level *e* mercury flows into bulb D, preventing further access of air to the water pump. The pressure in B immediately decreases so that the mercury is drawn back from A, which latter is now cut off from R by mercury in the capillary tube U. Simultaneously the mercury level in E is lowered below level *e*, and the mercury rising in tube L is finally forced into B so that the atmospheric pressure again presses on the mercury in B. The volume of R is larger than that of A, so that the air forced out of A into R does not increase the pressure in the latter to any great extent. In each cycle, when the pressure over C is decreased sufficiently, air is drawn out of R, so that the pressure in the latter always falls short of the column of mercury in capillary tube U. Each time that mercury is driven through the capillary tube it rises in V, out of which it is forced back into A when the mercury is leaving the latter, the difference in level of the mercury in U and in V becoming equal to the pressure in R. It is essential that tube G be connected to tube F at the same level that E is joined to F.

It was found to be serviceable to join the ends of tubes M and E to a common glass tap. This was closed at the start, enabling a thorough preliminary exhaustion by means of the water pump. Then, on opening the tap, air can enter M and E and the pump starts working. This saves a little time. Furthermore it is advantageous to have a tube and a glass tap attached near the top of tube T. This enables one to let air into the apparatus at the end of an experiment. These taps have not been included in the diagram since they are not necessary to the running of the pump, but are simply added conveniences.

The pump was found to work rapidly after the first exhaustion; it is possible to have two complete cycles occur in one minute.

That portion of the pump which has to do with the ejection of the air forced out of A is similar to an arrangement previously described in THIS JOURNAL.[1] Otherwise, as far as is known to the author, the device is new.

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ELECTRICAL TRANSFERENCE IN AMALGAMS.

BY GILBERT N. LEWIS, ELLIOT Q. ADAMS AND EDITH H. LANMAN.

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According to the electron theory, electrical conductivity of a metal is assumed to be due almost solely to the passage of the negative electrons through the body of the metal. Although the mobility of the free electron is doubtless far greater than that of any other carrier, still the other substances carrying electric charges are acted upon by the same forces which cause the motion of the electron and, having a finite mobility,

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[1] F. M. G. Johnson, THIS JOURNAL, 34, 909 (1912).

must take a certain part in electrical conduction. In the case of a pure metal it is hard to see how any experiments could be designed for the study of that part of the conduction due to these other carriers. But in the case of a solution of one metal in another it seemed not improbable that the passage of a heavy current for a number of days might result in appreciable concentration changes at the electrodes.

When a metal is dissolved in a nonmetallic solvent, as sodium in liquid ammonia, it dissociates, according to the well-substantiated theory of Kraus,[1] into a positive ion (sodium ion) and negative electrons, which may be in part combined with the molecules of the solvent. When an electric current is passed through such a solution, the dissolved metal is carried with the positive current. According to the prevalent theory of metals it seemed not unreasonable to expect that a highly electropositive metal, such as sodium, when dissolved in a far less positive metal, like mercury, would behave in a like manner. We were therefore at first surprised by the results of the experiments which we are about to describe and which show definitely that in both sodium and potassium amalgams there is in fact a change of concentration accompanying the passage of electricity, but that the dissolved metals travel with the negative current.

Preparation of Amalgams, and Transference Apparatus.

Sodium and potassium amalgams were prepared by electrolysis of concentrated solutions of the respective hydroxides with a cathode of pure mercury. The amalgams were transferred to evacuated glass containers equipped with vacuum stopcocks. After thorough shaking the container was sealed to the transference apparatus as shown in Fig. 1. H is the amalgam reservoir and ACB is a glass tube, 2 mm. in bore and 20 cm. in length. Stout, platinum electrodes are sealed in at A and B. In the first experiments, stopcocks below A and B permitted the withdrawal of amalgam from the two limbs. This method was later discarded, owing in part to the danger of contamination of the amalgam by the stopcock lubricant and in part to the difficulty of removing the last traces of adsorbed water which, clinging tenaciously to the walls of the glass tube, reacted with the amalgam, forming numerous small bubbles of hydrogen. In the later form of apparatus, shown in the figure, the whole tube up to E could be heated in an oil bath to over 200° while the apparatus was exhausted to 0.1 micron of mercury through F. After cooling the

