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Original Scientific Paper

Heterogeneous Exchange of Amalgams. II. Hydrogen Ion Concentration Effect on the Zn-Amalgam -Zn⁺⁺(SO₄⁻⁻) Solution Exchange

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The effect of hydrogen ion concentration on the exchange of a Zn-amalgam-Zn⁺⁺(SO₄⁻⁻) solution in both the presence and absence of oxygen has been investigated. The technique of radioactive indicators was used and it was found that in an atmosphere of nitrogen, the exchange rate does not change in the pH 4–6 range. From pH 2–4 the exchange rate is inversely proportional to the hydrogen ion activity. In the presence of oxygen from pH 2–6, zinc from the amalgam dissolves completely. At a partial oxygen pressure of 0.2 atm. at hydrogen ion concentrations ranging from 1×10^{-6} – 2.6×10^{-2} g. ion l.⁻¹ the zinc dissolves by two processes. The principal process due to depolarization takes place by the reaction $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$. At a partial oxygen pressure of 1.0 atm., zinc dissolves by only one process owing to the depolarization of oxygen by the same reaction.

INTRODUCTION

In their studies dealing with the effect of acidity on the solubility of metals dissolved in mercury A. N. Frumkin¹ and L. Hammet and A. Lorch² found that the equilibrium potential does not change during the spontaneous dissolution of amalgams of alkali and alkali earth metals. V. I. Kravsov and I. S. Loginova³ obtained the same results with cadmium amalgam dissolution in acidic solutions. In all the three cases, this is accounted for by the rate of the direct process which is assumed to be higher than that of hydrogen reduction. V. V. Losev and A. I. Molodov⁴ examined the mechanism of indium amalgam dissolution, and V. V. Losev and V. V. Gorodecki⁵ studied the same effect on the amalgam bismuth electrode. By investigating the dissolution of zinc and thallium amalgams I. Mádi^{6,7} found that in the presence of oxygen, the metal from the amalgam dissolved, due to the depolarization of oxygen, and that the velocity of dissolution was unaffected by the kind of acid and its concentration.

The objective of this study was to examine the effect of hydrogen ion concentration on the rate of the heterogeneous exchange of the Zn(Hg)/Zn⁺⁺ system.

The apparatus and experimental procedure was the same as in our previous paper⁸. Specified concentrations of hydrogen ions were obtained by adding different quantities of a 0.05 M solution of sulphuric acid.

RESULTS

Figure 1 shows the dependence of the exchange rate on the concentration of hydrogen ions in a deoxygenated solution. From pH 4—6, the exchange is practically constant for all $n_S = n_L$, ranging from 1×10^{-4} to 1×10^{-3} . From pH 2—4 the exchange rate increases with pH. To obtain a twofold increase in the exchange rate, the pH should increase in the range from 2 to 4 for 1 unit. With an increasing n_S value from 1×10^{-4} to 1×10^{-3} the form of the function does not change.

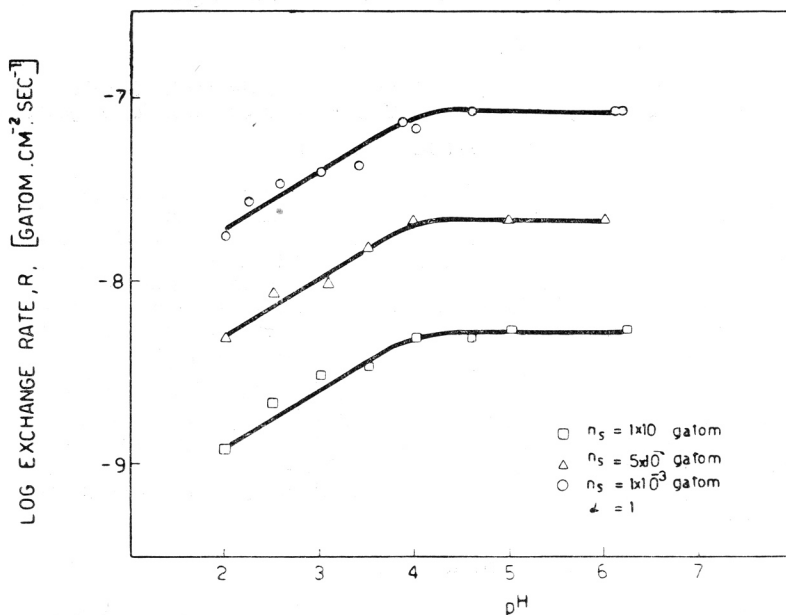


Fig. 1. Exchange rate R against pH plots for $n_S = n_L = 1 \times 10^{-4}$, 5×10^{-4} , and 1×10^{-3} g. atom Zn.

The pH values of the solution prior to and after the exchange are shown in Table I. The increase of pH values can be explained only by the reduction of hydrogen ions with zinc, as the equilibrium potential of the system $Zn(Hg)/Zn^{++}$ is more negative than the equilibrium potential of hydrogen. This reduction of hydrogen ions with zinc does not essentially affect the material balance of the exchange process between the zinc in amalgam and in solution. For example, for pH's varying from 6.29 to 6.65, 2.9×10^{-9} g. of hydrogen ions are reduced and, as a result approximately 1.5×10^{-9} g. atom of zinc dissolved. For a change of pH from 3.00 to 3.16 and from 2.03 to 2.12, 1.5×10^{-6} and 8×10^{-6} g. atom of zinc are dissolved respectively. For the amalgam solution system with $n_S = n_L = 1 \times 10^{-4}$ g. atom, these quantities are too small to be registered.

