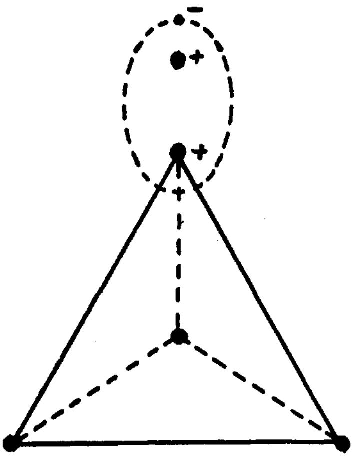

used to account for that localization of the affinities in particular parts of atoms which is indicated by many of the properties of organic compounds. Thus if we suppose that there are four (or eight) positive nuclei in a carbon atom, around which valence electrons may rotate, an atom of hydrogen may be held to the neighborhood of one of these nuclei as indicated in the figure.

I wish to acknowledge my indebtedness to Julius Stieglitz, R. D. Carmichael, J. B. Shaw, Jacob Kunz, A. P. Carman, A. A. Noyes and R. C. Tolman, who have read the first draft of this paper and several of whom have made helpful suggestions.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE ELECTRICAL CONDUCTIVITIES OF DILUTE SODIUM, POTASSIUM AND LITHIUM AMALGAMS.

BY THOMAS B. HINE.

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According to the current electron theory of metallic conduction as developed by Riecke, Drude, J. J. Thomson, Lorentz and others, the atoms of the metal are dissociated into positive ions and free electrons. These particles are supposed to be in disordered thermal motion. When an electromotive force is applied, a velocity of drift is superimposed upon the thermal motion and it is this drift of electrons that constitutes the electric current. The positively charged ions are in general assumed not to move, or at most to carry a negligible fraction of the current. In terms of this theory, therefore, the resistance of a metal depends upon the concentration and mobility of the free electrons. The changes in resistance of a metal under different conditions are variously ascribed by different investigators to one or the other of these factors, since the conductivity is the product of the two. A more precise conception of what is meant by a free electron seems desirable, and it may be that a closer examination will show that degree of ionization and mobility are two aspects of the same physical process. Before any definite mechanistic concept of the electric conduction can be obtained it will be necessary to study the phenomena in the simpler cases more thoroughly. With this idea in view the present investigation was undertaken. In a liquid conductor such as mercury and the dilute amalgams there are none of the crystalline forces that complicate the study of solid metals and alloys. The amalgams of lithium, sodium, and potassium offer an especially interesting field for investigation. These three metals are very similar in their chemical behavior with slight gradations of properties, and might be expected to affect the resistance of mercury in a similar manner, varying only in degree. This seemed to be indicated by the work of Bornemann and co-workers,[1] who first observed that potassium and sodium added in small amounts to mercury increase the resistance. This expectation was not realized, but instead a very striking difference in the behavior of the three metals was observed, which indicates the complex nature of conduction in alloys, and opens a new field from which to attack the general problem of conduction.

In all the investigations upon the conductivity of liquid amalgams, so far as I have been able to ascertain, the very dilute amalgams with less than one atom per cent. of dissolved metal have not been investigated. This particular region which is of primary importance in a consideration of the mechanism of electrical conduction has been neglected for two reasons. In the first place the previous investigations have been in the main carried out by those who were primarily interested in the metallurgical aspects of the subject and consequently directed their attention to the more concentrated amalgams in the search for metallic compounds of fixed composition. Another reason why the dilute amalgams have not been investigated is to be found in the experimental difficulties of preparation and measurement. The nature of the experimental problems involved is well illustrated in considering the case of sodium amalgam. A sodium amalgam of one atom per cent. contains 0.115% of sodium by weight. Amalgams in this region of concentration can be analyzed to within 2 parts in 1000 of alkali metal, and for the purposes of this investigation an accuracy of 5 parts in 1000 of alkali metal would be sufficient. The electrical resistance of a one atom per cent. sodium amalgam is approximately 0.6% greater than the resistance of mercury. Consequently if this increment in resistance is to be measured to within 0.5% the actual resistance must be measured to within 0.003%. The main experimental problem may therefore be stated as follows: First, devise a method of preparing a homogeneous dilute amalgam of any desired concentration and filling a measuring cell with it in such a way that its concentration will not vary by more than 5 parts in 1000. Second, devise an apparatus with which one may measure the resistance of a small cell full of amalgam to within 3 parts in 1000.

