agents show nearly the same specific rate and that the rate of oxidation increases somewhat with the amalgam concentration) that the reaction does not involve diffusion through a stationary layer near the amalgam–solution interface. (Presumably a zinc amalgam at rest reacts so slowly because diffusion of reactants or resultants through a film near this interface helps limit the rate.)

Mechanism.—Any mechanism for the oxidation of zinc amalgams by oxygen (and, through legitimate inference, by other oxidizing agents) must explain the following facts: (1) the rate of oxidation is limited by the rate at which new amalgam surface is produced, other factors remaining constant; (2) the rate increases only slightly with the concentration of the amalgam; (3) it is proportional to the concentration of the oxidizing agent; (4) it is little affected by temperature changes; (5) when oxygen is reduced, hydrogen peroxide appears as a reactive intermediate compound; (6) a dry amalgam oxidizes less rapidly than one in contact with an aqueous solution.

These results are far simpler than those previously obtained in investigations of similar reactions.[9] They support the idea that we are actually studying the transfer of electrons from the amalgam to the oxidizing agent with all the usual complicating factors of a heterogeneous reaction stripped away. An attempt will now be made to formulate a mechanism describing this process, with the understanding that other mechanisms may prove acceptable provided they explain the experimental results.

The transfer of electrons to oxygen in acid solution may be visualized as follows

$$\text{Rapid equilibrium: Amalgam} \rightleftharpoons \text{Amalgam surface}^{n+} + n\text{ electrons} \quad (1)$$

$$\text{Rate-determining: } O_2 + 2\text{ electrons} + 2H^+ \longrightarrow H_2O_2 \quad (2)$$

$$\text{Rapid follow reaction: Amalgam surface}^{(n+2)+} = \text{Amalgam surface}^{n+} + Zn^{++} \quad (3)$$

When the solution is not acid, it may be necessary to substitute water for hydrogen ion in reaction 2 with corresponding changes in the products. The substitution of hydrogen peroxide or of other oxidizing agents for oxygen presents no difficulty.

This mechanism, which should be applicable to many similar cases, has two necessary features: (1) the electrons transferred in reaction 2 need not originate with the zinc, but are furnished by the entire amalgam. The "electron concentration" at the amalgam surface appears to be nearly independent of the concentration of zinc; this explains why the rate does not increase more rapidly with the concentration and is in accord with the data on the electrical conductivity of zinc amalgams.[10] (2) The base-metal characteristics of zinc are responsible for the readiness with which reaction 3 proceeds. Shaking speeds up the oxidation because it continuously exposes a fresh surface, thus preventing the accumulation of reaction products, and because it provides a fresh supply of reactants. Several reasons suggest themselves for the accelerating effect of water; for example, water might make gaseous oxygen more reactive by activating it or by combining with it. The small energy barrier involved in the oxidation suggests, among other things, that the transfer of electrons to an oxidizing agent requires little or no activation when conditions are favorable.

This mechanism is conservative in that it is no more detailed than the experimental facts appear to warrant. The highly reactive substances H and HO_2, postulated by Furman and Murray, which have long been used in explaining photochemical and chain reactions[11] have not been assumed as intermediate for the following reasons. (1) It has not been proved that the reduction of oxygen by mercury or an amalgam involves a chain reaction (further experimental work bearing on this point would be welcome). (2) The assumption that H exists on a mercury or amalgam surface in contact with an aqueous solution containing an excess of reactive oxidizing agents appears implausible. (3) Intermediate products (like HO_2), to form which oxygen must accept an odd number of electrons, could scarcely have an appreciable life on a zinc amalgam surface, provided no chain or photochemical reaction is occurring. The evidence from many inorganic oxidation reactions in aqueous solutions favors the idea that oxygen is reduced to oxide in two steps (peroxide first and oxide afterward), whenever

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(9) See, for example, Fraenkel, Wengel and Cahn, *Z. anorg. Chem.*, **171**, 82 (1928).

(10) In this connection, *cf.* Schulze, *Z. Metallkunde*, **17**, 170 (1925), where data are given showing that the addition of 1% zinc to mercury increases its electrical conductivity by about 15%.

(11) See, for example, Marshall, (a) *J. Phys. Chem.*, **30**, 34 (1926); (b) THIS JOURNAL, **49**, 276 (1927); (c) Haber and Weiss, *Proc. Roy. Soc.* (London), **147A**, 332 (1934).

this is possible; in each of these steps two electrons are transferred.

There is no reason, *a priori*, why the oxidation of other amalgams—at least of amalgams baser than mercury—should not be closely analogous to the reaction under discussion. Indeed, examination of the literature reveals that the amalgams of cadmium, lead, copper, tin, thallium, sodium, potassium, lithium, calcium and barium[12] all show peculiarities of behavior indicating that their dilute amalgams are much more unstable than the concentrated.

Other Explanations.—Polymerization of zinc amalgams[1a] might serve as a qualitative explanation of the inertness of concentrated zinc amalgams, but it falls so far short of being quantitative that it must be rejected. A preferential accumulation (analogous to a Gibbs adsorption) of zinc in the surface layer of the amalgams so that the surface concentration of a very dilute amalgam is not much smaller than that of one more concentrated is another possible explanation; but it seems quantitatively unsatisfactory and conflicts with the fact that the amalgams obey the Nernst equation quite well in the concentration range $10^{-6} - 2(10^{-3})\%$.[1b] Overvoltage as a possible explanation provides little more than a restatement of the problem. The suggested explanation of Erdy-Grúz and Vázsonyi-Zilahy for the electromotive forces of cells with dilute amalgams involves several implausible features and will be examined elsewhere.

I am indebted to Dr. A. L. Marshall of this Laboratory for many valuable discussions bearing on the foregoing material.

Conclusions and Summary

The reactivity of zinc amalgams toward several oxidizing agents has been studied under experimental conditions that lead to extremely simple results. With violent agitation, the rate of oxidation for a given oxidizing agent appears to be limited mainly by the rate at which a fresh surface can be exposed; when this is constant, the rate of oxidation increases only slightly with the concentration of the amalgam, is proportional to the concentration of oxidizing agent and almost unaffected by a change in temperature. The conclusion has been drawn that the reaction being studied involves the capture of electrons by the oxidizing agent at the amalgam surface, followed by the expulsion of a zinc ion.

Work on other amalgams is required to test the generality of this conclusion. Meanwhile, the experimental facts for zinc amalgams are interesting because they show that concentrated zinc amalgams appear to be inert (although they react somewhat more rapidly than those more dilute) only because the amount of zinc disappearing from them is proportionally small enough to escape detection. Results like these have a number of applications. In the cleaning of mercury, for example, they indicate that the removal by oxidation of a metal like zinc becomes progressively easier as the concentration of zinc decreases, a situation highly unusual in purification processes.

SCHENECTADY, N. Y. RECEIVED JANUARY 6, 1937

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[12] (a) Hulett and DeLury, THIS JOURNAL, **30**, 1805 (1908); (b) Tammann and Hinnüber, *Z. anorg. Chem.*, **160**, 249 (1927); (c) Ambruster and Crenshaw, THIS JOURNAL, **56**, 2525 (1934); (d) Erdy-Grúz and Vázsonyi-Zilahy, *Z. physik. Chem.*, **177**, 292 (1936).