THE CONTACT ELECTROMOTIVE FORCE BETWEEN THE SOLID AND LIQUID PHASES OF THE SAME METAL AND BETWEEN THE OUTGASSED SURFACES OF TWO DISSIMILAR METALS

By Philip H. Dowling

Abstract

Change in contact e.m.f. at the melting point of three low melting point metals.—Measurements were made on tin, Wood's metal and a Sn-Pb alloy (1/4th Pb) in comparison with a nickel surface, using the standard Kelvin null method. The metal, previously purified electrolytically, was melted in vacuum and then run into a cup below the nickel surface. No evidence of a sudden change of contact potential at the melting point was observed. However even with vacua of the order of 5×10^{-6} to 10^{-6} mm, a residual gas effect caused the contact potential on cooling to be less than on heating, in one case by .14 volt, and this may have masked a slight jump. It is probable, however, that with the metals studied the change cannot be more than .005 volt.

Effect of heat treatment in high vacuo on the contact e.m.f. between Cu and Ni.—The Pyrex glass apparatus was put together without wax joints and arrangements were made for heating either plate separately by high frequency induction. A pressure of less than 10^{-6} mm was maintained. As the outgassing of either metal progressed at a constant temperature, the potential passed through a pronounced minimum. After 80 hours continuous pumping including some 10 hours heating at about 1000°C, the contact potential approached .25 volt as a limiting value (Ni positive). (In air the usual value is .15 volt.) These results are compared with those of others on the effects of outgassing on the Volta effect and on photo-electric sensitivity.

Tribo-electric effect when Sn is solidified in a glass vessel.—Distinct clicks were heard as the Sn cooled, accompanied by sudden violent deflections of the electrometer connected to the Sn.

Part I. Effect of Fusion on Contact Electromotive Force

THE problem undertaken in the first part of this research was the measurement in vacuum of the contact potential between two dissimilar metals one of which could be carried through the melting point, to determine whether or not a measurable jump in the contact potential occurred at this point. Richardson's electron atmosphere theory of the Volta effect leads to the relation

$$V=(\phi_1-\phi_2)/e+TdV/dT$$

where V is the contact potential between two metals whose respective surface work functions are ϕ_1 and ϕ_2, e is the electronic charge, and T the absolute temperature. One is interested, of course, in the change at

the melting point in both terms on the right hand side of this equation. Regarding the first of these terms, one might expect, owing to the altered surface structure of the melted metal, a measurable change in the surface work function as the metal passes from the solid to the liquid state. The experimental evidence on this point is inconsistent. Goetz[1] has concluded, from calculations made from observations on the thermionic properties of metals in the region of the melting point, that a change of four or five fold does occur in the surface work functions of Cu, Fe, and Mn as the metals melt. On the other hand, similar observations made by Young[2] show no evidence of such a change in the work function of K. Whether or not this discrepancy arises simply from the difference in properties of the metals studied in the two sets of observations does not seem clear. As for the second term, Harrison and Foote,[3] working on the thermoelectric power of a Sn-PtRh couple in the region of the melting point of the tin, found a discontinuity in the thermo-electric power of the couple at the tin's melting point amounting to 1.2 microvolts per degree. Since the Richardson theory makes $dV/dT = dE/dT$, where dE/dT is the thermo-electric power, the expression $T\ dV/dT$ can change at the melting point of the tin by only .0006 volt, a change too small to be detected by the precision attained in the present experiment, part of which also dealt with tin. The detection, in the author's work, of a change in V at the melting point depended, then, upon the existence of an appreciable change at that point in the surface work function of the low-melting point metals which could be studied with the apparatus.[4]