Preparation of the Amalgam.

The simplest procedure in the preparation of a series of dilute amalgams seemed to be to prepare a supply of the most concentrated amalgam

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[1] *Metallurgie,* 7, 730 (1910); 9, 473 (1912).

to be used and then to obtain the other concentrations from this one by adding a known weight of mercury to a known weight of amalgam. The concentrated amalgams of sodium and potassium were obtained by electrolysis of concentrated solutions of the respective bicarbonates with a cathode of pure mercury. The lithium amalgam was similarly prepared by electrolysis from a solution of lithium sulfate with lithium carbonate suspended in it. The lithium carbonate was used to keep the solution from becoming acid. During electrolysis the mercury cathode was vigorously stirred mechanically, thus preventing the formation of a concentrated surface layer which would redissolve rapidly. After the amalgam had reached the desired concentration it was drawn off through a stopcock at the bottom of the vessel used for electrolysis into an evacuated container equipped with a vacuum stopcock. The amalgam was then heated to boiling in the container under a pressure of about 1 millimeter of mercury to insure complete reaction with any traces of water vapor that might be present. The amalgam was shaken vigorously for some time to aid the rather slow diffusion in establishing a homogeneous amalgam, and was then ready for use.

The mercury used in these experiments was purified by washing with a solution of nitric acid and mercurous nitrate and then twice distilled under reduced pressure with a current of air. This method of purification has been investigated by Hulett and Minchin[1] and found to give very pure mercury. The sodium bicarbonate and potassium carbonate used in the preparation of the amalgam were of the best grade of chemicals obtainable. A portion of the purified mercury was placed in a glass bulb equipped with a vacuum stopcock and then the bulb was evacuated and the mercury heated to boiling to drive off any water vapor that might adhere to the walls of the container. This bulb was then inverted and attached to the mixing apparatus serving as a reservoir for mercury used in diluting the amalgams.

The mixing apparatus shown in the accompanying drawing consisted essentially of two pipets for measuring out known volumes of amalgam and mercury, respectively, and a bulb where these portions could be mixed and stirred by bubbling hydrogen gas through the mixture. By a system of glass tubing and a two-way vacuum stopcock, not shown in the figure the tubes C, D and E could be attached either to the supply of hydrogen or to an oil vacuum pump of large capacity capable of quickly evacuating to 0.001 mm. mercury pressure. The tube F was connected to the hydrogen supply and the tube G led to the measuring cell in a thermostat, as shown in Fig. 2. The upper end of the measuring cell was attached by glass tubing and a two-way vacuum stopcock to either the vacuum or hydrogen supply. The apparatus, together with the amalgam and mer-

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[1] *Phys. Rev.*, 21, 388 (1905).

cury containers, was supported by six iron clamps attached to a steel frame-work, which, in turn, was firmly attached to the laboratory bench. The mixing apparatus was hermetically sealed to the measuring cell, the hydrogen supply and the vacuum pump after it had been clamped in position. The amalgam and mercury containers were then attached to the mixing apparatus as shown in Fig. 1.

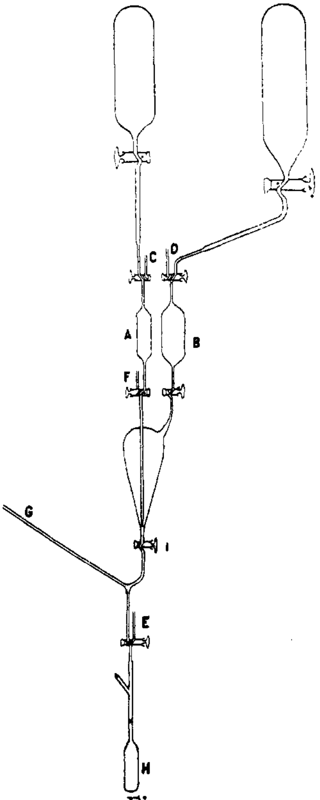

Fig. 1.

