

THE CONTACT POTENTIAL BETWEEN THE SOLID  
AND LIQUID PHASES OF BISMUTH

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## ABSTRACT

**Contact potential between the solid and liquid phases of bismuth.**—In order to obtain as gas-free metal as possible, the bismuth was distilled into the highly exhausted apparatus. The contact potential was measured, by the standard Kelvin method, against a copper plate whose absolute potential was maintained constant by protecting it from the temperature changes incident to melting and solidifying the bismuth. The results were remarkably free from disturbing factors which arise from residual gas effects. Solid bismuth was found to be of the order of  $-0.020$  volts with respect to the molten metal. Small variations from this value were caused, presumably, by the chance crystalline state of the solid surface.

**Relation between thermo-electric power and temperature change at contact potential.**—The equation  $dV/dt = dE/dt$ , which expresses the equality of the thermo-electric power to the temperature rate of change of contact potential, has so far failed of experimental verification. The present experiment, though not adapted to a real test of the equation, yielded evidence that the discrepancy can be greatly reduced by improvement of experimental conditions.

**The effect of surface charges on melting conditions.**—From the results on the contact potential between the two phases of bismuth, it can be shown thermodynamically, following Bridgman's treatment of the matter, that, when one coulomb per  $\text{cm}^2$  is added to the surface of bismuth at constant volume, pressure, and capacity the melting point of the metal increases by  $(1/v) \times 0.02^\circ\text{C}$  where  $v$  is the volume per unit area of the solid bismuth at its melting point.

**I**N A previous paper,<sup>1</sup> the author reported some work on the contact potential between the solid and liquid phases of various low melting-point metals such as tin and lead-tin alloys. At that time it could not definitely be established that a metal, in passing through its melting point, changed its contact potential relative to another metal whose condition had remained fixed. This negative result was ascribed to the masking of any small, real effect by a residual gas effect.

To eliminate this gas effect, it was decided actually to distill the metal under investigation into the highly exhausted apparatus. Bismuth presented itself as a most satisfactory metal for the experiment. Its melting point ( $271^\circ\text{C}$ ) is not too high to render impracticable the use of the direct Kelvin method for the measurement of the contact potential. At this temperature its vapor pressure is negligibly small ( $10^{-10}$  mm of mercury), so that contamination of the measuring plate is not to be feared, although at  $900^\circ\text{C}$ , it is high enough for reasonably rapid distillation. Furthermore, one has an instinctive feeling that if there is an effect to be shown, bismuth will show it. As will appear later, the one bad feature in using bismuth for the author's purpose is its expansion as it solidifies.

<sup>1</sup> Dowling, Phys. Rev. 25, 812 (1925).

Since it had to withstand, evacuated, a temperature of 900°C; the still, *S* (see figure), was constructed of quartz. At first this was sealed to the main tube of Pyrex glass by a graded quartz-to-Pyrex seal and considerable time was wasted in the construction of such seals by the author and in trying out seals purchased on the market. In either case, no matter how rugged a seal appeared to be, the present requirements were too severe for it and it would eventually crack. The problem of sealing the quartz still to the tube was finally solved by the use of a ground joint, *B*, surrounded by a glass cup. This cup was filled with molten tin which rendered the joint vacuum tight, allowed the joint to be baked out, and made dismantling of the apparatus relatively easy. The tin was kept melted throughout the entire course of the experiment by a small electric furnace. Since the vapor pressure of tin at its melting point is but  $10^{-20}$  mm of mercury, contamination of the bismuth from this source was negligible. The still was heated by an electric furnace and had, also, to be kept hot (above 271°C) throughout the entire experiment; for if the bismuth remaining in the still had solidified, it would have cracked the quartz. The construction of the still gave an excellent re-gurgitating action during distillation and the results gave every indication that the bismuth had been very well outgassed.

The preparation of the bismuth surface was as follows. The still was filled with small pieces of bismuth which was the residue from a previous distillation. After the all-glass tube had been sealed, it was exhausted by a conventional pumping system and baked to a temperature of 400°C by means of an electric furnace which completely surrounded it, including the still furnace. A higher baking temperature was not thought necessary from the point of view of the subsequent temperatures to which the tube was to be exposed and would have endangered the working of the various mechanical parts of the apparatus. As soon as the McLeod gauge showed a "sticking vacuum," the carriage *C* was moved with a magnet until the little cup *D* was under the discharge of the still. The latter was then heated to 900°C while the whole tube was kept just above 271°C. In this manner bismuth was distilled as a liquid into the small cup and the initial, poorly outgassed metal was removed, together with any dust which might have accumulated in the still. When *D* was filled, *C* was moved until the glass tube *F* brought the still discharge into communication with the crucible *L* in which the metal was to be held during measurement. Possibly six hours were required to fill the latter. After cooling the main tube but keeping both the residual bismuth in the still and that in the measuring crucible above 271°C and the tin joint above 230°C, the McLeod gauge showed a "sticking vacuum" of between four and five cms.\* After the distillation, *C* was moved out of the way of the measuring apparatus.