The apparatus, Fig. 1, consisted of a straight Pyrex tube, some 8 cm in diameter and 45 cm long, sealed with red sealing wax into brass ends upon the lower of which the working parts were mounted. The metal to be melted was held in a small crucible within an earthed metal shield. A Ni-Fe thermocouple was placed in contact with the crucible within a small projection into its interior and gave consistent temperature readings, using galvanometer and scale. The calibration curve was linear within the temperature range 0°-300° C. In order to render the surface of the metal to be melted free from contaminations, the melted metal was drained, in

[1] Goetz, Phys. Zeits. **24,** 377 (1923)

[2] Young, Proc. Roy. Soc. **104**A, 611 (1923)

[3] Harrison and Foote, J. Opt. Soc. Amer. and Rev. Sci. Instr. **7,** 389 (1923)

[4] Bridgman (Phys. Rev. **14,** 346 (1919)) has developed thermodynamically a formula for the change in the contact potential at the melting point, involving the change of volume on melting and the change in melting pressure when unit charge is added to the free surface at constant temperature, volume, and capacity. Although there are no definite data which would allow the application of this formula, it would seem to point to a very small change in the contact potential at melting.

high vacuum, into the observation crucible from an auxiliary crucible. This was accomplished by raising magnetically (control A_2) a glass stem which normally closed a small hole in the bottom of the auxiliary crucible. The temperature of the metal under observation was controlled by a split furnace, external to the tube. It was wound noninductively, as a furnace wound in the ordinary way was found to interfere with the observations. The standard Kelvin null method of measuring the contact potential was used with a dependable accuracy of .005 volt, using an electrometer

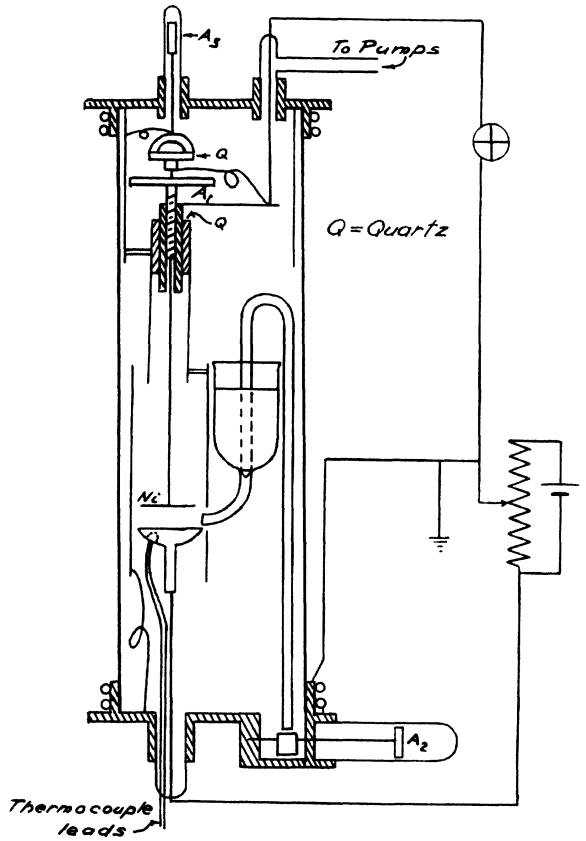

Fig. 1. Apparatus for studying effect of change of phase.

sensitivity of about 2000 mm to the volt. The movable plate in this case was a nickel plate some 3 cm in diameter. Its motion was controlled by the armature A_3 and its initial separation from the other metal by A_1. No particular care was taken in the preparation of the nickel surface beyond cleaning it thoroughly with fine emery cloth, and during the experiment no particular outgassing was accorded it. Applied voltages

were read from a voltmeter on whose scale .005 volt could easily be estimated. The pumps consisted of the usual oil fore-pump and an air cooled mercury diffusion pump, the tube being protected by liquid air. Pressures were read by means of a McCleod gauge on whose scale 2 mm represented a pressure of .00001 mm of mercury. The gauge was connected between the liquid air trap and the diffusion pump.

