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THE MIGRATION OF SODIUM IN DILUTE AMALGAMS UNDER THE INFLUENCE OF AN ELECTRIC CURRENT

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED THE MIGRATION OF SODIUM IN DILUTE AMALGAMS UNDER THE INFLUENCE OF AN ELECTRIC CURRENT.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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CONTENTS.

I INTRODUCTION

PURPOSE OF THE INVESTIGATION. This investigation was undertaken at the suggestion of Prof. G. McP. Smith for the purpose of obtaining accurate and, if possible, consistent data concerning the migration of metallic sodium in sodium amalgam under the influence of an electric current.

HISTORICAL. This problem was investigated several years ago by G. N. Lewis (1) who considered the phenomenon as one of electrical transference and calculated his results as transference numbers, based upon the concentration changes of sodium at the anode and cathode. His experiments were carried out in a transference apparatus of such a form that there was considerable local heating; in fact a temperature gradient was maintained from the bottom of the apparatus to the top. This, of course, in case there was more heating at the bottom than at the top would give rise to convection currents; also, the amalgam at the top would be more concentrated than at the bottom since sodium is more soluble in warm than in cold mercury. It appears that convection would also occur upward from the more concentrated amalgam since this is less dense than the dilute. With all of these possibilities for error, it was nevertheless quite apparent that the dissolved metal moved with the negative current, in the opposite direction to that in which it would move if present as the positive ion. The considerable lack of agreement in the results might be laid to the errors mentioned above.

II THEORETICAL.

Any attempt at an explanation of this "negative transference" of metals must recognise the fact that the amalgams are a mercurial solution of a compound $MeHg_x$ [2] in which x may be quite large, and that the compounds are, at least slightly, dissociated into Me^+ and Hg^- ions.[3] Lewis has called attention to the fact that those metals (only Na and K have been studied) which exhibit this effect also have the property of decreasing the conductivity of the mercury. If then we consider a current through pure mercury to consist of a stream of negative electrons, the phenomenon here presented must possess three components.

I. A purely metallic conduction through the mercury, consisting of a stream of electrons.

II. An obstruction to this stream of electrons which is due in some way to the dissolved metal; and

III. A true transference effect on the few positive metallic ions in the system.

The action I has no effect on the concentration of the amalgam. The function is merely that of a shunt which relieves the current of the necessity of ionic transportation and renders the probable error large on account of the excessive current required to produce a measureable effect.

The second action is the cause of the effect which has been observed, a migration of the dissolved metal in the direction of the negative current. With whatever force the solute obstructs the flow of the current, by that force it is carried

with the current. The mechanics of this may be, as suggested by Lewis, a mere bombardment of the unwieldy molecule $MeHg_x$ by the passing electrons. There is also the possibility of the strongly positive nucleus of such a group fixing the mobile electrons of the mercury in such a manner that, rather than yield them to adjacent molecules in a true metallic conduction, the entire mass moves as a negative ion. Whatever this mechanism may be, it is evidently not a true transference as is the third action, which however operates toward a concentration effect in the opposite direction. Inasmuch as this drifting of the molecules with the negative current is not essential to the passage of the current, as is the migration of ions in an aqueous solution of an electrolyte, it appears that the magnitude of the effect is not to be measured by the quantity of current passed but rather by those conditions which render the molecules more mobile or more amenable to drifting with the flow of electrons, and also by those conditions which tend to retard the true transference in the opposite direction. A careful control of these unknown factors might reveal a consistent relation between the quantity of migration and the quantity of electricity but such a relation would probably be of little value compared with a knowledge of the actual transference in the solution.