Figure 2 shows the logarithmic quantity of reduced hydrogen ions as a function of the initial pH in the solution. It can be seen that in the pH range 4—6 this dependence is linear i.e. in the same range in which the exchange rate is also independent of pH. At lower pH values the increase in the reduced

quantity of hydrogen decreased in the same region in which the exchange rate decreased in Fig. 1.

TABLE I
The pH Values and the Quantity of Reduced Hydrogen During Exchange
in the Absence of Oxygen
 $\alpha = 1$

$n_S \cdot 10^4$ g. atom	pH		Deviations from the equivalent quantities*	Quantity of re- duced hydrogen gatom
	initial	final		
1.0	6.29	6.65	-0.02	3.10^{-9}
1.0	5.00	6.78	-0.10	5.10^{-8}
1.0	4.00	4.88	+0.03	8.10^{-7}
1.0	3.00	3.16	+0.02	3.10^{-6}
1.0	2.03	2.12	—	$1.5 \cdot 10^{-5}$
5.0	6.00	6.20	+0.03	$3.5 \cdot 10^{-9}$
5.0	4.97	6.37	+0.10	1.10^{-7}
5.0	3.98	6.44	+0.03	1.10^{-6}
5.0	3.50	3.99	+0.04	$2.1 \cdot 10^{-6}$
5.0	3.07	3.28	-0.05	$3.2 \cdot 10^{-6}$
5.0	2.51	2.71	+0.04	$1.1 \cdot 10^{-5}$
5.0	2.03	2.09	-0.02	$1.2 \cdot 10^{-5}$
10.0	6.12	6.18	-0.08	1.10^{-9}
10.0	4.74	6.24	-0.05	$1.8 \cdot 10^{-7}$
10.0	4.00	6.20	-0.05	1.10^{-6}
10.0	3.40	3.84	-0.08	$2.5 \cdot 10^{-6}$
10.0	2.23	2.35	-0.16	$1.5 \cdot 10^{-5}$
10.0	2.01	2.11	—	$2.3 \cdot 10^{-5}$

* The deviation of the equivalent quantities is the measure for the corrosion of zinc and can be calculated from the total activity of the solution after the exchange is over and the activity of amalgam at the beginning of exchange using $[(a_L)^\infty - (a_S)_0/2] / (a_S)_0/2$. The indexes L and S refer to the solution or amalgam.

Table I contains the initial and final pH values, the quantity of reduced hydrogen and the deviations from the equivalent quantities, which is a measure of the zinc corrosion. Table I shows that for the pH 4—6, the hydrogen ions are reduced until the pH of the solution, after a sufficiently long exchange, approaches a value of 6—7, i.e. becomes practically neutral. However, in solutions which has a pH smaller than 4 at the beginning of the experiment, only a fraction of the hydrogen ions are reduced because the pH of the solution at the end of the exchange is far from a neutral value. It is obvious from Fig. 2 that in the case of total reduction, the amount of reduced hydrogen vs. pH should follow the broken line, and for initial pH values 2 and 3 one gets values of 1×10^{-4} and 1×10^{-5} g. atom of reduced hydrogen respectively. These are equal to the total concentration of hydrogen ion in the 10 ml. aliquots of these solutions.

An investigation into the effect of pH in the same system with $n_S = n_L = 1 \times 10^{-4}$ g. atom of zinc in the presence of oxygen at pressures 0.2 and 1.0 atm. has shown that from pH 2—6.5, zinc from the amalgam phase is completely dissolved.

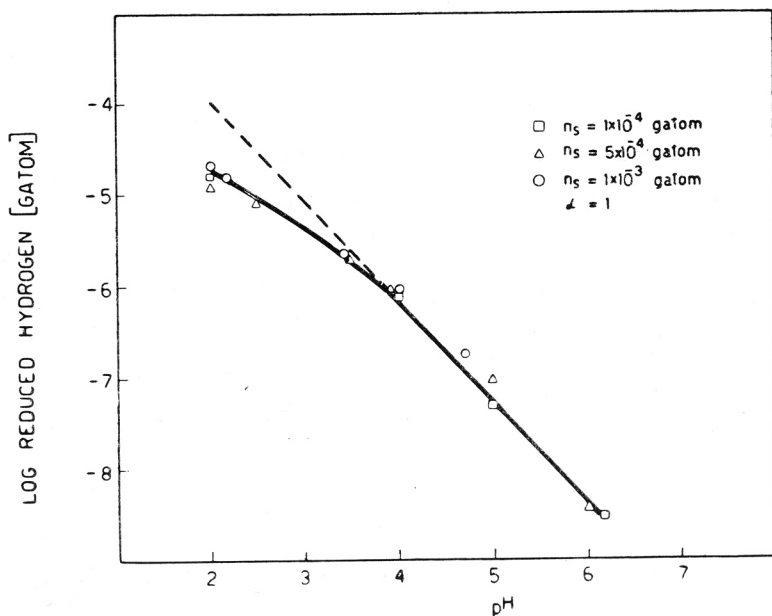


Fig. 2. Reduced hydrogen amount against pH plot for $n_s = n_L = 1 \times 10^{-4}$, 5×10^{-4} and 1×10^{-3} g. atom Zn in the absence of oxygen.

