

THE THERMAL COEFFICIENT OF CONTACT ELECTROMOTIVE FORCE.

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IN looking back over the development of electrical knowledge we find many experimenters who have made a study of contact electromotive force. Their work has been extensive in its range and carefully done and the discussion of it has contained the defense of many widely differing theories. Yet, with all the investigation that has been given to this subject, the effect of temperature upon the potential difference of contact has received but scant attention. A few investigators have attempted to determine it but their efforts, with one exception, have proven almost fruitless. It would seem unquestionable that this temperature effect would have an important bearing upon the explanation of the original phenomenon and that its determination is worthy of extended effort.

Peculiarly enough, from the first attempt ever made to measure this temperature effect came some of the most satisfactory results. This attempt was made by Cavallo,¹ an experimenter in England, at some time previous to the year 1795. He used the very simple means of dropping a piece of metal from his hand upon an insulated tin plate, shaking it off, and then by applying the plate to a multiplier, increased the charge sufficiently to be tested with an electroscope. This process would, of course, give the contact potential difference between tin and the metal used. He found in this way, zinc positive to tin and silver; bismuth negative to tin, but lead and platinum positive to it. On heating the different metals, he found zinc, tin, silver and bismuth to become more positive, while lead and platinum became more negative. It appears then that he placed most of the metals in their proper order both as to their potential and the change of it by increased temperature, though the magnitude of this change could not be measured with his apparatus. This, of necessity, terminated his work and it was not until 1879 that further attempts were made to perform this experiment. At that time Knott² made measurements on the potential difference between two plates of the same metal, one being heated. He found iron, copper,

¹ Nicholson's Journal, Vol. I., page 184, 1802.

² Knott, Proc. Royal Soc. of Edin., No. 105, p. 362, 1879.

zinc, and tin to become negative when heated, and the effect to increase with the temperature. This change, however, was permanent, as it persisted after the metals were cooled, hence what he determined was the relation of a hot and oxidized surface to a normal one of the same metal. This then was not a true temperature effect and as his work ceased here it is of no practical value. Again in 1882, Von Zahn tried the same experiment, hoping to find it related to the Seebeck effect. His conclusions are not available.

It is evident therefore that the data given by Cavallo nearly a century before are as valuable as these later data so that it is in the results of Erskine-Murray's¹ work alone that anything dependable is to be had regarding the temperature effect. The range of his experiments was not large either in the number of metals used or in the temperature differences. No temperatures were carried beyond 70° and some to only 30°. Also the determination of the temperature was very rough, being estimated by touching with the fingers in all plates except one.

When these conditions are considered in regard to the data given by Erskine-Murray, and it is remembered that these are the only data of any consequence that have been published, it would seem that the present endeavor to measure the temperature effect would be far from mere repetition. It was undertaken with the purpose of adding to the other data upon contact electrification, some reliable values of its temperature coefficient.

The method of the following experiments was essentially the same as that used by Erskine-Murray, namely, a null method. It differs from it, however, in one respect and in that same respect from all other experiments on the potential difference of contact. Instead of using parallel plates two telescoping cylinders were used, the inner being much shorter than the outer so that it could be put well inside it. No matter what theory of contact potential difference one holds to, it is agreed that between the two surfaces there is an electrical field. This form for the two metals was chosen therefore that the metal composing the inner cylinder might be wholly in the field of the other, and not partially so as in the case of plates.

A sensitive electroscope was tried at first but discarded in favor of a Dolazalek electrometer. The sensitiveness of this instrument more than compensated for its larger capacity, and its reliability left no question as to the advantage of its use. The heating of the inner cylinder was first done by raising it into a steam jacket but it proved more satisfactory to fill the cylinder with water and use an electric heater, and this method was followed throughout.

¹ Erskine-Murray, *Phil. Mag.*, Vol. 45, p. 398, 1898, "On The Volta Electricity of Metals."