The procedure was as follows. After the parts had been lined up and the auxiliary crucible filled by pouring the melted metal, the Pyrex tube was slipped over them and sealed into the lower brass end, with no danger of breakage, by running hot steam through the water jacket coils. The tube was then evacuated and pumped for a period of twenty hours or more at a temperature about 30°C above the melting point of the metal under observation.[5] The construction of the tube obviously prevented thorough outgassing of the entire tube, although there was no difficulty in obtaining a vacuum of a few millionths of a millimeter of mercury. The pumps were run continuously throughout observations. After evacuation, enough of the metal to fill it was allowed to run down into the crucible in the measuring chamber. The Ni plate, which had been raised during this process, was then lowered by the control A_1 to within .5 mm or so of the metal surface. Readings on the contact e.m.f. were taken at regular intervals as the temperature was varied continuously from room temperature to above the melting point of the metal under observation and back to room temperature. Observations were made on three metals —tin, Wood's metal, and a lead-tin alloy (3 parts Sn to 1 part Pb by weight)—and with the exception of the Wood's metal, the metals used were electrolytically purified—the tin from a stannic chloride and the lead from a lead acetate solution. The crystals obtained from the electrolytic deposition were melted under hydrogen.

Wood's metal was the first to be studied. The measurements show no definite change in the contact e.m.f. at the melting point, 84°C (Fig. 2). There is, however, a very marked and quite regular variation in the contact e.m.f. as the metal is heated to above its melting point and cooled again. Although their form is always the same, these curves are not exactly reproducible in successive heating-cooling cycles. The magnitude of the variations and the absolute values of the contact e.m.f. seem to depend on the rapidity of heating and the previous history of the metals. Further, the curves exhibit a marked hysteresis-effect; i.e., the cooling do not coincide with the heating curves. At the melting point, for

[5] No detectable evaporation of the metals studied was encountered at these temperatures, nor did the contact e.m.f. in subsequent readings give any indication of contamination of the Ni plate from that source.

example, (Fig. 2A) we have on the heating side a contact potential of .12 volt and on the cooling side of −.02 volt. During the evolution or absorption of heat at the melting point, the contact e.m.f. becomes sensibly constant. Fig. 2B shows a run where the temperature was maintained constant at points just above and below the melting point. Here too, the contact potential becomes constant during the period of constant temperature, showing that the effect at the melting point is not due to any structural change in the metal.

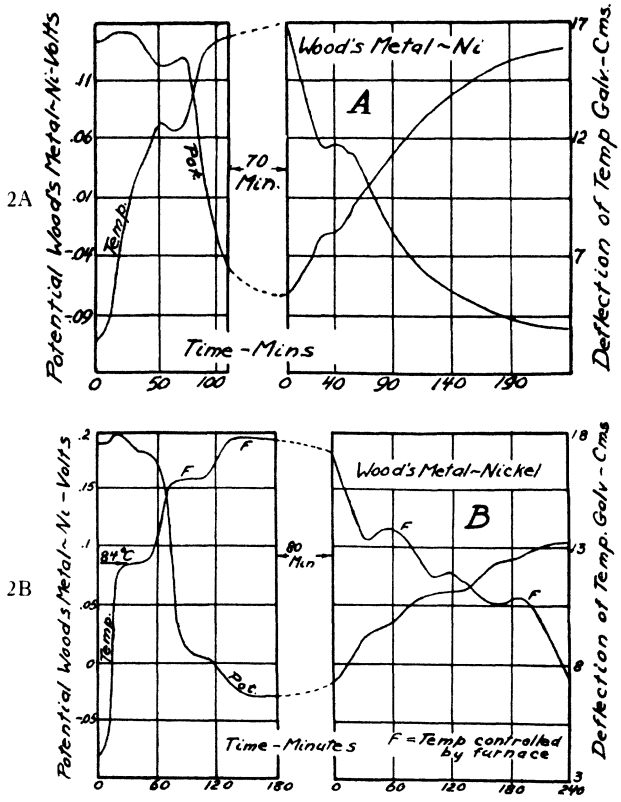

Fig. 2. Equilibrium contact e.m.f. of Wood's metal-Ni.