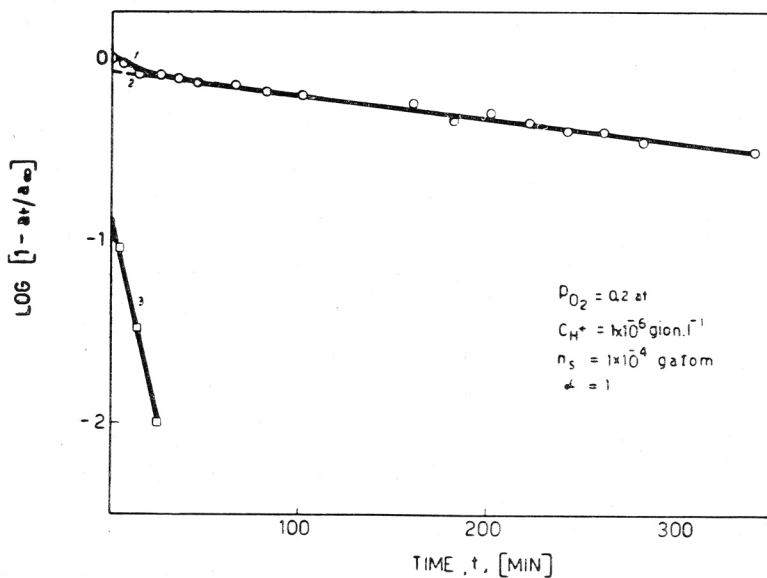


Fig. 3. Fraction of the undissolved Zn from the starting Zn amount calculated as $1 - a/a_\infty$ against time plot; Hydrogen ion concentration 1×10^{-6} g. ion l^{-1} ; $p_{O_2} = 0.2$ atm.; 1. — experimental plot; 2. — extrapolated slow dissolution process; 3. — from 1 and 2 deduced fast dissolution process.

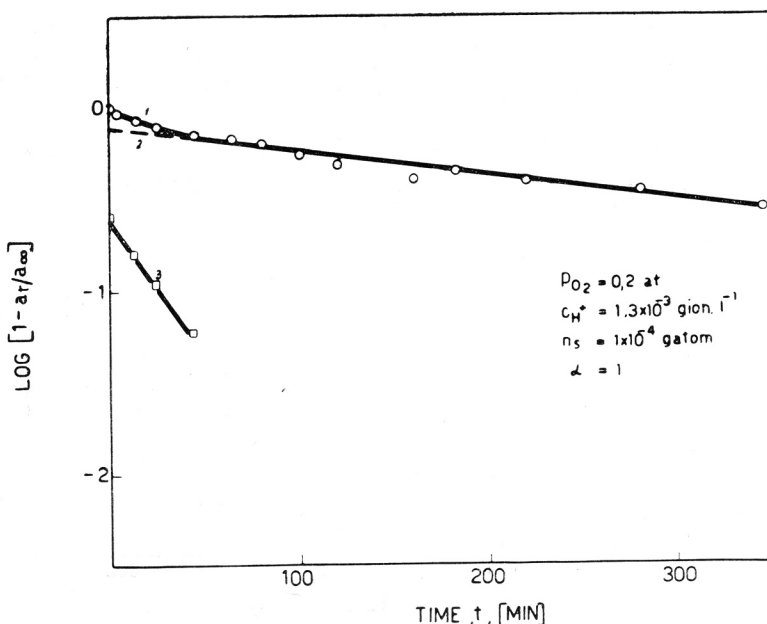


Fig. 4. Fraction of the undissolved Zn from the starting Zn amount calculated as $1 - a_t/a_\infty$ against time plot; Hydrogen ion concentration 1×10^{-6} g. ion l^{-1} ; $p_{O_2} = 0.2$ atm.; 1. — experimental plot; 2. — extrapolated slow dissolution process; 3. — from 1 and 2 deduced fast dissolution process.

The mode in which zinc dissolves depends on both the partial oxygen pressure and on the concentration of hydrogen ion. Figures 3, 4, 5 and 6 show the plots $\log(1 - a_t/a_\infty)$ against t under a partial oxygen pressure of 0.2 atm. in concentrations of hydrogen ions: 1×10^{-6} ; 1.3×10^{-3} ; 1.1×10^{-2} ; and 2.6×10^{-2} g. ion l^{-1} . In this expression, a_t is the radioactivity of the solution due to dissolved zinc at time t , a_∞ the radioactivity of the solution after it becomes practically constant. The dependence of the logarithm of the non-dissolved zinc fraction on time for hydrogen concentrations 1×10^{-6} ; 1.3×10^{-3} and 1.1×10^{-2} g. ion l^{-1} indicates that zinc dissolves in two ways. A graphical resolution of the curves indicates two processes of different velocities of zinc dissolution. The curve for the faster process is obtained from the difference of the nondissolved zinc fraction measured and the fraction derived under the assumption that the slow process takes place at a constant rate from $t = 0$. The dissolution of zinc for a hydrogen ion concentration of 2.6×10^{-2} g. ion l^{-1} takes place by a single process only, as shown in Fig. 6.