The entire apparatus, which had been cleaned and rinsed with distilled water, was evacuated for some time and filled with dry hydrogen gas and again evacuated. The mercury pipet B was then filled with mercury from the container and this amount allowed to run by gravity into the mixing bulb. By opening the stopcock I at the base of the mixing bulb and applying hydrogen pressure through D this mercury was then forced up into the evacuated measuring cell through the tube G. The resistance of the measuring cell full of mercury was then compared with a standard resistance of mercury in a cell of similar construction and the constant of the measuring cell thus determined. The mercury was then allowed to run into the evacuated sealing-off tube H, which was removed and weighed, thus giving the weight of mercury contained in the mercury pipet B. The volume of the amalgam pipet was obtained in a similar manner. Mercury was forced up into the evacuated pipet A from the mixing bulb by hydrogen pressure admitted at D, the mercury remaining in the mixing bulb and tube below the stopcock at F was removed and the mercury in A allowed to run into another sealing-off tube at H and weighed. By opening the stopcock at C the amalgam pipet could be filled with the concentrated amalgam in the container. This was the amalgam that had been prepared by electrolysis as has been described.

The amalgam in A and the mercury in B were allowed to run into the mixing bulb and stirred by hydrogen admitted at F which bubbled through the amalgam, stirring it vigorously, and passed through B and D to the vacuum pump. Opening the stopcock at I and applying hydrogen pressure, this amalgam was then forced up into the cell where its resistance was measured. To be certain that the amalgam was of homogeneous constitution and to avoid the chance of a gas bubble having lodged in the narrow tube of the measuring cell, the amalgam was next forced back into the now evacuated mixing bulb and again stirred. The cell was evacuated and again filled with amalgam and the resistance measured. In filling the cell the amalgam was allowed to rise very slowly to avoid trapping any gas bubbles. This procedure could be repeated as often as desired. In general, at least three measurements were thus taken.

After the resistance of an amalgam had been determined, the pipet A was filled with it and the remainder of the amalgam run into sealing-off tubes at H and sealed off *in vacuo* to be analyzed later. The amalgam reserved in A could then be diluted again with mercury or dropped into the mixing bulb and mixed with more of the concentrated amalgam run into A from the amalgam container.

In working with such reactive amalgams as sodium, lithium and potassium it was very necessary to exclude any traces of air or water vapor from the apparatus and as the apparatus was evacuated to very low pressures this was found to be impossible without the use of vacuum stopcocks carefully ground and lubricated. In case any gases that react with the amalgam get into the apparatus they not only change the concentration of the latter by the amount that they react but generally form a scum or black skin on the surface of the amalgam which sticks to the glass, thus hindering the transference of the amalgam and making it impossible to obtain an amalgam of constant composition. In the earlier part of the experiments a great deal of trouble was caused by the formation of such a scum on the amalgam after stirring with hydrogen. The hydrogen was produced in an electrolytic generator which will shortly be described by G. N. Lewis and R. L. Sebastian. The gas thus obtained and dried over phosphorus pentoxide formed a scum on the surface of the amalgam. The action was ascribed to phosphoric acid or the anhydride carried along by the stream of hydrogen, and a gas wash bottle containing a rather concentrated liquid sodium amalgam was placed in the line. This reduced the action of the gas very greatly, but it still reacted somewhat with the amalgams to be measured. Two gas absorption bulbs were then filled with a liquid alloy of sodium and potassium and placed in the line which consisted entirely of glass connections. This removed the last trace of reactive substance and the amalgam retained its bright surface no matter how often it was stirred or how long it was in contact with the hydrogen.

Measurement of Resistance.

In most of the investigations on the conductivity of amalgams a simple potentiometer method has been used to measure the resistance. In the extensive investigation of Bornemann and Müller[1] on the electrical conductivity of alloys in the liquid state, an accuracy of 0.3% in the measure-

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[1] *Metallurgie*, 7, 396, 730, 755 (1910).

ment of the resistance was claimed for the method of reading current and voltage. This was sufficient accuracy for the purpose of their investigation on concentrated amalgams and alloys, and even enabled them to discover that small quantities of sodium added to mercury increased the resistance. They seemed to get a similar result with lithium, but the effect was less than the error of measurement. In undertaking measurements in this region of very dilute amalgams, as has been pointed out, an accuracy of about 0.003% in the measurement of resistance was desirable. A more refined method of measurement, therefore, than those previously employed was one of the problems of the investigation. In measurements of the resistance of solid metals the greatest accuracy is generally obtained with the Kelvin double bridge. Some preliminary experiments were made in the endeavor to apply the bridge method to the measurement of amalgams, but the trouble caused by thermoelectric effects at the junctions and the difficulty of temperature regulation with the apparatus necessary made it seem more advisable to try and develop the potentiometer method. After considerable experimentation this was satisfactorily accomplished.