This latter consisted of a nickel plate, *H*, connected to the electrometer through a fine nickel spring and insulated from its housing *I* and lifting armature *A* by quartz *Q*. Any change in capacity between *I* and *H*, as the

\* Two mm at the top of the gage capillary represented a pressure of 0.00001 mm of mercury.

latter was raised in the process of taking a reading, was minimized by the shield *J* connected to *H*. Such a change would have affected the electrometer and falsified the readings. *J* also insured a minimum effect on the readings of the edges of the crucible holding the bismuth. *I*, being earthed, served as an electrostatic shield from stray charges on the walls of the surrounding glass tube. An earthed wire gauze around the outside of the glass tube provided further shielding. This mounting for the movable plate was very compact, fitting inside a two-inch tube, and gave very satisfactory results. The whole affair could be moved along the tube, sliding on the same tracks *P* as did the delivery tube *F*, so as to be over either the bismuth or a standar-

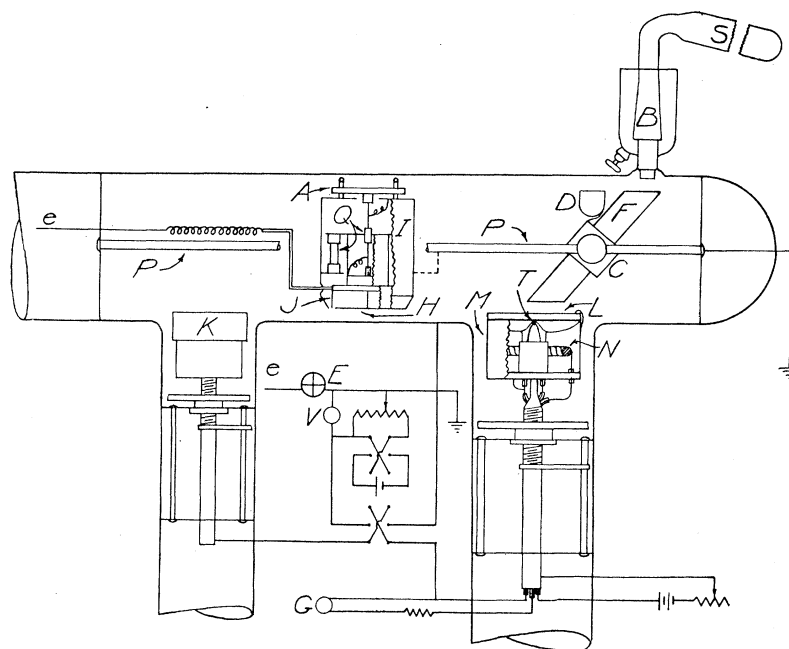


Fig. 1. Diagram of apparatus.

dizing plate. Details of the guides for the measuring apparatus have been omitted in the figure for the sake of clarity.

Since the contact potential between two metals is given to a first approximation by the difference between the work functions of the two surfaces, a measured change in the contact potential cannot be traced to either surface unless some means is at hand for standardizing one or the other. In the present work, the temperature of the nickel measuring plate varied with that of the bismuth and since it could not be thoroughly outgassed without increasing the complexity of an already too complicated apparatus, its work function could not be expected to remain constant. A solid piece of copper, *K*, was used as a standard plate whose large thermal capacity and radiating surface were relied upon to keep its temperature sensibly constant

even though small amounts of heat were conveyed to it by the nickel plate. *K* was mounted on a screw so that by means of a magnet outside the tube its height could be adjusted to correspond with that of the measuring plate. No special care beyond careful mechanical cleaning was taken in the preparation of either the copper or nickel surface. The former was found to be indispensable and the nickel plate was checked against it before and after every reading on the bismuth surface.