If the above representation of the process of migration is correct the system would not act, as Lewis assumes, in the manner of a storage cell. If the concentration gradient is produced by an effect which is not electrolytic, then the equalization of this gradient will not produce an electrolytic current in the

opposite direction to that originally impressed. In fact, considering the true ionic transference postulated above, the current from such a concentration cell should be in the same direction as the impressed current. The solute which was mechanically driven toward the anode will return electrolytically toward the cathode thus reversing the polarity of the cell. The determination of the polarity of a concentration cell would then be sufficient to show whether or not the migration effect was electrolytic and whether, in case the migration was not electrolytic, there was an electrolytic effect in the opposite direction.

At the conclusion of the work herein described, such an experiment was actually performed. A concentrated amalgam was placed in one pole of the transference apparatus and pure mercury in the other, the two electrodes attached to a high sensitivity galvanometer and the polarity determined. The result was in accordance with the above prediction; the current in the external circuit flowed from the dilute to the concentrated amalgam, in the same direction as the current which would have built up such a concentration gradient as then existed. This determination cannot be taken as conclusive however for the following reasons:

(1) In such a cell the dilute amalgam, upon becoming more concentrated, rises in temperature and the concentrated amalgam, upon dilution, becomes cool.

(2) Such a metallic circuit consisting of two amalgams of different concentrations forms a thermo-couple.

(3) The heating of the dilute junction of such a thermo-couple produces a current in the same direction as that observed.

The polarity measured is then the resultant of this thermal effect and whatever electrolytic effect there may be. To render the results of such an experiment conclusive the determination of polarity must be made when the temperature of the dilute amalgam is slightly though measurably below that of the concentrated amalgam.

Our argument then, that this is a mechanical rather than an electrolytic phenomenon must rest upon the fundamental ideas of the ionic hypothesis and the lack of quantitativeness of the data to be presented later.

III EXPERIMENTAL

MATERIALS. The amalgams were prepared by electrolysis of a saturated salt solution using a cathode of purified mercury.[4] For the methods of purification of the NaCl see the work of G. McP. Smith and T. R. Ball of this laboratory.[5] The amalgams, which ranged in concentration from 22 to 24 milli-equivalents of Na per 100 grams of amalgam, to avoid oxidation were sealed into glass bottles from which they were poured as required. In this investigation only sodium amalgams were used.

APPARATUS AND METHODS. Most of the experiments were performed in a small transference apparatus of the ordinary ∩ form having one pole at the top and the other at the bottom, the purpose being to avoid convection by obtaining the more concentrated hence less dense amalgam at the top. At the present time only two runs have been made with a second apparatus in the form of a U with both poles at the top but arranged with a glass joint in the middle so that either pole could be turned down. Both pieces of apparatus were about 6" long and had an inside diameter of approximately 1/4". Although this diameter was found sufficient to prevent heating with the current used, the runs were all made in a small thermostat at approximately 25°C so that convection was more completely prevented.

The transference apparatus before being filled was heated in an electric oven to 160°C, which treatment effectually removed the adsorbed water on the glass and prevented the form-

ation of hydrogen bubbles in the amalgam. It was not found necessary to evacuate the apparatus before filling; the amalgam was poured directly from the container and most of the oxide that formed was found to remain behind on the subsequent drawing of the samples. As oxide, or more likely, hydroxide is usually present in amalgams prepared in this manner, it is essential to exercise care in the taking of samples for analysis. Where the analysis is made by alkalimetric titration a very small quantity of solid hydroxide will introduce an error entirely commensurate with the effect of the migration.

Runs were made for periods varying from 30 to 720 hours with a current of about 6 amperes. The current was generally shut off by turning the stop-cocks in the transference apparatus. The stop-cocks were designed, as is usual in transference apparatus, with the holes as large or larger than the inside diameter of the tube so as to avoid the possibility of constriction and consequent heating.