Similar effects were noted in the observations made on tin and on the lead-tin alloy (Fig. 3). In neither case was any change in the contact potential found which could definitely be ascribed to the change in phase of the metal. In all cases, the contact potential becomes sensibly constant during the period of constant temperature at the melting point.

The regular variation in contact e.m.f. as exhibited by the curves in Figs. 2 and 3 is undoubtedly a gas effect, since the variations diminished

in magnitude in succeeding runs (between which a good vacuum was maintained) and increased again in runs taken after the metals had been exposed to gas. The magnitude of the variations is so large as to preclude their being due to any thermal e.m.fs. which might have been produced in the circuit. The particular forms of the curves obtained in these experiments may be regarded, of course, as resulting from the superposition of the effects of changing gas conditions on the absolute potential of the two dissimilar metals.

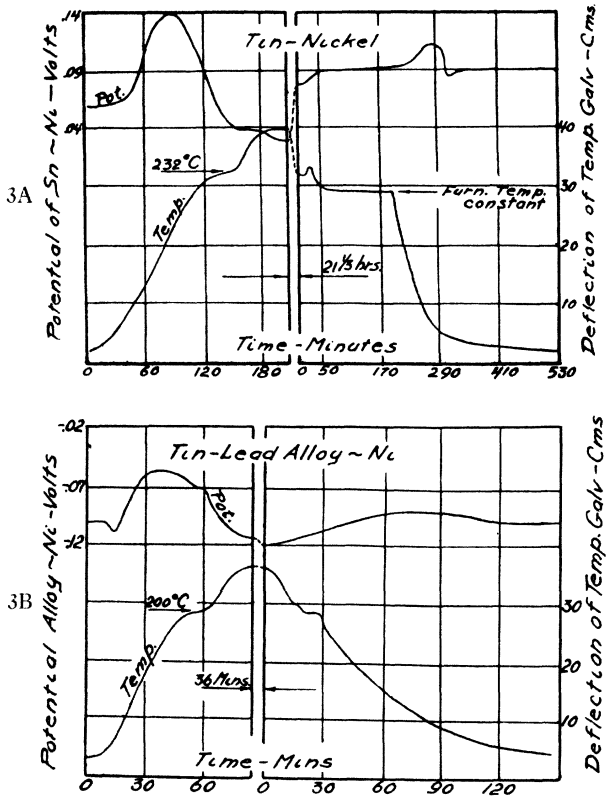

Fig. 3. Contact e.m.f. as a function of time for (A) tin-nickel; (B) tin lead alloy-nickel.

Although the curves in Figs. 2 and 3, as pointed out, do not seem to indicate a unique variation of the contact potential with temperature, it is hard to conceive that with constant vacuum conditions the gas conditions of a metal surface should not reach a constant state, characteristic of the metal's temperature. In fact, experiments to be described later indicate that such equilibrium can be reached although, even at much higher temperatures than those reached here, it is a relatively slow

process. Evidently the heating and cooling in the present experiments were too fast for the curves of Figs. 2 and 3 to represent a series of equilibrium contact e.m.f. values. The slow rate of reaching equilibrium at a given temperature is also undoubtedly responsible for the apparent constancy of the contact e.m.f. at the melting and other points of constant temperature. The cooling side of Fig. 3A, where the temperature was held constant at one point for a comparatively long time, shows, in fact, a small shift in the contact potential even though the temperature was constant. The hysteresis-effect noted previously may result from a difference between the particular way in which gas equilibrium is reached as the temperature rises and as it falls, coupled with a possible temperature lag between the movable Ni plate and the metal in the crucible.