Figure 7 shows the same dependence at a partial oxygen pressure of 1.0 atm. From the plots it appears that zinc dissolves at this pressure by a single process, faster than at a partial oxygen pressure of 0.2 atm. In the measured region of 1×10^{-6} to 2.6×10^{-2} g. ion l^{-1} of hydrogen ion the dissolving rate increases to 5.3×10^{-3} g. ion l^{-1} and a further increase in the concentration does not affect the dissolution rate.

Figure 8 shows the quantity of reduced hydrogen as a function of the initial activity of hydrogen ions in the solution at partial oxygen pressures of 0.2 and 1.0 atm. From pH 4—6.5 the curves coincide with the corresponding

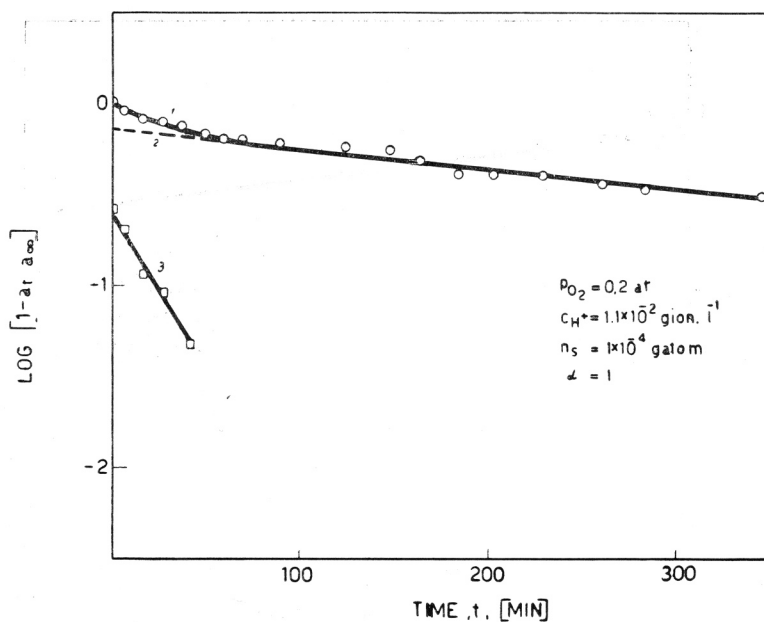


Fig. 5. Fraction of the undissolved Zn from the starting Zn amount calculated as $1-a/a_\infty$ against time plot; Hydrogen ion concentration 1.1×10^{-2} g. ion l^{-1} ; $p_{O_2} = 0.2$ atm.; 1.— experimental plot; 2. — extrapolated slow dissolution process; 3. — from 1 and 2 deduced fast dissolution process.

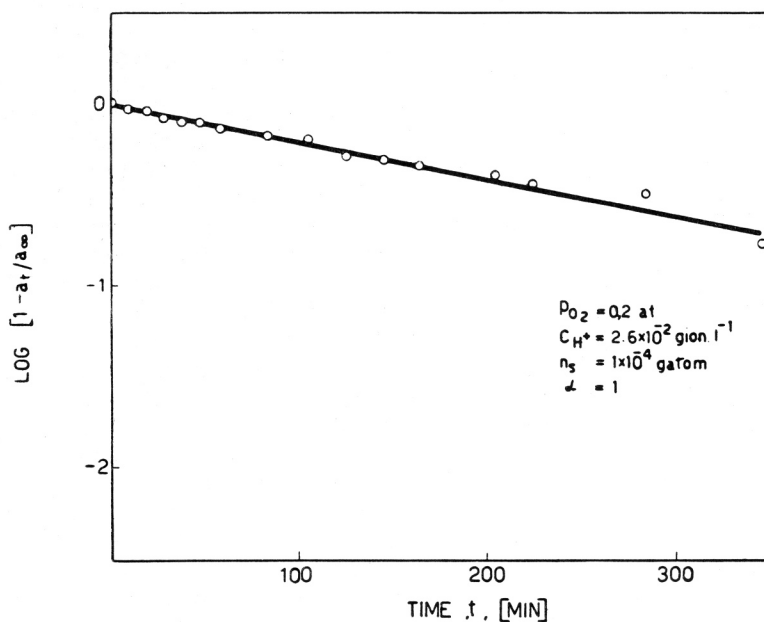


Fig. 6. Fraction of the undissolved Zn from the starting Zn amount calculated as $1-a/a_\infty$ against time plot; Hydrogen ion concentration 2.6×10^{-2} g. ion l^{-1} ; $p_{O_2} = 0.2$ atm.