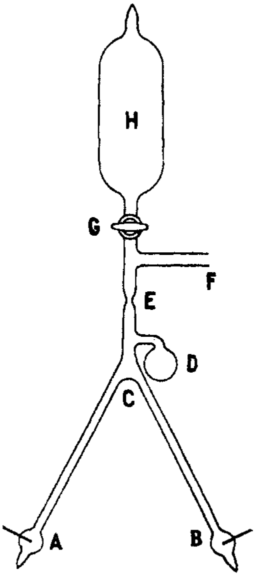

Fig. 1.

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[1] Kraus, This Journal, 30, 1323 (1908).

apparatus, the amalgam was allowed to enter through stopcock G and the transference apparatus, sealed off at E, was ready for use. A current of 4 to 8 amperes was allowed to run several days so as to give approximately 1000 ampere hours. The current was read with an ammeter. Minor uncertainties, owing to fluctuations, and in one or two cases to actual cessation of the current, were negligible compared with other experimental errors.

In order to prevent convection of amalgam, it seemed advisable not to attempt to maintain constant temperature throughout, but rather to establish a temperature gradient from the upper to the lower portions of the apparatus, so that the density increased gradually from top to bottom. This was accomplished by encasing the tube, at the bend C, in asbestos, thus retarding the escape of the heat generated by the current.

At the conclusion of the experiment the apparatus was tipped so that the amalgam in the tube at C flowed into the empty bulb D. The two limbs were sealed off and their contents were weighed and then analyzed by treating the amalgam with a slight excess of standardized hydrochloric acid (0.2 *M*), measured from a weight buret, the residual acid being titrated back with carbonate-free sodium hydroxide (0.01 *M*). The method of procedure will be described in the next section.

An Improved Procedure for Alkalimetric Titration.

Since the portions of amalgam which were analyzed contained but small quantities of dissolved metal (from 0.3 to 4 milli-equivalents), the determination of the small changes in these quantities, due to the passage of the current, was a matter of some difficulty. The ordinary methods of alkalimetric titration are open to criticism, owing to an improper choice of indicator and to the absorption of carbon dioxide from the air. Especially when titrating small amounts of dilute acid and alkali, it is important that the indicator should change color rapidly through a small range of hydrogen ion concentration and that the point of maximum color change should be near the neutral point. An investigation of a number of the common indicators has convinced us that rosolic acid best satisfies these conditions. The color change occurs almost at the point of equal hydrogen and hydroxyl ion concentration, and 0.01 cc. of 0.01 *M* alkali produces a marked change of color in a total volume of 20 cc. This indicator unfortunately fades appreciably in the course of a few minutes, but this difficulty may be overcome by adding only a part of the indicator at first and the remainder when the titration is nearly at an end.

The titration was carried out in narrow flat-bottomed cylinders which were carefully steamed (a high grade of resistance glass would be preferable). When only a slight excess of acid remained a stream of air, freed from carbon dioxide by soda-lime, was led through a glass tube into the solution. This not only effectively stirs the solution, but in the course of five minutes completely sweeps out whatever carbon dioxide may be dissolved. The end point is then very sharply obtained.

The whole procedure is extremely simple and satisfactory, and such discrepancies as are to be observed in the tables given below are to be attributed not to the analytical method, but rather to the difficulty of dealing with so reactive a substance as sodium or potassium amalgam.

Results of the Transference Experiments.

Our experiments show definitely that both sodium and potassium dissolved in mercury are transferred from one electrode to the other during the passage of a current and that both are carried with the negative current.

Table I gives the results of three experiments with sodium amalgam which had, according to three analyses (average deviation from mean 0.05%), 3.240 atom per cent. of sodium. The first column gives the number of grams of amalgam, respectively, in the anode and cathode portions; the second, the number of milli-equivalents of sodium originally contained in these portions; the third, the increase in the number of milli-equivalents in these portions accompanying the passage of the quantity of electricity given in column four. The fifth column shows the number of equivalents transferred per faraday, namely, the ordinary transference number, together with the mean of the transference numbers obtained from the anode and cathode portions. It is to be noted that this mean may be calculated without any knowledge of the original composition of the amalgam.