Considerable difficulty was encountered in the choice of a material for the measuring crucible *L*. Although no apparent trouble had been experienced in previous work with graphite crucibles, it was found impossible, in the present instance, to prevent small particles of graphite from shearing off and floating on the surface of the molten bismuth. Carbon, though harder, could not be rid of carbon dust left by the tool in its forming and moreover was much more difficult to outgas than the graphite. Metals were shunned for fear of contamination of the bismuth by alloying. On the supposition that its coat of oxide might protect it, aluminum was tried but under high vacuum conditions it alloyed in spots with the bismuth. Although previous experience had shown that one must be wary of tribo-electric effects<sup>1</sup> in using glass for such a purpose, the crucible was finally made of Pyrex glass. The tribo-electric effects were avoided by the simple expedient of never cooling the bismuth more than a few degrees below its melting point. The crucible was made an inch and a quarter in diameter and an eighth of an inch deep with a small reentrant tip in the bottom to accommodate a thermocouple. Electric contact was established with the bismuth by a fine tungsten wire bent over the crucible edge. Since the nickel measuring plate was but seven-eighths of an inch in diameter, the crucible edge was fairly well removed from it and moreover the molten bismuth surface was sensibly flat over the area of the plate in spite of surface tension effects. Curvature of the bismuth surface was to be avoided since it reduced the sensitivity of the measuring apparatus. The crucible was mounted as the cover to a cylindrical nickel box, *M*, which contained a small nichrome helix wound on a quartz ring, *N*. A current of about an ampere through the helix sufficed to keep the bismuth in the neighborhood of the melting point. Care was taken, of course, to heat the nichrome during the outgassing process well above its final operating temperature. The iron-nickel thermocouple *T*, though hardly fit for precise measurements, by reason of the necessary unprotected junctions with foreign metals, was found fairly reliable and was used satisfactorily to pick out the melting point by the flattening of the cooling curve. In order to adjust its height to that of the measuring plate, the entire crucible system was mounted on a screw similar to the mounting of the standard plate.

In the author's previous work, it was possible to take readings right through the melting point. The bismuth, at least in the apparatus used, did not allow this because of its large expansion on solidification. The consequent change in level of the surface, made necessary a readjustment, just at the melting point, of the screw upon which the measuring crucible was mounted. This condition was aggravated by the propensity of the metal

to commence solidification near the edges of the crucible and then, just before the last surface metal in the centre of the crucible hardened, to push up a small peak, as much as an eighth of an inch high and an eighth in diameter. Not only did this reduce enormously the sensitivity of the Kelvin method for measuring the contact potential of the solid surface but it was found that any scum-like impurity (which surface tension effects would ordinarily keep down under the curved edge between the molten metal and the glass) would follow the line of solidification and finally locate at the very top of this peak. Nor was the author ever able; even with the utmost care in cleaning the parts to come in contact with the bismuth, in predistilling the metal, or in discarding the first droplets of the metal as they distilled over; to get a surface entirely free from a small trace of a brownish scum which coagulated into a few minute spots and fortunately ordinarily remained under the curved edge of the molten metal. The origin of this scum remained a mystery. It could not be dissipated by making the melted bismuth the cathode of an electric discharge in hydrogen. Finally all attempts to get rid of it were abandoned and a policy of strict scrutiny of the surface adopted. As stated, it caused little trouble with measurements on the molten state and it was found possible to *occasionally* induce the metal to start solidification in the centre of the metal surface, leaving the undesirable peak at the edge of the crucible, safely out of range of the measuring apparatus. In such cases, it was indeed a beautiful sight to watch the growth of crystals in the surface. A tiny crystal might start in the centre, its presence betrayed only by the little surface tension ridge between it and the molten metal, and grow undistorted until its points reached the edges of the metal, when the remaining molten molecules would be forced to break the precedent set by their solid neighbors. In other cases, practically the whole surface might be covered with small crystalline facets. Great care was taken in watching the surface during solidification to see that no floating scum contaminated it.

During the four days of observations on the surface, only two complete runs; that is—comparisons between the contact potential, with respect to the copper plate, of the solid and liquid metal; were considered unimpeachable. By unimpeachable is meant, not that the measurements checked, but that the solid metal had a clean, flat, crystalline surface with no peaks beneath the measuring plate. Of these two solid surfaces, one was almost entirely a single triangular crystal, the edges near the crucible being filled in with a varied assortment of small crystals. It showed a contact potential with respect to the melted metal of  $-0.025$  volts. The other was a maze of tiny facets and had a contact potential with respect to the liquid metal of  $-0.015$  volts. These measurements had an accuracy such that  $0.040$ , say, could be distinguished from  $0.045$  volts with certainty. That the results on these two surfaces do not check exactly may be ascribed to one of three possible reasons—difference in crystal structure, contamination in the form of scum, or residual gas effects. Contamination, the author feels certain, is ruled out.