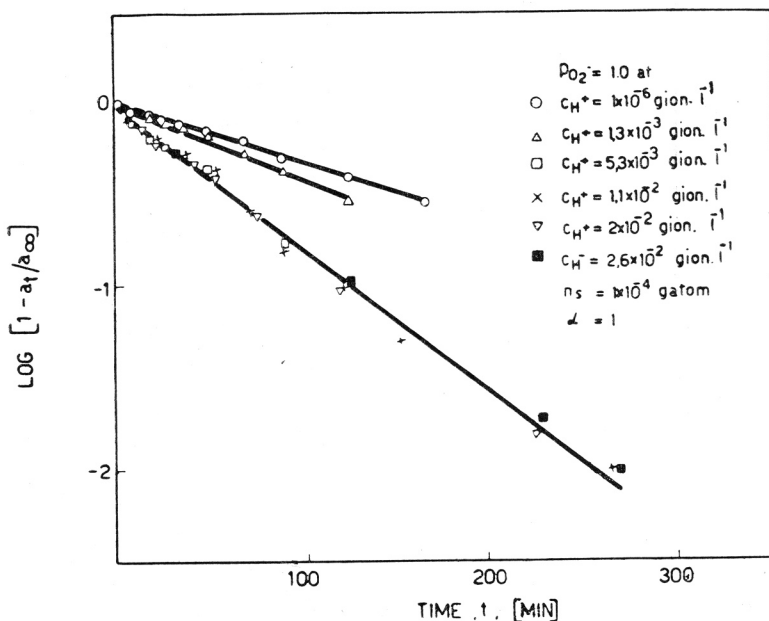


Fig. 7. Fraction of the undissolved Zn from the starting Zn amount calculated as $1 - a_t/a_\infty$ against time plot; Partial oxygen pressure 1.0 atm.

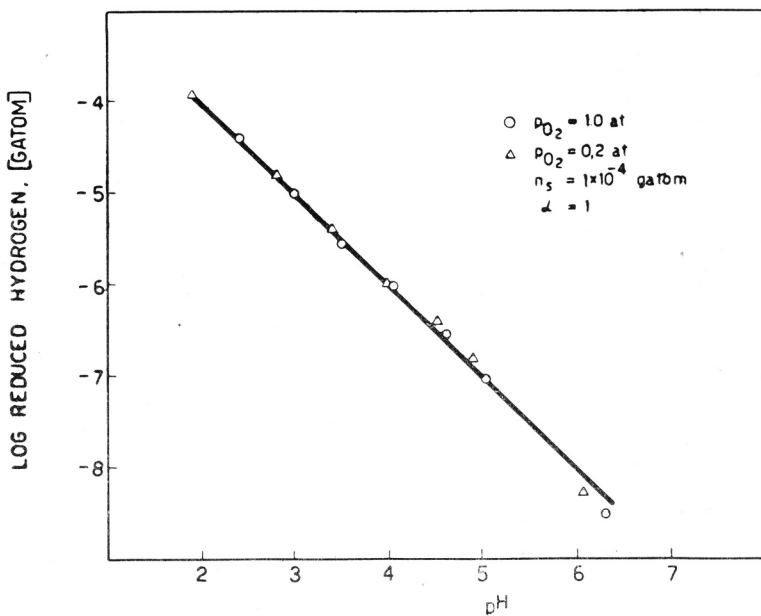


Fig. 8. Reduced hydrogen amount against pH plot for $n_s = n_L = 1 \times 10^{-4} \text{ g. atom Zn}$ and partial oxygen pressure 1.0 atm.

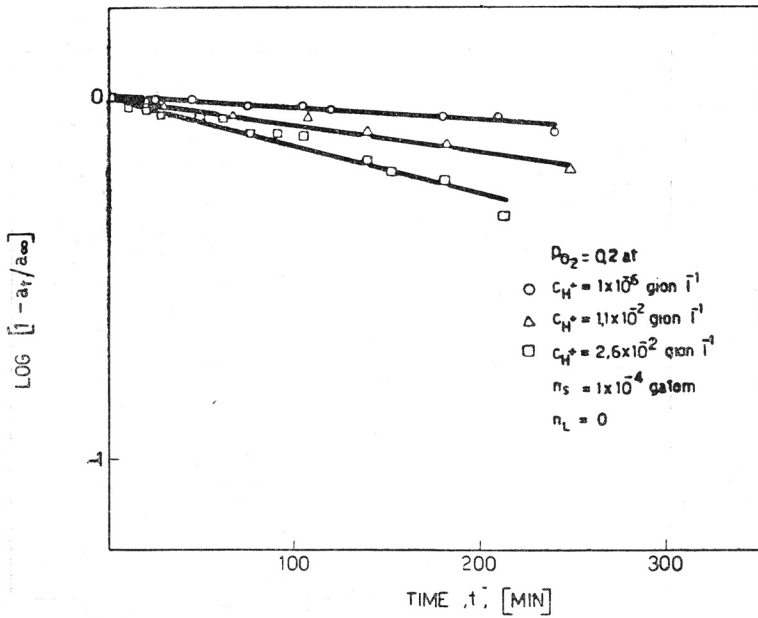


Fig. 9. Fraction of undissolved Zn from starting Zn amount calculated as $1 - a/a_\infty$ against time plot; $n_s = 1 \times 10^{-4}$ g. atom Zn, $n_L = 0$, $p_{O_2} = 0.2$ atm.