TABLE I.

	Wt. of each portion.	Milli-equiv. Na (orig.).	Incr. in milli-equiv. Na.	No. of ampere hrs.	Transference number × 10^6.
a........	24.072	4.112	0.152	600	6.78
c........	25.684	4.387	—0.025	..	1.10
					Mean, 3.94
a........	9.588	1.638	0.098	850	3.08
c........	8.421	1.439	—0.066	..	2.08
					Mean, 2.58
a........	9.566	1.634	0.093	1250	1.99
c........	8.368	1.429	—0.118	..	2.53
					Mean, 2.26
					Average, 2.93

Whatever theory we may offer for the mechanism of this transference, we should expect that in very dilute amalgams, where the conductivity does not differ materially from that of pure mercury, the amount of sodium transferred per faraday would be proportional to the concentration of sodium in the amalgam, and even at such concentrations as are here employed we might predict that this would still be approximately true. A few measurements were made with sodium amalgam, 0.577 atom per cent. (average of four analyses, average deviation 0.4%). Owing to the very small amount of sodium in the electrode portions, these measurements were extremely difficult, but we believe we may rely upon the approximate validity of the three results which were obtained and are given in Table II, in which the several columns have the same significance as in Table I. The anode portion of the second run was lost.

TABLE II.

	Wt. of each portion.	Milli-equiv. Na (orig.).	Incr. in milli-equiv. Na.	No. of ampere hrs.	Transference number × 10^6.
a..........	26.384	0.7610	0.0126	1035	0.325
c..........	20.468	0.5804	—0.0134	..	0.347
					(Mean, 0.336)
c..........	25.352	0.7308	—0.0063	805	0.211
					Average, 0.294

The ratios of transference number to atom fraction from Tables I and II, respectively, are $2.93 \times 10^{-6}/0.0324 = 0.90 \times 10^{-4}$; $0.294 \times 10^{-6}/0.00577 = 0.51 \times 10^{-4}$. The difference between these two numbers is barely within the limits of probable experimental error.

The next experiments were made with potassium amalgam, 2.1604 atom per cent. (two analyses, average deviation 0.04%). The results are given in Table III.

TABLE III.

	Wt. of each portion.	Milli-equiv. K (orig.).	Incr. in milli-equiv. K.	No. of ampere hrs.	Transference number × 10^6.
a........	10.963	1.205	0.173	1250	3.72
c........	10.447	1.148	—0.177	..	3.80
					Mean, 3.76
a........	10.892	1.197	0.042	1000	1.13
c........	9.087	0.999	—0.239	..	6.40
					Mean, 3.76
a........	13.601	1.495	0.191	2000	2.56
c........	17.274	1.899	0.283	..	3.79
					Mean, 3.17
					Average, 3.56

Since these measurements were made, it has seemed not unlikely that in spite of repeated shaking the amalgam may not have reached complete uniformity of concentration. The mean of transference numbers from anode and cathode portions of each run can be obtained without a knowledge of the original composition. The three results so obtained show an average deviation from the mean of only 7%. Dividing the average transference number, 3.56×10^{-6}, by the atom fraction, 0.0216, gives 1.65×10^{-4}, which is about twice the corresponding number for sodium.

Theoretical Considerations.

A clue to the interpretation of this apparently mysterious transference effect in amalgams is found when we examine the curves relating the electrical conductivity and the composition of liquid amalgams of sodium and potassium. Bornemann and Müller[1] have shown that the electrical conductivity of mercury is lowered by the addition of sodium.

Now, unless the sodium diminishes the number of electrons which take part in the conduction, which seems improbable, this change of conductivity must be due to a diminution in the average mobility of the electrons. Probably the atoms of sodium which are dissolved in mercury are not there chiefly as such, but rather as nuclei of large aggregates of mercury atoms. Be this as it may, we can consider a dilute amalgam as composed of small regions whose centers are the sodium atoms, embedded in a mass which has all the properties of pure mercury. If an electron meeting one of these regions during the passage of the current is on the average retarded, whether by the greater impenetrability of that region or by any kind of reflection or refraction, then, by the law of action and reaction, the region containing the sodium atom will be impelled in the direction of the negative current.