The analyses were made in a manner similar to that of Lewis, by neutralization of the sodium with an excess of 0.5N H_2SO_4 and titration back with 0.01N NaOH in a hot CO_2-free solution, using rosolic acid as an indicator. This operation was greatly facilitated by the use of an apparatus which combined the three features of heating to boiling, steaming down the sides, and washing the solution with CO_2-free air. (see Fig. I)

A hard glass test-tube 30x160 mm. was fitted through a rubber stopper into a small, wide-mouthed bottle so that about 4 1/2 inches of the tube were in the bottle and 1 1/2 inches

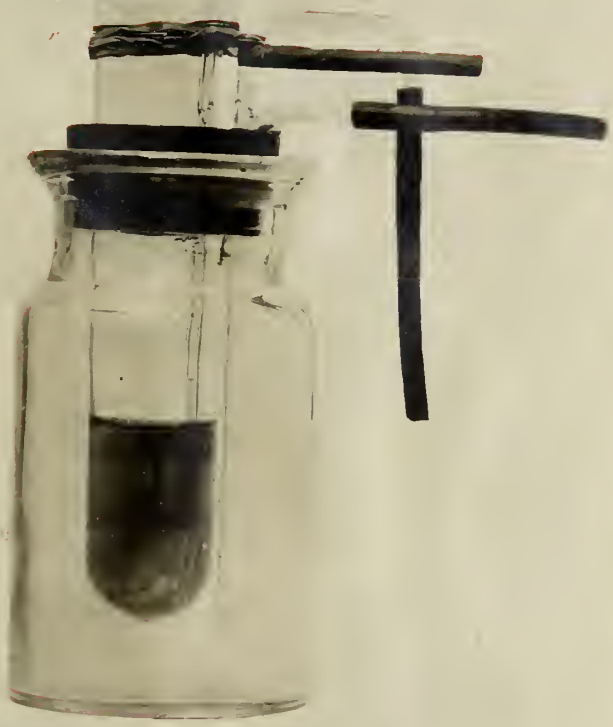

Figure I.

projected above the stopper. This bottle by the insertion of two small tubes through the stopper was made to serve as a steam jacket for the test-tube. The motivating feature of the apparatus consisted of a small glass tube which ran down the side of the test-tube and, following the curve of the glass, ended in a small tip at the very bottom of the test-tube. CO_2-free air was passed through this tube, the rate of flow being controlled by a pinch cock on the rubber tubing connection; in this way the air could be regulated by a pressure of the elbow, both hands being free for the burette. The portion of the titration tube projecting above the steam jacket afforded a condensation area which, when the apparatus was in use, was completely covered with a descending film of water thus effectually and continuously washing down the sides.

The sample, usually about 30 grams of amalgam, was poured into the steam heated tube, covered with about 20 cc. of water containing a drop of indicator, and allowed to decompose with the air bubbling through it. The acid was added in very slight excess (to avoid any action on the mercury) from a small weight burette, H_2SO_4 being used because of its non-volatility and also because of the unsatisfactory behavior of rosolic acid with HCl. The excess of 0.5 normal acid was neutralized with 0.01 alkali from a weight burette, the solution being at all times heated to boiling, thoroughly stirred and washed free from CO_2, and completely steamed from the sides of the tube. Check analyses usually agreed within a few tenths of one per cent and, when unusual care was employed in taking the samples, within .01% or less. The larger errors are attributed to the inclusion of oxide or hydroxide of sodium in the sample.

IV EXPERIMENTAL DATA.

The complete results of the experimental work are shown in Table I.

The values of "milli-equivalents originally present" were calculated from analysis of the middle portions after the runs were completed. These middle portions were sufficiently larger than the end portions so that the inequality of the migration did not appreciably change their concentration from that of the original amalgam. The milli-equivalents present at the end of the run were calculated from the final analyses of the electrode portions. The migration of metal in milli-equivalents is represented by the difference in these two values and is shown for both anode and cathode. Migrations are all measured in the direction of the anode; negative values represent a migration toward the cathode. To reconcile the extreme discrepancies between the changes at the anode and at the cathode, the average of the two migrations is given for comparison with the quantity of current.