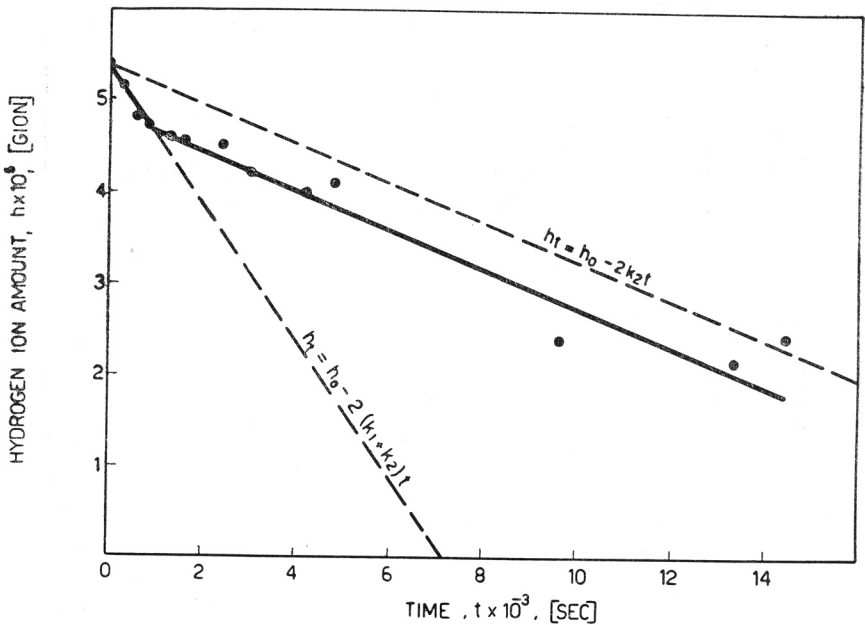


Fig. 10. Hydrogen ion amount against time plot. $n_s = n_L = 1 \times 10^{-4}$ g. atom Zn, $p_{O_2} = 0.2$ atm.

one in the absence of oxygen shown in Fig. 2. The reduction of hydrogen ions is not disturbed in the presence of oxygen from pH 2—4. This section of the curve coincides with the broken line in Fig. 2 which would represent the quantity of reduced hydrogen for the deoxygenated case when no other factor would interfere with its total reduction.

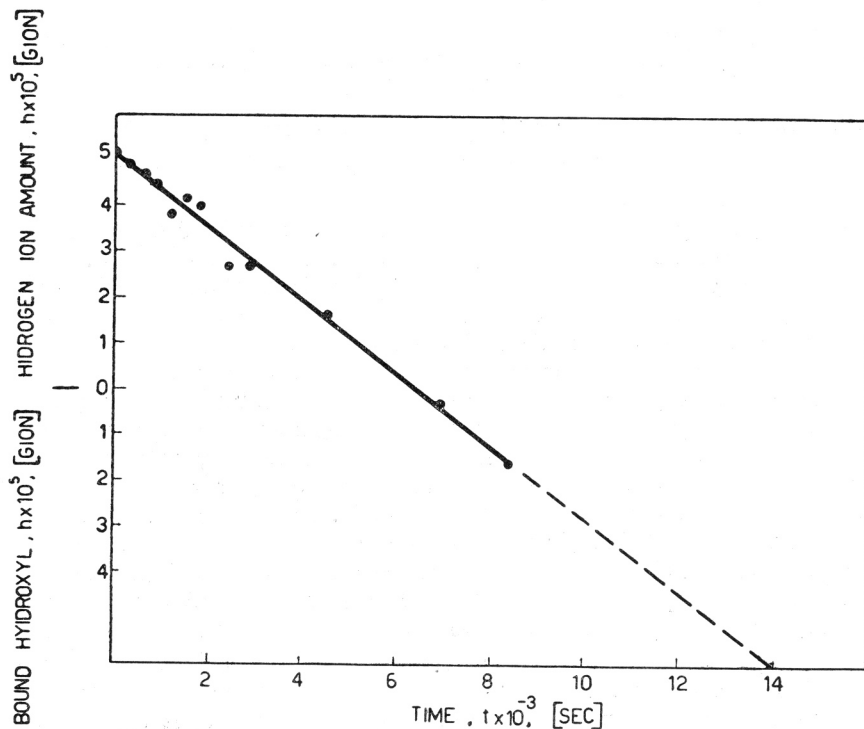
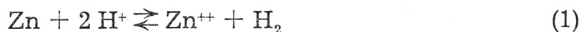


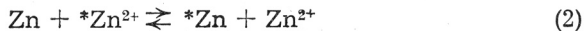
Fig. 11. Hydrogen ion amount and bounded hydroxyl against time plot. $n_s = n_L = 1 \times 10^{-4}$ g. atom Zn, $p_{O_2} = 1.0$ atm.