There seems to be no satisfactory reason why a definite jump in the contact potential at the melting point was not found except that such a jump, if it exists in the three metals studied, is quite small and was masked in these experiments by the rather large gas effect. Arguing, however, from the fact that at points where the temperature was purposely held constant, the influence of the latter was almost negligible, one would not expect it to interfere at the melting point. On the whole, the results indicate that if the contact e.m.f. does suffer a change at the melting point, that change in Wood's metal, tin, and a lead-tin alloy is at the most of the order of .005 volt.

An interesting difficulty was encountered in the use of glass crucibles to hold the metal to be melted during observations. Although its exact nature is unknown, it is apparently to be classed with such tribo-electric phenomena as were discussed by H. F. Richards.[6] While heating the metals, no startling changes were observed; as the metals cooled, however, audible clicks were given out within a certain rather wide temperature range, which were also accompanied by rather large electrical effects. The electrometer, unearthed and connected to the Ni plate, was caused to deflect violently and usually to return almost immediately to zero. It was finally found, in air, that the clean bright metal stuck tenaciously to the glass as it was cooled under the melting point, although after it had cooled sufficiently, it was quite easily removed from the glass. The inference is that as the metal cooled, it pulled away from the glass at one or more points, producing the click and an evolution of charge. This was borne out by the fact that as the metal became oxidized, it failed at any time to stick to the glass and gave out no clicks. The substitution of a graphite crucible eliminated the effect entirely and gave much more

[6] Richards, Phys. Rev. **22**, 122 (1923)

consistent results in general. (Figs. 2 and 3 all represent data taken with the graphite crucible.) Mechanical stretching of a thin sheet of tin in air and suddenly releasing it gave no indication of an evolution of charge as would be expected were the sudden contraction of the metal itself, rather than a tribo-electric effect of the glass-metal combination, responsible for the effect. As it was a side issue of the main problem, the effect was not investigated with care.

Part II. Effect of Heat Treatment

The problem of the effect of gas on the contact difference of potential between two different metal surfaces is, of course, an old one. Yet it seemed to be worth while to attack it again, utilizing modern high vacuum technique. Further interest is added by the recent work which has been done by various investigators on the effect of heat treatment in high vacuum on the photo-electric sensitivity of a metal surface. Three methods have been used to obtain a "gas-free" surface; evaporation, used by Hughes[7] and Perucca[8]; mechanical scraping, used by Hennings[9]; and heat treatment, used by some photo-electric investigators and in the author's work. Although the relative merits of evaporation and heat treatment are by no means certain, it does seem fairly evident that mechanical scraping is of avail only in removing surface contaminations. Scraping in vacuum can at most disturb the surface gas conditions and expose gas-filled body-metal layers. The original surface conditions may then be slowly re-established and such measurements as that of the contact e.m.f. may be only temporarily displaced. Evaporation leaves us uncertain as to whether gas cannot actually be carried to the new surface from the parent metal by the escaping molecules, and as to how rapidly the thin, newly-formed surface can pick up gas from the receiving surface. These effects could at least be minimized by careful heat outgassing of the parent metal and of the receiving surface before distillation and also by plotting the contact e.m.f., for instance, against time immediately after the evaporated surface was formed, and extrapolating to zero time. The latter has been done by Perucca and, virtually, by Hughes, both of whom found contact e.m.fs. of the order of a few tenths of a volt between the newly evaporated surfaces of dissimilar metals. Heat treatment seems also to be uncertain, for, in the author's experience, if the metal be heated to a given temperature for a long time, a point will be reached where apparently no further gas, as indicated by

[7] Hughes, Phil. Mag. **28,** 337 (1914)
[8] Perucca, Comptes Rendus **173,** 551 (1921)
[9] Hennings, Phys. Rev. **4,** 228 (1914)

a McCleod gauge, is given off and the contact e.m.f. to any other surface will remain constant with continued heating at that temperature. Yet on raising the temperature, more gas is given off and the contact e.m.f. comes to a new equilibrium value. Similar equilibrium values are found in the photo-electric sensitivity.[10] The aim of the heat treatment method seems to be to find a point at which increasing the temperature of heating has no effect on the phenomenon under observation. With the heat treatment method, there is, however, the uncertainty as to whether the changes in the observed phenomenon are due to the outgassing of the metal surface or to an actual structural change.