As for residual gas effects, the author was very well pleased with the constancy of conditions in the tube. Throughout all the many measurements made on the molten surface, its contact potential with respect to the copper plate remained constant at  $+0.370$  volts. In view of the notorious fickleness of contact potential measurements, this seemed quite remarkable. Further, the contact potential of either the solid or melted surface was insensible to temperature changes. The temperature of the solid surface was lowered  $70^{\circ}\text{C}$  below the melting point with no effect on its contact potential. It might have continued constant below this but the author was afraid of running into tribo-electric effects because of the glass crucible. The molten metal was carried  $23^{\circ}\text{C}$  above the melting point without changing its contact potential, above this, the nickel plate began to change so rapidly that it could not be checked precisely against the copper standard.

Since a difference of  $0.005$  volts could be detected in the present experiment; we can say, from the results stated in the previous paragraph, that, in the neighborhood of  $270^{\circ}\text{C}$ , the temperature rate of change of the contact potential between bismuth and copper, when the temperature of the bismuth only is varied, is less than  $0.00007$  volts/ $^{\circ}\text{C}$ ; *i.e.*— $0.005/70$ . Although this process is not strictly that denoted by  $dV/dt$ , it is interesting to note that the figure  $0.00007$  is of the same order of magnitude as the thermoelectric power of a bismuth-copper couple.<sup>2</sup> This seems fairly strong evidence that the existing discrepancy of  $50$  fold<sup>3</sup> in the experimental verification of the equation  $dV/dt = dE/dt$  may be greatly reduced. Here  $dV/dt$  is the temperature rate of change of contact potential and  $dE/dt$  the thermoelectric power between the same two metals.

The results on the change in the contact potential at the melting point are applicable to the hypothetical effect of surface charges on surface melting conditions. The relations between such effects and contact potential were discussed by Bridgman.<sup>4</sup> A slight modification of his treatment yields an equation from which may be calculated the magnitude of the change in the surface melting point, under constant pressure, volume, and capacity conditions, when unit density of charge is added to the surface. Setting up a condenser of which our bismuth is one plate, we may choose as independent variables;  $c$ , the capacity per unit area of the condenser;  $\rho$ , the density of charge on the bismuth surface;  $v$ , the volume per unit area of the bismuth;  $\pi$ , the hydrostatic pressure; and as dependent variables,  $V$ , the contact potential of the bismuth relative to the other condenser plate;  $u$ , the internal energy of the system per unit area;  $dW$ , the work per unit area done by the system in any infinitesimal change;  $dQ$ , the heat absorbed per unit area by the system in any infinitesimal change;  $t$ , the absolute temperature. It can then be shown thermodynamically that

<sup>2</sup> Existing thermo-electric data on bismuth seems to be rather sketchy.  $dE/dt$  for a bismuth-copper couple as calculated from Caswell's work (Phys. Rev. **33**, 381, 1911), is  $0.00006$  volts per  $^{\circ}\text{C}$  at  $18^{\circ}\text{C}$ .

<sup>3</sup> K. T. Compton, Phys. Rev. **7**, 209 (1916) and **9**, 78 (1917).

<sup>4</sup> Bridgman, Phys. Rev. **14**, 306 (1919).

$$\partial V/\partial v = (1/t) [(V + \partial u/\partial \rho - \rho/c) \partial t/\partial v - (\partial Q/\partial v) \partial t/\partial \rho].$$

At the melting point,  $\partial t/\partial v$  is zero, so for this temperature the equation reduces to

$$t \partial V/\partial v = -(\partial Q/\partial v) \partial t/\partial \rho.$$

Here the partial derivatives imply the constancy of the remaining independent variables. The equation may be rewritten

$$\partial t/\partial \rho = -t(V_L - V_S)/Lvd;$$

where  $V_L - V_S$  is the change in the contact potential on solidifying the bismuth (+0.02 volts);  $L$  the latent heat of fusion of bismuth (-12.64 cal/gr.);  $d$  the density of solid bismuth at its melting point (9.8 gr/cm<sup>3</sup>);  $t$  the melting point of bismuth (544°K);  $v$  the volume per unit area of solid bismuth at its melting point (a constant depending upon the size and shape of the bismuth condenser plate). Substitution of these values gives,

$$\partial t/\partial \rho = (1/v) \times 0.02^\circ\text{C}/\text{coulomb per cm}^2.$$

The smallness of the effect is evident both from the smallness of the figure itself and from the magnitude of the coulomb. Since  $V$  is independent of  $v$ , we can say that the effect should be larger the larger the ratio of surface area to volume of the solid bismuth condenser plate at its melting point.

YALE UNIVERSITY,  
June, 1927.