DISCUSSION

In the absence of oxygen the hydrogen ions are reduced on the amalgam surface according to the reaction



and hydrogen atoms or molecules are adsorbed on the surface. The adsorbed hydrogen interferes therefore with the basic exchange process between zinc ions in solution and atoms dissolved in mercury (*Zn labelled atoms):



Accordingly, with an increasing quantity of adsorbed hydrogen, the exchange rate should decrease. At hydrogen ion concentrations exceeding 1×10^{-4} g. ion l^{-1} the free hydrogen ions present are not entirely reduced in the observed time of up to 300 min. probably because the adsorbed hydrogen ions on the surface hinder the further dissolution of zinc.

The quantity of adsorbed hydrogen which is necessary to stop the total reduction of hydrogen ions can be estimated from Fig. 2; it corresponds to the limit of the linearity of the plot »logarithm of reduced hydrogen against pH« with decreasing pH values. This limiting value is 7×10^{-7} g. atom or 2×10^{-7} g. atom/cm.² at pH 4.

Since the variation of the zinc concentration from 10^{-4} to 10^{-3} g. atom on a constant contact surface does not affect the limiting quantity of adsorbed hydrogen of about 7×10^{-7} g. atom, we can draw the conclusion that this quantity is determined by the contact surface.

The present results seem to confirm the supposition that adsorbed hydrogen is the cause for the deceleration of the reduction and exchange process.

In their study on the mechanism of the anodic dissolution of the indium amalgam in acidic solutions, V. V. Losev and A. J. Molodov⁴ found that at perchloric acid concentrations less than 0.1 M the slope of the curve of logarithm of the exchange current* vs. the logarithm of perchloric acid concentration is $b = -0.99$ and that the equilibrium potential does not depend on the acidity. Figure 1 shows that solutions with pH values lower than 4 give a similar linear dependence. These authors assumed, however, that the partially hydrolyzed ions, whose concentration was reduced with increasing acidity, rather than the metal cations, take part in the exchange process. Consequently, the exchange current and exchange rate are also decreased. On the other hand, V. V. Losev and V. V. Gorodecki⁵ found that with increasing pH the exchange current on the bismuth amalgam electrode decreased although in this case, with increasing pH, partially hydrolyzed bismuth ions $[\text{BiOH}]^{2+}$ are formed. It was found that the concentration of $[\text{BiOH}]^{2+}$ is directly proportional to the rate of the cathodic process.

In the presence of oxygen, a complete dissolution of zinc from the amalgam was observed. From the dependence of the logarithm of non-dissolved zinc versus time shown in Figs. 3, 4 and 5, it appears that at partial pressures of oxygen of 0.2 atm., zinc is dissolved by means of two parallel processes of different rates. Of the total zinc, 10–30% dissolved by the faster process in much shorter times.

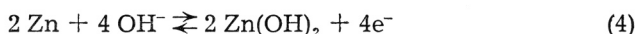
The faster process, which takes place in the measured region in solutions ranging from neutral to those containing 2.6×10^{-2} g. ion l.⁻¹ of hydrogen, can be explained by the influence of zinc sulphate in the solution. According to R. Schinder¹⁰, a solution of zinc sulphate dissolves zinc forming zinc monoxysulphate, $\text{ZnSO}_4 \cdot \text{ZnO}$. In order to find out whether the presence of zinc sulphate in the solution affects the dissolution process of zinc from amalgam, experiments were carried out under the same conditions using solutions which do not contain zinc sulphate. Figure 9 shows that in the absence of zinc sulphate, at $p_{\text{O}_2} = 0.2$ atm., zinc from amalgam dissolves by a single process over the entire region of measured hydrogen ion concentration.

The slower process inducing dissolutions of larger quantities of zinc can be explained according to J. K. Vetter¹¹ by the reduction of oxygen according to the reaction:

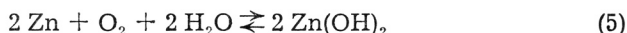
* The exchange current, i_0 , and the exchange rate, R, are connected by the relation $i_0 = zFR = 1.93 \times 10^5 R$.



and the subsequent precipitation of $\text{Zn}(\text{OH})_2$ according to the reaction:



The resulting process can be given as:



This reaction is supported by the presence of zinc hydroxide precipitate in the solution after dissolution. The greater the amount of the precipitate, the smaller the quantity of hydrogen ions present in the solution at the beginning of the experiment.

Potentiometric titrations of the solution containing the precipitate show that the total amount of hydrogen ions necessary for neutralization (*i.e.* the quantity added for decomposition of the compound formed under the action of zinc sulfate on zinc in amalgam, and for the decomposition of zinc hydroxide formed by reaction 4 or 5 plus the quantity of hydrogen ions present in the solution at the beginning of the experiment) is always equivalent to the amount of zinc dissolved from amalgam. Hence, it may be assumed that hydrogen ions present in the solution are used in the decomposition of the compound formed under the action of zinc sulfate, and in the neutralization of hydroxyl ions formed in reactions 3 and 4. In both cases 2 g. ion, of hydrogen are needed for 1 g. atom of dissolved zinc. The quantity of hydrogen ions reduced in the first process of zinc dissolution (eq. 3 or 4) depends on the quantity of compound formed. In the second, they neutralize hydroxyl ions up to the equilibrium pH value for the precipitation of zinc hydroxide.