The apparatus was arranged as shown in Fig. 1. The outer cylinder (*A*) was made of commercial sheet copper about 1.2 millimeters thick and formed into two half cylinders 94 mm. in diameter and 240 mm. in length. The halves were held together by two adjustable copper bands. The base (*B*) was turned from plate copper 8 millimeters thick and the

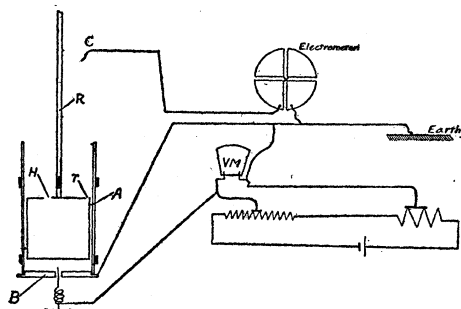


Fig. 1.

outer part thinned to 5 mm., leaving a circular table 3 mm. high in the center, over which the cylinder (*A*) fitted. This base (*B*) rested on a triangular wooden table with three screw-feet for leveling. In the center of the base was a three-millimeter hole fitted with a hard-rubber insulator. Through this passed a No. 22 brass wire, the portion below the base being coiled into a spring to make the contact adaptable.

This construction of cylinder and base allowed for easy cleaning. On removing the cylinder (*A*), the base was unobstructed and the cylinder itself being in two parts, both inside and outside surfaces were readily accessible.

The different metals investigated were made into the form of hollow cylinders as (*I*), closed at both ends. They were each 86 mm. in length and diameter, thus leaving about 8 mm. between the walls of (*A*) and (*I*). These inner cylinders were cast from the metals used, with one end left open and a plate cast for this. Both parts were turned down to about 5 mm. thickness, the top plate carefully fitted in and then spun firmly in place. When necessary the inside edge of the top plate was coated with solder to insure a strong joint, but in such cases care was taken that no solder was exposed on the outer surface of the finished cylinder. In some cases where casting was not convenient or where a very pure, metallic surface was desired, cast cylinders were electroplated with the metal to be tested.

When in use, the cylinder (*I*) was carried on the vertical rod (*R*) which slid in guides. A cord fastened to the side of (*R*) raised and lowered this

cylinder by passing over a pulley above the top guide and thence to a counter-weight hung over a second pulley at the edge of a table. On this table were placed the telescope and scale for use with the electrometer and also the voltmeter and potential divider. With this arrangement the cylinder (*I*) could be raised and lowered and the movement of the electrometer needle observed at the same time. Adjustable stop-blocks with rubber pads were placed on the rod (*R*) and were set to allow the cylinder (*I*) to be lowered as close to the base (*B*) as desired and raised to just touch the flexible wire contact (*C*) leading to the electrometer.

Each inner cylinder (*I*) had a rod of the same metal 13 mm. long screwed into the center of the top. Into this was screwed a wooden piece of about the same length and the wood in turn joined to the rod (*R*) by a connection of hard rubber. The rubber served to insulate the cylinder electrically, while the wood was found necessary to keep the rubber from being softened too much by the heat from the cylinder.

In the top of the inner cylinder (*I*) and near the center a hole (*H*) was bored large enough to admit a heater made from a quarter-inch fiber rod wrapped with No. 22 resistance wire. On the opposite side of the center and flush with the inner surface a smaller hole (*T*) was bored through which a stirrer or thermometer could be inserted. The stirrer was made of stiff wire with a strip of sheet metal soldered on one end at right angles and short enough not to strike the heater. By rolling the handle of the stirrer between the thumb and finger, the blade could be moved rapidly through the water in the cylinder at any depth. This rapid stirring allowed the cylinder to be heated very uniformly. When the desired temperature was reached the stirrer was replaced by a thermometer. The opening (*T*) was located with the purpose of bringing the thermometer as close to the outside surface as possible so that the temperature it registered would be closely that of the surface.

The potential divider was of 90 ohms resistance with a ten-ohm auxiliary of coarser wire to allow more delicate adjustment. One storage cell and these rheostats were connected in series and the potential difference between the sliding contacts on the rheostats was indicated by a voltmeter reading direct to .02 volt. Thus by estimating the tenths of a division the potential difference could be determined to .002 of a volt.