The amalgams were placed in a glass cell, shown in Fig. 2, consisting of a narrow tube widened at each end to admit the electrodes and coiled into a spiral to shorten it. There were two electrodes of platinum sealed through the glass at each end, of which the two outer ones served to conduct the current and the two inner ones acted as points of contact, between which the drop in potential was measured. By the use of two sets of electrodes in this way the resistance of the platinum does not enter into the resistance measured, and any thermal or contact electric effects at the point where the current enters the amalgam are also eliminated from the resistance. As a standard resistance with which the resistance of the cell was compared, a second coil of similar form and dimensions was made and filled with mercury. The current was then passed in series through

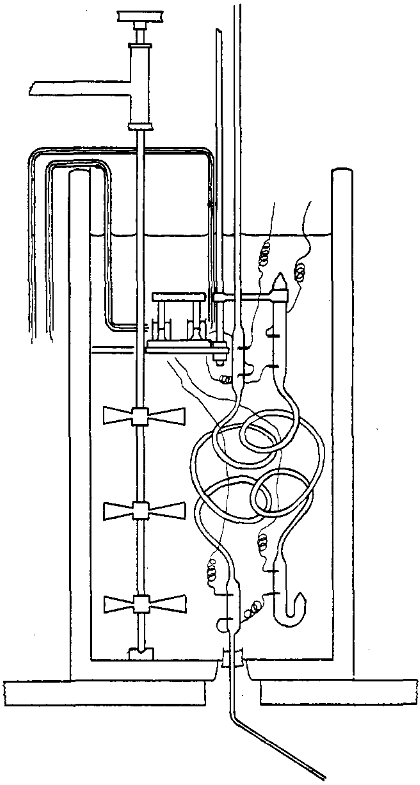

Fig. 2.

this mercury cell and the amalgam cell and the drop in potential in each measured.

This cell has the very great advantage over any of the usual standard constant resistances that when it was placed in the same thermostat as the amalgam cell, the temperature did not have to be kept very constant, since a slight change of temperature would effect both resistances in the same way, and hence would not change the ratio. In the construction of the cell to contain the amalgam it was desirable to have as large a resistance as feasible, since a large resistance drop can be measured with greater accuracy than a small one. The tube could not be made very small, however, without danger of the thread breaking, and could not be made very long without becoming awkward to handle and difficult to keep at constant temperature. The cells as constructed were about 61 cm. long and each had a resistance of about 1 ohm. The potential drop across a given resistance is proportional to the current. This makes it desirable to have as large a current through the two cells as possible. A large current, however, due to its heating effect, would make it difficult to maintain constant and uniform temperature in the cells during measurement.

In the preliminary experiments a lead storage battery was used as a source of current both for the main circuit and for the circuit through the potentiometer but the voltage was found to vary too much for the precision of measurement desired. Eight Hulett[1] standard batteries were then made up and proved very satisfactory, giving a very constant voltage with constant current. It was found, however, that the voltage dropped somewhat upon first withdrawing current from these batteries. The battery was therefore short-circuited through a resistance approximately equal to that of the cells for about twenty minutes before a measurement was made. By this time the voltage of the battery had reached a constant value. A switch permitted the sending of the current through the cells for the few seconds necessary to make a reading and then back again through this auxiliary resistance without leaving the battery on open circuit.

In order to measure the resistance to the desired accuracy of 0.003%, it was necessary to measure the potential drop to within 0.0015%. With a current of 0.01 ampere through a resistance of 1 ohm, there would be a potential drop of 0.01 volt which would require the measurement of 1.5×10^{-7} volts to give an accuracy of 0.0015%. A Leeds and Northrup potentiometer was used with a d'Arsonval galvanometer to measure this potential. This type of potentiometer with a current of 0.02 ampere through the potentiometer will give directly the potential to six significant figures, or, in other words, will measure 0.1 volt to within 10^{-6} volts.

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[1] G. A. Hulett, *Phys. Rev.*, 27 (1910).

Since for a smaller current through the potentiometer the readings are proportional to the current, it was possible by reducing the potentiometer current to 0.002 ampere to measure a potential of the order of 0.01 volt to within 10^{-7} volts. The galvanometer used was tested and found capable of detecting the current caused by placing the potentiometer 10^{-7} volts off balance. Since in the determination of the resistance two readings of potential are necessary with a consequent chance of accumulative error, the potentiometer arrangement used was capable of measuring a resistance of 1 ohm to within 0.002%. The measurements of resistance of the amalgams, however, due to the rise in temperature of the amalgam with the current or the fluctuations of voltage in the battery were not always reproducible within this limit, but were accurate within 0.005%, which was sufficient for the purpose in hand.