This was the explanation of our results which we adopted before the experiments with potassium were made, and on the basis of this explanation we predicted that a similar amalgam, which at the same equivalent concentration shows a greater effect than that of sodium in diminishing the conductivity of mercury, would have a larger transference number than that found for sodium amalgam. Bornemann and Müller have shown that potassium, in its dilute amalgams, lowers the conductivity of mercury about twice as much as an equivalent amount of sodium, and the fact that our potassium amalgams gave twice as great a transference number as sodium amalgams at the same concentration is a striking corroboration of the explanation which we have offered.

In order to establish a quantitative relationship between the electrical conductivity and the transference number of amalgams, it would be necessary to consider the mobility of the solute as shown by measurements of the diffusion coefficient. Without entering into a further discussion of this point at the present, we may nevertheless call attention to one simple corollary of our theory, namely, that a dilute amalgam which has the same electrical conductivity as pure mercury would show no electrical transference.

Certain metals like lithium and calcium increase the conductivity of mercury[2] and it will be very interesting to see whether these amalgams show, as our theory would predict, a transference in the opposite direction to that of potassium and sodium.

In conclusion we may point out an interesting thermodynamic consequence of the electrical transference. It is commonly stated that a

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[1] *Metallurgie*, 7, 396 (1910).

[2] Bornemann and Rauschenplat, *Metallurgie*, 9, 505 (1912).

completely metallic circuit, all at one temperature, can give no electromotive force. This is a thermodynamic necessity if there is no process accompanying the passage of a current, except the absorption of heat from the surroundings, which could serve as a source for the electric work. We may, however, construct a new type of concentration cell, composed entirely of metals, which, according to the results of our transference experiments, should give a definite and measurable electromotive force. If we have in contact with one another two sodium amalgams of different concentrations and a platinum electrode in each, we may expect to obtain an electromotive force between the electrodes, owing to the fact that a current passing through such a cell in the right direction will carry the sodium from a region of higher to one of lower concentration. Experiments with such concentration cells are now in progress, and may afford a more exact method of determining the transference number of amalgams.

Summary.

An electric current passing through a dilute amalgam of sodium or potassium causes a transfer of the dissolved metal in the direction of the negative current. The number of equivalents carried per faraday is 2.9×10^{-6} in sodium amalgam of 3.24 atom per cent., and 0.29×10^{-6} in sodium amalgam of 0.577 atom per cent. In potassium amalgam of 2.16 atom per cent. it is 3.6×10^{-6}. An explanation of this transference is offered and the relationship between transference number and electrical conductivity is pointed out.

[Contribution from the Department of Chemistry of the University of Washington.]

MOLECULAR WEIGHTS OF GASES BY AN EVAPORATION METHOD.

By H. L. Trumbull.

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Before the researches of Stefan[1] on the rates of evaporation of ether and carbon disulfide into different gases, it was generally believed by physicists that the rate of evaporation of a liquid is independent of the character of the gas above the liquid.[2] Stefan demonstrated that the velocity of evaporation varies with the nature of the gas above the liquid,

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[1] M. J. Stefan, *Wien. Akad. Ber. Math. Naturw.*, **68**, 385 (1872). See also *Ibid.*, **63**, 163 (1871) and **65**, 323 (1872).

[2] Stefan quotes from Marbach's physikalischen Lexicon under the heading, "Verdunstung and Verdampfung," as follows: "Die Natur der Luftarten äussert übrigens keinen Einfluss auf die Verdunstung der Flüssigkeiten, sobald nur die Umstände also der Druck, die Temperatur u. s. w. gleich sind. Mag die Verdunstung in einer Atmosphare von Sauerstoff, Wasserstoff, Stickstoff, Kohlensäure, oder an der Luft selbst, vor sich gehen, die Menge der entweichenden Dämpfe bleibt sich bei den