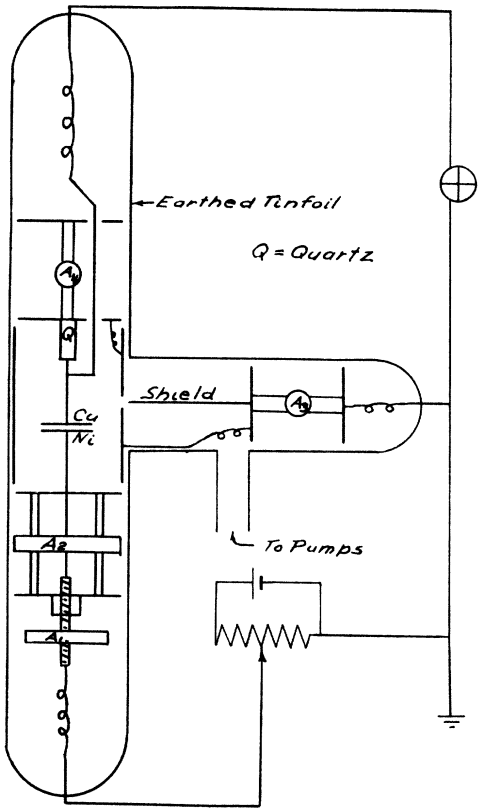

Fig. 4. Apparatus for studying effect of heat treatment.

The apparatus (Fig. 4) was enclosed in a T-shaped Pyrex tube sealed to the soft glass pump system with a small ground glass joint, itself sealed with Wood's metal. Special care was taken to have no wax joints in the vacuum system, which comprised the same pumping apparatus as

[10] Sende and Simon, Ann. der Phys. **65**, 697 (1921)

that used in the first part of this research. The Cu and Ni plates upon which observations were taken were about 22 mm in diameter and .5 mm thick. Undoubtedly it would have given better outgassing to have used thinner plates, but even as it was, difficulty was experienced owing to the warping of the plates at high temperatures. The two plates were carried on two small carriages so that they could be slid in and out of the earthed measuring chamber (controls A_2 and A_4) and a small shield was mounted on tracks in the arm of the tube so that it could be slid between the two plates (control A_3) to protect one plate from the vapors of the other as it was being heated. The Kelvin method was used to measure the contact e.m.f., the carriage carrying the movable and grounded plate being provided with a screw adjustment so that the initial separation between the two plates could be accurately set (control A_1). This same control provided for the motion required by the Kelvin method. About the same sensitivity was attained here as in the previous work. There were no sliding electrical contacts. The plates were heated by high frequency induction, the current being furnished by two 1 kw step-up transformers giving 25,000 volts at their secondary terminals.

The procedure was to bake out, while pumping, the entire tube until the pressure was reduced at most to a few millionths of a millimeter while the tube was hot. Then the plates were heated, one at a time, during which process the cold plate remained within the measuring chamber protected by the shield and the hot plate was, of course, out in the open tube. The earthed tinfoil electrostatic shield around the end of the tube enclosing the plate connected to the electrometer had to be removed for each heating of that plate. The observations were conducted with two objects in view. First, to determine the contact potential between the two gas-free surfaces of two dissimilar metals. This involved heating the plates alternately at a constant temperature until the contact potential between them reached an equilibrium value, the attempt being made to reach such a value that a subsequent increase in the outgassing temperature would not affect it. Readings on the contact potential were taken on the cool metal after each period of heating. These periods ranged from a few seconds to 15 minutes in length. Secondly, to determine how the intrinsic potential of one of the surfaces is affected by outgassing at a constant temperature. For this it was necessary to heat one plate continuously and to measure at intervals its contact potential against the other which was kept cool and assumed to remain at constant potential.