In measuring such small voltages the danger of leakage from external circuits on the laboratory bench had to be guarded against. This was done by shielding the entire apparatus with an equipotential metallic shield as recommended by W. P. White.[1] The potentiometer was connected by carefully insulated copper wires through a double switch of special design with the inner sets of electrodes in the amalgam cell and the standard mercury resistance cell. The conducting parts of this switch were made of heavy copper and the copper contacts were made in cups filled with mercury. This switch was of very low resistance and free from contact electromotive forces. To insure the entire absence of any thermoelectric effects the entire switch was placed in the oil thermostat with the mercury and amalgam cells, as shown in Fig. 2. As was pointed out in connection with the standard mercury resistance cell, it was not necessary to maintain the two cells at any one temperature so long as they were both at the same temperature throughout their length and there was no change of temperature during the measurement. This was accomplished by placing both the cells in an insulated vessel filled with "petrolatum" oil and stirred mechanically with the aid of a small motor. The "petrolatum" oil is an excellent insulator, especially with such small potential differences as were present in this case.

Experimental Results.

After a series of preliminary experiments had demonstrated the reliability of the apparatus to maintain the amalgam at constant composition and permit of resistance measurements within an accuracy of 0.005%, a series of sodium, lithium and potassium amalgams were investigated. With the exception of the most dilute amalgam in each series, the concentrations were all obtained by analysis. The concentration of the very dilute amalgam was calculated from the volume of amalgam of known concentration and the volume of mercury used in preparing it. After

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[1] THIS JOURNAL, 36, 2011 (1914).

the resistance of an amalgam had been determined, two or three samples were sealed off *in vacuo* in glass tubes for analysis. These tubes were weighed and the contents treated with a slight excess of standardized hydrochloric acid (0.1 *N*) measured from a weight buret. A piece of platinum was introduced to hasten the reaction by lowering the overvoltage of hydrogen and the amalgam was shaken until all the alkali metal had dissolved. The excess acid was then titrated with 0.01 *N* sodium hydroxide solution, using rosolic acid as an indicator and bubbling carbon dioxide-free air through the solution. This method of analysis has been investigated in this laboratory and found to be very accurate.[1]

The sodium amalgam series was most thoroughly investigated. Eleven different concentrations, ranging from about 0.09% to 4.9%, were measured. Each amalgam was measured several times, being removed from the cell and stirred between measurements to insure a homogeneous amalgam. The results of these measurements are given in Table I. The amalgams are arranged in order of increasing concentration. The first column gives the order in which the amalgams were measured. The fourth column gives the ratio of the resistance of the amalgam cell to the standard mercury resistance. In the last column the resistances are expressed in terms of mercury taken as unity.

TABLE I.—SODIUM AMALGAMS.

Order of measurement.	Per cent. of sodium by weight.	Atom per cent. of sodium.	Resistance in terms of standard resistance.	Resistance referred to mercury.
Mercury	0.00000	0.00000	0.992067	1.00000
9	0.01070	0.09325	0.992768	1.00071
8	0.03339	0.2905	0.994091	1.00204
5	0.04430	0.3851	0.994783	1.00274
7	0.09990	0.8646	0.997371	1.00535
4	0.1387	1.197	0.998587	1.00657
11	0.1944	1.670	1.00000	1.00800
10	0.2468	2.113	1.00067	1.00867
2	0.2824	2.409	1.00093	1.00893
6	0.3104	2.644	1.00070	1.00824
3	0.4338	3.661	0.999542	1.00657
1	0.5893	4.916	0.997226	1.00621

The values of resistance given in Col. 4 have been plotted against the corresponding concentrations expressed in atom per cent. as is shown in Fig. 3.

The lithium and potassium amalgams were not measured over as large a range of concentrations as the sodium amalgam, since the form of the resistance concentration curve could be determined with fewer points. The results of the measurements of six lithium amalgams are given in Table II.

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[1] Lewis, Adams and Lanman, THIS JOURNAL, **37**, 2658 (1915).