The needle of the electrometer was charged to 250 volts and with the scale distance used gave a deflection of 50 cm. to the volt. The ratio of its capacity to the capacity change on separating the cylinders (*A*) and (*I*) was such that the throw equalled what the permanent deflection would have been for the same difference of potential. Thus .01 of a volt between the quadrants gave a deflection of 5 mm. and this same

difference between the inner and outer cylinders (*A*) and (*I*) gave a throw of 5 mm. From this it is evident that a throw of 1 mm. corresponds to .002 of a volt between the cylinders, which was the smallest quantity that could be read on the voltmeter. Though contact difference of potential is usually given to .001 of a volt there was nothing found to justify this. When it is considered that a clean surface at room temperature will often vary .003 or .004 of a volt in a few minutes, and when heated, as much as .006 or .008 inside of a minute, it will be seen how useless any effort toward accuracy to thousandths would have been.

The outer cylinder was carefully prepared by thoroughly cleaning with emery cloth, both the inner and outer surface of the walls and base, until every portion was bright. The surfaces were finished with the finest emery cloth and kept clean by handling only with soft, dry cloths. This left a surface almost polished in appearance, but covered with light scratches from the very fine particles of emery. It was expected that these surfaces would have to be repolished frequently, but this was not found necessary. By allowing nothing moist to come in contact with them no change could be noticed after the elapse of two or three months. The close agreement of the readings taken on the potential difference between the cylinder and a given metal, even when these readings were some weeks apart, indicated also that there was no change electrically. For surfacing the inner cylinders the finest emery cloth was likewise used. Their appearance was as described above for the outer cylinder. This surface was taken as standard, and all measurements were upon metal surfaces so prepared.

With this outer cylinder as the metal of reference, the procedure for taking a set of readings was as follows: a cylinder of the metal to be tested was put in a lathe and turned with the emery cloth held against it. The cloth was moved very little lengthwise so that the scratches were all nearly parallel to the base. On the ends the cloth was kept stationary so that all the scratches were concentric circles. The particles of metal clinging to the cloth were removed every few seconds by snapping with the finger and a fresh piece taken frequently to insure as clean a surface as possible. This process was continued until every part was bright, then a soft cloth was rubbed over the cylinder to remove all metallic dust and particles of emery. The cylinder was then reversed to complete the polishing, the finished end being wrapped in cloth to protect it from the jaws of the lathe.

The cylinder was then screwed firmly onto the sliding rod (*R*) and usually its potential with reference to the outer cylinder was determined at that time. It was then lowered into the outer cylinder and allowed

to stand over night. As has been frequently noted before, the value immediately after polishing was not permanent, consequently sufficient time was allowed before taking a set of measurements to permit the potential difference to become more nearly fixed. On beginning a set of measurements the following day, readings were taken ten or fifteen minutes apart for a half hour or longer until the potential difference seemed quite constant. This was done because it was found that the first reading always indicated the inner cylinder more positive to the outer than was permanent. The potential difference would usually fall very rapidly at first, then more slowly to a quite permanent value in about twenty minutes. The reason for this is not apparent.

When this value was reached the temperature of the inner cylinder was taken by inserting a thermometer. The temperature of the outer cylinder was obtained by using a thermometer with its bulb resting against the base (*B*). Most of the bulb was exposed to the air but the cylinder was also, so that this seemed as good a means as was necessary to determine the average temperature throughout the cylinder. It proved sufficiently accurate to show that the radiation from the hot cylinder, though it was inside the outer one only long enough to make contact and be lifted out, continually warmed it. This increase in temperature amounted to as much as five or six degrees when the readings on the inner cylinder were taken as high as 90° .

With these records made, the heater was placed in the inner cylinder and the thermometer replaced by the stirrer. The current was allowed to flow through the heater for the time found necessary by trial to raise the temperature of the cylinder and its contained water about ten degrees. The stirrer was used continually that the whole surface of the cylinder might be heated uniformly. The heater was then removed, and the water well stirred and the stirrer removed. The potential divider was at once adjusted until on lifting out the inner cylinder and touching it to the contact point (*C*), the electrometer was unaffected. The potential difference was read from the voltmeter and a thermometer placed in the cylinder. The voltmeter reading and that of the thermometer against the outside cylinder were recorded, and that of the inner cylinder as soon as it reached its highest point. This gave the temperature of the inner cylinder immediately after the potential difference was measured so that the cooling during the time required to adjust the potential divider did not necessitate a correction. The cooling itself was never rapid enough to prevent the easy adjustment of the potential divider as, at the highest temperature, the rate was only one degree in four minutes which was usually longer than necessary to set the divider. This process

was repeated until the maximum temperature was reached. The cylinder was then brought back to room temperature in intervals of approximately 10° by taking out some of the hot water and replacing it with cold. All readings were taken after each interval in the same manner as during the heating.