At a partial oxygen pressure of 0.2 atm. and a concentration of hydrogen ions up to 2.6×10^{-2} g. ion l^{-1} zinc is dissolved by two parallel processes. If hydrogen ions are used in both, then the quantity of hydrogen ions present in the system (h_t) at time t , is

$$h_t = h_0 - 2(k_1 + k_2)t \quad (6)$$

where h_0 is the quantity of hydrogen ions in the solution before it was brought into contact with the amalgam. If the solution contains 1.08×10^{-2} g. ion l^{-1} hydrogen, h_0 has the value of 5.4×10^{-5} g. ion (it is the hydrogen ion amount in a 5 ml. aliquot of this solution) and k_1 and k_2 are the rates of zinc dissolution by the faster and slower process which, according to Fig. 5 have the values of 2.4×10^{-9} g. atom $\text{cm}^{-2} \text{sec}^{-1}$ and 1.1×10^{-9} g. atom $\text{cm}^{-2} \text{sec}^{-1}$ respectively. In the same manner, the relationship for the decrease in hydrogen ion quantity by the slower process is

$$h_t = h_0 - 2k_2t \quad (7)$$

In Fig. 10, the broken lines show the expected decrease in hydrogen ions with time according to equations 6 and 7. The full points were obtained by determining the free hydrogen ions in solutions which were in contact with amalgam for different time intervals, *i.e.* in which hydrogen ions are used up due to the dissolution of zinc. The concentration of hydrogen ion was determined by potentiometric titration of 5 ml. solution aliquots. The arrange-

ment of these points linked by a full line confirm the results shown in Figs. 3, 4 and 5. It may be concluded that at a partial oxygen pressure of 0.2 atm., zinc dissolves in the presence of hydrogen ion of conc. 1×10^{-6} — 2.6×10^{-2} g. ion l^{-1} by means of two processes in which hydrogen ions are used.

At a partial oxygen pressure of 1.0 atm. the dependence of non-dissolved zinc with time indicates that the dissolution takes place only by one process, with a rate of 4×10^{-9} g. atom cm^{-2} . sec^{-1} when the hydrogen ion concentration in the measured region exceeds 5.3×10^{-3} m units. These velocities are greater than those of the dissolution of zinc at a partial oxygen pressure of 0.2 atm. This can be explained by the higher oxygen concentration in the solution. The oxygen concentration ratio in the solution is approximately equivalent to the ratio of the partial pressures, i.e. 1:5 in our experiments. The ratio of the dissolution rate of zinc by process 3 at partial pressures of 0.2 atm. and 1 atm. is 1:3.7, i.e. close to the ratio of the concentrations of dissolved oxygen. It may be assumed that at the partial oxygen pressure of 1.0 atm. zinc also dissolved by process 1 and the free hydrogen ions are used for neutralization of the hydroxyl ions formed. In Fig. 11 the broken line shows the expected fall in the concentration of free hydrogen ions and an increase in the concentration of hydroxyl ions bonded according to a similar dependence given by 3. It appears that after neutralization of the free hydrogen ions, further dissolution of zinc is followed by the formation of zinc hydroxide. The full points are the quantities of free hydrogen ions or bonded hydroxyl ions at time t , calculated from potentiometric titrations. The experimental points are in good agreement with the expected decrease in the concentration of hydrogen ions and the increase in the concentration of hydroxyl ions.

While I. Mádi^{6,7}, accepting the interpretation of G. Wagner and W. Traud⁹, assumes that only reaction (8):



is responsible for depolarization, our results undoubtedly show that the basic process occurring in the Zn-amalgam-Zn²⁺(SO₄) solution system in the presence of oxygen is zinc dissolution by reaction 3, which continues until all the zinc from the amalgam dissolves. This reaction is followed by the dissolution of zinc, due to the presence of zinc sulfate in the solution at $pO_2 = 0.2$ atm. and concentrations of hydrogen ions 1×10^{-6} — 2.6×10^{-2} g. ion l^{-1} .

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IZVOD

Heterogena izmena amalgama. II. Uticaj koncentracije hidrogen-jona na izmenu Zn-amalgam Zn^{2+} (SO_4^{--}) rastvora*A. Filip i M. Mirnik*

Ispitivan je uticaj koncentracije hidrogen-jona na izmenu Zn-amalgam- $Zn^{2+}(SO_4^{--})$ rastvora u prisustvu i odsustvu oksigena. Korišćena je tehnika radio-aktivnih indikatora. Utvrđeno je da se u atmosferi nitrogena u oblasti pH 4—6 brzina izmene ne menja. U oblasti pH 2—4 brzina izmene obrnuto je proporcionalna aktivnosti hidrogen-jona. U prisustvu oksigena u oblasti pH 2—6 dolazi do potpunog rastvaranja cinka iz amalgama. Pri parcijalnom pritisku oksigena 0,2 at i koncentracijama hidrogen-jona od $1,0 \times 10^{-6}$ — $2,0 \times 10^{-2}$ gjon l^{-1} rastvaranje cinka se odvija sa dva procesa od kojih primarni ide usled depolarizacije oksigena po reakciji $O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$. Pri parcijalnom pritisku oksigena 1.0 at cink se rastvara samo po jednom procesu za račun depolarizacije oksigena po istoj reakciji.

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I

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