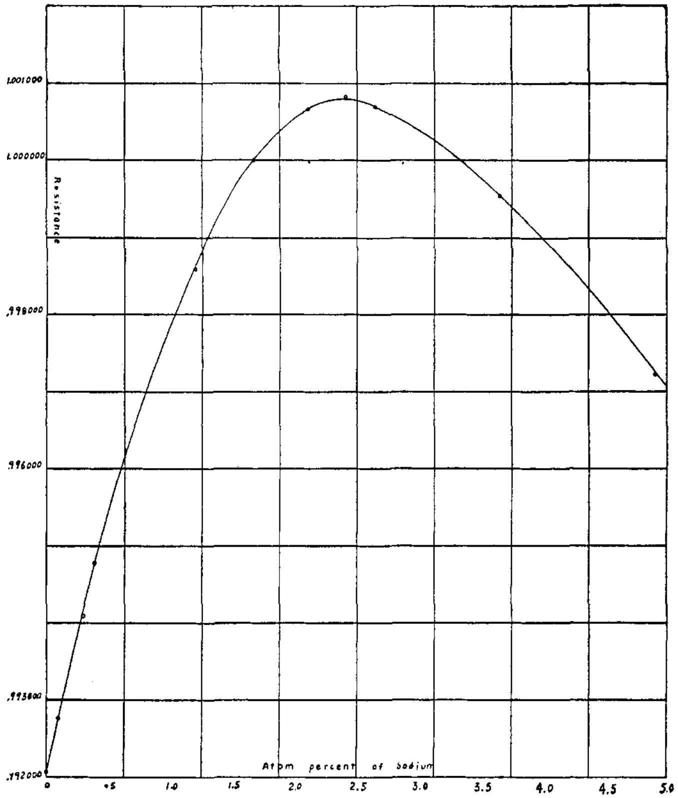

Fig. 3.

TABLE II.—LITHIUM AMALGAMS.

Order of measurement.	Per cent. of lithium by weight.	Atom per cent. of lithium.	Resistance in terms of standard resistance.	Resistance referred to mercury.
Mercury	0.000000	0.00000	0.992067	1.00000
3	0.001131	0.03269	0.991538	0.999468
2	0.003459	0.09988	0.990359	0.998280
1	0.01069	0.3080	0.986012	0.994006
4	0.01684	0.4844	0.982249	0.990105
5	0.02474	0.7103	0.977784	0.985603
6	0.02867	0.8221	0.975299	0.983097

The concentration resistance curve has been plotted from these data and is shown in Fig. 4. The scale of resistance is the same as that used in Fig. 3, but the concentrations are plotted on a much larger scale. On account of the length of the curve, it is here shown in two sections.

The results of measurements on potassium amalgam are given in Table III.

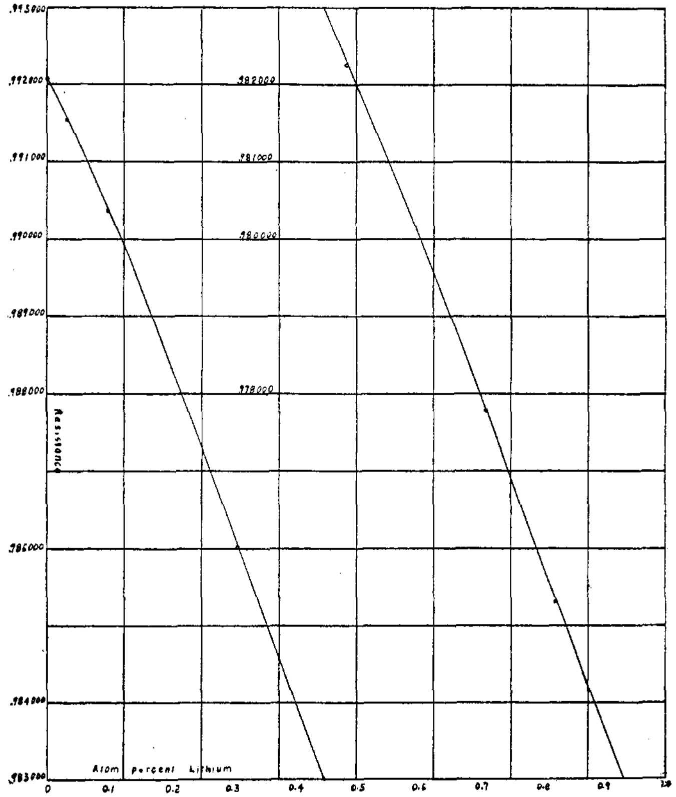

Fig. 4.