After 80 hours of continuous pumping while the Cu plate was heated 10 hours and the Ni plate 7 hours at an estimated temperature of 1000°C,

the contact potential between the two came to an equilibrium value of approximately .25 volt, the Ni being positive to the Cu.[11] As this was the highest temperature which could be reached with the apparatus and the last hour's heating at this temperature produced some change in the contact potential, it is somewhat doubtful what would have happened could the heating have been carried on at still higher temperatures. The usual value for the contact potential between Cu and Ni in air is in the neighborhood of .15 volt, the Ni being positive; some recent work puts it at .21 volt.[12] The Ni surface remained unchanged in appearance throughout the heating; the Cu, however, developed a beautifully crystalline surface.

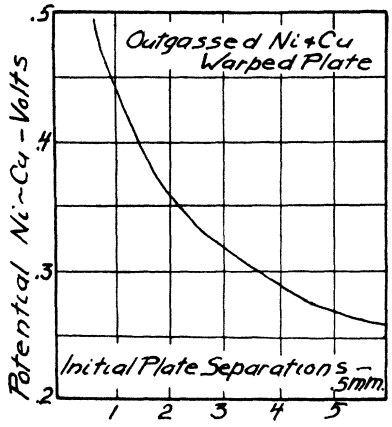

Fig. 5

Due to an unfortunate, though interesting, occurrence, the final contact e.m.f. could not be determined as exactly as had been wished. The skin effect of high frequency currents coupled to the loss of heat by conduction along the plate-supporting rods, led to the centers of the plates being somewhat cooler during outgassing than the peripheries. The centers were consequently not as well outgassed. The warping of the Ni plate, owing to its heat treatment, brought the centers of the two plates closer together than the outside portions. Hence, in taking a reading, if the plates were pulled apart from a very small initial separation, the change in capacity was largely between these central parts and the contact potential reading obtained was characteristic of them, while

[11] Since outgassing by heat treatment is, in a measure, cumulative and these were the same plates which had been used in four or five previous runs, the total periods of heating were effectively longer than as though this had been their first outgassing.

[12] Vieweg, Ann. der Phys. **74**, 146 (1924)

increasing the initial separation tended to give an average reading for the whole surface. These latter readings (Fig. 5) are those to be taken as characteristic of the most thoroughly outgassed conditions obtainable in the apparatus. This explanation of the curve in Fig. 5 was borne out by the fact that after the apparatus had stood at atmospheric pressure for some time after these readings had been taken, there was no variation of the contact potential with initial separations. We thus have two parts of the same plate differing in potential by a matter of tenths of a volt, the more thoroughly outgassed portions being negative with respect to the remainder of the plate.

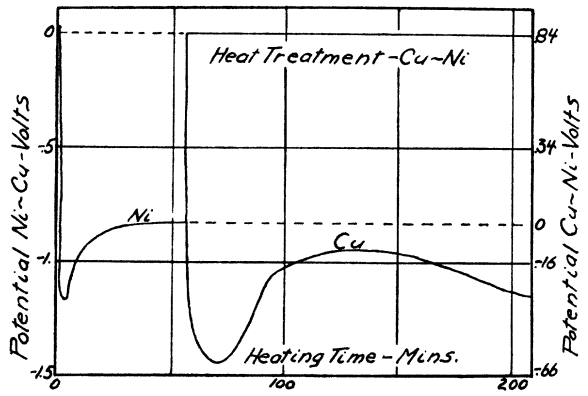

Fig. 6

Fig. 6 shows how, at a given temperature, the intrinsic potential of the metal surfaces reached equilibrium. Both the Ni and Cu acted similarly and the results from all of the several runs made substantiated these curves. The first few seconds of heating rendered the plate being outgassed much more electronegative, at one time as much as 1.5 volts. Further heating of the plate at the same temperature made it slightly more electropositive until equilibrium at that temperature was reached. An increase in the temperature of outgassing would now cause the intrinsic potential to pass through similar though smaller variations and come to a new, more electronegative equilibrium value. Fig. 6 shows these variations in such a way that the difference at any time between the two curves there drawn gives the contact e.m.f. between the Cu and Ni.