Since all of these experiments with the exception of numbers VI and VIII were made with the same apparatus an opportunity is afforded to compare, if not electrodes in general, at least two individual electrodes as to their ability to promote or retard the migration of the dissolved sodium. For this purpose the migrations of the portions contained in the upper pole have been underlined.

TABLE I.

Run No.	CATHODE				ANODE					
	m.e. Na orig. present	wt. of portion.	m.e. present, end of run.	m.e. migrated out of cath.	m.e. Na orig. present	wt. of portion.	m.e. present, end of run.	m.e.Na migrated into anode.	Av. of anode & cath. migration.	Ampere hours.
I	7.845	33.027	7.759	0.086	6.973	29.362	6.967	-0.006	0.040	1000
II	6.628	29.802	6.589	0.039	7.706	34.651	7.869	0.163	0.101	1008
III	8.068	33.831	7.798	0.270	7.071	29.652	7.074	0.004	0.137	576
IV	7.868	33.244	7.875	-0.007	8.135	34.371	8.142	0.007	0.000	160
V	7.510	33.862	7.395	0.115	6.694	30.182	6.854	0.160	0.138	1460
VI	10.536	45.630	10.527	0.009	9.986	43.252	9.952	-0.034	-0.013	4690
VII	7.000	29.987	6.940	0.060	7.994	34.246	8.052	0.058	0.059	2650
VIII	5.260	44.175	5.263	-0.003	5.606	47.077	5.652	0.046	0.022	648

(Note: By "m.e." is meant "milli-equivalents".)

V DISCUSSION OF RESULTS.

From the point of view of transference the relation between the last two columns of Table I is hopeless. The migration varies, to be sure, but not with the quantity of electricity. Rather it seems to be a function of the electrode, as may be seen by comparing the underlined migrations in Table I with the corresponding migrations in the opposite pole. Experiments I, II, III, IV, V, and VII, having been made in the same apparatus, show that the upper electrode (whose migrations are underlined) in every case of significant magnitude suffered the greater migration. A comparison of the two electrode compartments failed to reveal any more striking difference than a slight constriction at the stopcock of the upper compartment. Since the constriction was very slight and no heating effect noticeable it is entirely possible that it produced no measureable variation. It is however obvious that the cause of the inequality in anode and cathode migrations and perhaps the cause of the entire migration is to be sought in some such physical characteristic of the electrodes or the apparatus. Inasmuch as there was an increase in mobility in the upper pole when used either as anode or cathode, the inequality cannot be ascribed to convection; for the same reason it may not be laid to any thermal effect of increasing solubility.

Since we assume on the basis of the ionic hypothesis that a small true transference effect is operative on the few positive sodium ions in the solution, the result of experiment VI suggests the following possibility: that the action of the

stream of electrons on the amalgam is similar to the action of cathode rays on dilute gases, that it produces a degree of ionization which promotes the transference of Na^+ ion toward the cathode. In this experiment where the greatest quantity of electricity was passed there was obtained a negative migration (or a positive transference). Runs VI and VIII were made in the U-shaped transference apparatus which for some reason shows a smaller migration effect than the first apparatus.

VI CONCLUSIONS.

In conclusion it may be considered as demonstrated:

(1) That the migration effect is mechanical rather than electrolytic; that it bears no relation to the quantity of electricity passed but is dependent on some characteristic of the electrodes or apparatus.

(2) That a concentration gradient built up by this migration effect would act in no sense like a storage cell and that any current which might be taken from such a cell would be in the same direction as the impressed current and due to an entirely separate effect.

As a result of the foregoing study the following hypotheses are presented as indicated though not definitely proved:

(1) That a true transference effect is operative on the few positive sodium ions in the amalgam solution but is generally so small as to be negligible compared with the migration effect.

(2) That the ionization of the mercurial compound is increased by the continual passage of a current until the actual transference attains measurable proportions.

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