TABLE III.—POTASSIUM AMALGAMS.

Order of measurement.	Per cent. of potassium by weight.	Atom per cent. of potassium.	Resistance in terms of standard resistance.	Resistance referred to mercury.
Mercury	0.00000	0.00000	0.992067	1.00000
5	0.01137	0.05831	0.994252	1.00220
4	0.03496	0.1791	0.997761	1.00574
3	0.07956	0.4068	1.009595	1.01767
1	0.10945	0.5590	1.018093	1.02623
7	0.1274	0.6502	1.022150	1.03032
6	0.1726	0.8777	1.033210	1.04147
2	0.2334	1.186	1.045045	1.05341

These results are shown graphically in Fig. 5. The resistance of the potassium amalgams increased so rapidly with the concentration that the scale used for resistances is one-sixth that employed in Figs. 3 and 4. The scale of concentrations is slightly greater than that employed in Fig. 4.

These measurements show a striking difference in the effect of the metal added to mercury for metals of such general similarity. Other metals than these, without exception as far as known, lower the resistance of mercury when added in small amounts. It must be recalled, however, that the dilute amalgams, with these three exceptions, have not been accurately investigated. The measurements of Müller give the trend of the concentration-resistance curve for more concentrated amalgams.

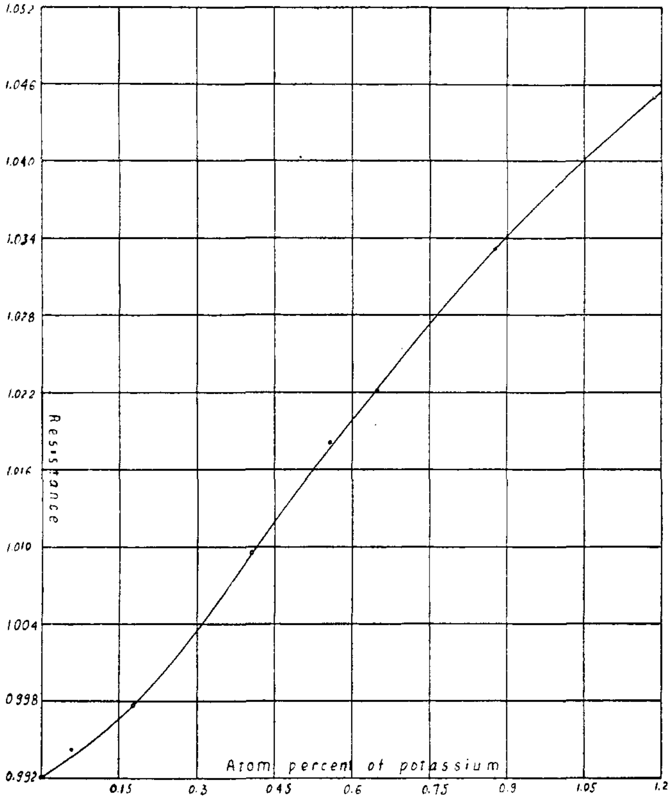

Fig. 5.

The resistance of mercury increases with the temperature while the density decreases. In terms of the electron theory the increase in the resistance with the temperature is usually accounted for by the effect of thermal agitation on the mobility of the electrons and not by an effect upon the number of electrons present. C. A. Kraus[1] has calculated the temperature coefficient at constant volume for mercury from the formula

$$\frac{dR/R}{dT} = \frac{\partial R/R}{\partial T} + \frac{\partial R/R}{\partial P}\,\frac{\partial V/V}{\partial T}\bigg/\frac{\partial V/V}{\partial P}$$

where R represents resistance, T temperature, P pressure and V volume. This gives a value of -6.9×10^{-4} for the temperature coefficient of resistance at constant volume, from which he concludes that since the in-

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[1] *Phys. Rev.*, [2] 4, 159 (1914).

crease in temperature would shorten the mean free path, at constant volume the number of carriers in liquid mercury increases with the temperature. The temperature coefficient at constant pressure is 8.9×10^{-4}, hence the total resistance change due to change in density is 0.158% per degree. Kraus concludes that this increase in resistance with decreasing density is due to decreasing ionization and that at 20° only a small fraction of the atoms of liquid mercury are ionized to furnish the carriers for the current.