The question as to how much of the variation noted in this experiment is due to structural changes and how much to a real outgassing effect is, of course, of interest. The fact that one of the curves of Fig. 6 taken on Cu which was not heated hot enough to cause crystallization of the

surface is consistent with the curve obtained for the same plate after it had been heated hot enough to cause the surface to become crystalline, indicates that the outgassing is largely responsible. The variations were, furthermore, reproducible; that is, after the metals had once been heat treated until their contact difference of potential had been brought to an equilibrium value at some temperature, if they were then exposed for some time to air and again heated in vacuum, the contact e.m.f.passed again through variations similar to those shown in Fig. 6.

The recent work of Vieweg[12] is quite at variance with these results. He also studied the variations of the contact e.m.f. between Ni and Cu with heat treatment of both metals. He finds that the metal becomes more electropositive with the progress of outgassing; his data do not, as published, indicate a minimum or maximum corresponding to those of Fig. 6. The discrepancy may arise from several factors which were different in the two experiments. In the first place, his vacua were of the order of 10^{-4} mm whereas those of the present experiment were at the worst of the order of 10^{-6} mm of mercury. Further his apparatus involved the use of sealing wax joints, against which, on account of the apparently large effects of wax vapors on measurements of this sort in high vacuum, a considerable prejudice has arisen. On the other hand, he does not mention baking out his apparatus previous to taking his observations and it may be that that process in the author's work is responsible for the accumulation on the Ni and Cu surfaces of vapors released from the hotter glass walls, the subsequent removal of which by heat treatment is responsible for the observed large decrease in potential of the surfaces. Further experimental work is required to settle the point. Vieweg reports a limiting contact potential between Cu and Ni of .06 volt, the Ni being positive. He apparently reached a point where increase of outgassing temperature did not affect the contact potential. The discrepancy in final values is perhaps not surprising, due to the difference in vacuum conditions in the two experiments.

It is of interest to compare the curves of Fig. 6 with work which has been done under comparable experimental conditions on the effect upon the photo-electric properties of metals of outgassing by heat treatment. F. G. Tucker[13] has found that as the outgassing by heat treatment of a platinum foil proceeded, the long wave limit shifted from long wavelengths into the violet, indicating an increase in the work function. Although Tucker's results are not of a nature to indicate the minimum of the curves of Fig. 6, they are consistent with the author's work which

[13] Tucker, Phys. Rev. **22**, 574 (1923)

shows a metal to become more electronegative as a result of outgassing Comparison with such data as that obtained by Hallwachs and Sende and Simon,[10] showing the variation in photo-electric sensitivity of metal foils as outgassing at constant temperature proceeds, is not certain. Although the curves in Fig. 6 are of the same general form as those of Hallwachs, if we confine our attention to the effect of outgassing on the work function alone, his curves indicate an initial decrease in that function rather than the initial increase indicated in Fig. 6. The discrepancy may lie in the possibility that in the case of photo-electric sensitivity, outgassing affects not only the work function but also the number of electrons excited by the incident light and reaching the surface with sufficient energy to escape. Comparison with the work of Hughes[7] and Hennings[9] is also difficult as the experimental procedures are so different as to require speculation on the detailed mechanism of the outgassing effects, for which it is perhaps too early.

The author wishes to express his sincere thanks to Professor C. E. Mendenhall under whose sympathetic supervision the work has been done.

UNIVERSITY OF WISCONSIN,
June, 1924.*

* Received January 14, 1925—Ed.