It is interesting to apply similar considerations to those advanced by Kraus to the case of dilute amalgams. In the case of an amalgam, however, the matter is not as simple as in the case of a pure metal. If we desire to eliminate the effect of volume change upon the resistance, it is not sufficient to calculate the change in resistance with additions of alkali metal at constant volume since the number of atoms in this unit volume is no longer constant as in the case of pure mercury considered by Kraus. The effect upon the resistance of mercury of the addition of the three alkali metals may, however, be calculated at constant average atomic volume: that is, the volume occupied by 1 average gram atom. If, for example, N is the fraction of dissolved sodium atoms in the amalgam, the average gram atom is $23\,N + 200.6\,(1 - N)$ grams. It is evident that the average gram atom contains the same total number of atoms no matter what the value of N.

If R is the resistance of pure mercury, V and V′, the atomic volumes, respectively, of pure mercury and of amalgam, P the pressure in kilograms per square centimeter, and N the atomic fraction of the dissolved metal, then, according to the measurements of Bridgman,[1] $d \ln R/dP = -3.34 \times 10^{-5}$, while from the measurements of Richards, of Buchanan, and of Bridgman,[2] $d \ln V/dP = -3.8 \times 10^{-6}$. Hence, $d \ln R/d \ln V = 8.79$. In Table IV the second column gives the value of $d \ln V'/dN$ calculated from the work of Maey,[3] and the third column the values of $d \ln R/dN$, which are obtained from the second column through multiplication by 8.79. These figures therefore show the change in the resistance of mercury which would be produced by the three metals, assuming that the effect of the dissolved metal is due solely to the accompanying volume change. The fourth column gives the values of $d \ln R/dN$ obtained directly from our measurements, by finding the slope of the resistance curve at $N = 0$. These figures will vary somewhat according to the relative weight given to the measurements at the lowest concentration. The fifth column gives the values of $\left(\frac{d \ln R}{dN}\right) V'$, namely, the

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[1] Bridgman, *Proc. Amer. Acad. Arts Sci.*, 44, 221 (1909).

[2] Landolt, Börnstein, and Roth, "Tabellen."

[3] *Z. physik. Chem.*, 29, 119 (1899).

fractional change in the resistance per gram-atom of dissolved metal when the average atomic volume is kept constant. These figures are obtained by subtracting the third column from the fourth.

TABLE IV.

	$\frac{d \ln V'}{dN}$.	$\frac{d \ln R}{dN}$ (calc.).	$\frac{d \ln R}{dN}$ (obs.).	$\left(\frac{d \ln R}{dN}\right)_{V'}$
Lithium............	-0.534	-4.70	-0.82	$+3.88$
Sodium............	-0.014	-0.12	$+0.92$	$+1.04$
Potassium..........	$+0.643$	$+5.66$	$+2.73$	-2.93

It is evident that when added at constant atomic volume lithium would increase and potassium decrease the resistance of mercury, the very reverse of that which happens at constant pressure.

This observation does not appear susceptible of simple explanation in terms of the free electron. Since the number of atoms in the average atomic volume is constant, the addition of an alkali metal to mercury at constant average atomic volume is equivalent to substituting atoms of the alkali metal for some of the mercury atoms. In terms of the theory of the free electron there would result no change in the mean free path of the electron and in consequence no change in the mobility. The alkali metals show a higher conductivity and a greater photo-electric effect than mercury, which would indicate higher concentration of free electrons in the alkali metals than in mercury. We should therefore expect an increased ionization upon the addition of alkali metals to mercury at constant average atomic volume, but this expectation is not realized. The mechanism of conduction in the case of these amalgams would seem to be much more complicated than that presented by the drift of free electrons due to an electromotive force superimposed upon their disordered thermal motion.

The parallelism between the figures of the second and the third columns is striking; we need not, however, consider the change in volume and the change in resistance to be directly related as cause to effect, but rather we shall regard them as concomitant effects of some condition in the immediate neighborhood of the dissolved particles, a condition which probably is closely connected with what is known as the solvation of the dissolved metal. The amount of this solvation or combination with the solvent undoubtedly increases in the same order as the electrical resistance, being least in the case of lithium and greatest in the case of potassium. Thus, to cite one of the most direct pieces of evidence, it is shown by Lewis and Keyes[1] that the heats of solution in mercury of lithium, sodium and potassium are, respectively, 19,600, 19,800 and 26,000 calories.

PITTSBURG, CALIFORNIA.

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[1] Lewis and Keyes, THIS JOURNAL, 35, 340 (1913).