All the original data were corrected as found necessary when the instruments used were tested. The fixed points of both thermometers were determined and corrections made accordingly. In addition the readings of the one used in the inner cylinder were corrected for the length of the mercury thread exposed. This was done by putting the same length of the stem as went into the cylinder, into a steam bath and noting the difference between the reading then, and that when the whole length was immersed. The readings of the cylinder temperatures were then corrected by the fractions of this difference corresponding to the length of the exposed mercury thread. With these corrections probably no temperatures are in error by more than one or two tenths of a degree. Because of the corrections to the voltmeter readings they neither end in all odd nor all even numbers, but as stated before they are accurate to only 2 units in the last place.

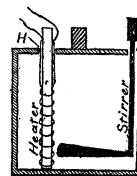


Fig. 2.

As would be expected, the temperature of the outer cylinder did not remain constant while a set of readings were being taken. This meant that the cylinder's potential changed somewhat from one measurement to the next and consequently, the potential difference observed was in error by the amount of this change. The correction to be applied would have been easily found had the coefficient of copper been known, but not being so, a proper method of determining it seemed difficult to find. It is not to be overlooked that placing the inner cylinder, at perhaps 80 or 90 degrees temperature, within a few millimeters of the outer copper base even for only a second or two necessary for each contact might easily heat the very surface of this base far above the temperature of the remainder. If then it is the surface that determines the potential difference, this effect might cause the readings to be considerably below the true value because the real temperature difference would be far less than the one measured. However, as there seemed no way to prevent this if it should exist and no way to measure it so that a correction could be applied, it is disregarded in the following.

After some consideration the following method of correcting for the temperature change of the outer cylinder appeared the most reasonable one to be applied. It was assumed that its temperature coefficient was

the same as that of the inner cylinder made of copper. Then the four most consistent sets of data on the temperatures and the potential differences of the two copper cylinders were tabulated for increasing temperature only. Each number was subtracted from the one below it in its own column, thus giving a table of the change in voltage from each temperature reading on the inner cylinder to the following one, and also whatever increase in temperature the outer cylinder had taken on. Each of these potential changes were then corrected by proportion. Thus, if from the previous reading the potential had risen .008 volt, the temperature had increased 10.8° , and the outer cylinder at the same time had become 0.6° warmer, then the increase in voltage was not due to 10.8° because the voltage is measured from a base that has risen 0.6° . The measured rise in potential was then due to 10.8 less 0.6 degree, or 10.2° . Hence, if the base had not risen in temperature the voltage change would have been $(.008 \times 10.8)/10.2$ volts. This method of correction was applied to each change of potential and then by adding these differences the readings were obtained that would have resulted, had the outer cylinder remained constant in temperature. These values were plotted and the straight line drawn that best fitted each set of readings up to about 50° temperature. The slope of the line for each set was determined and the average of these slopes taken. This average value was then considered the temperature coefficient of the outer copper cylinder. All the readings of the potential difference were corrected by the use of this coefficient for the number of degrees which the outer cylinder differed from 20° . Thus all potentials given are with reference to this copper cylinder at 20° temperature.

In getting at the correction for the change in temperature of the outer cylinder it was assumed that the relation between the voltage and temperature was a straight line for the range used, of about 30° , and the data justified this assumption. However it would not seem allowable to assume a straight line relation for the whole range. When it is considered that a satisfactory explanation of the Volta effect has not yet been set forth, it would not seem worth while to hazard a guess as to the action that underlies the effect of temperature. Hence no form of curve can be assumed, and the variations from it considered merely errors of measurement.

Besides this, another difficulty arises in the interpretation of the results obtained, because the values are not uniform and consistent but widely varying. Despite the utmost care in preparation to have the surface always the same yet the potential difference at room temperature for the same metal against the copper outer cylinder would be quite different

from one day's surfacing to another. This was not so serious a difficulty, as it was the change and not the absolute potential difference which was sought. The serious thing was the widely differing values of the temperature coefficient obtained which made a reliable determination of it most difficult. The temperature-voltage curve for a given metal, with falling temperature, neither came back accurately on the rising temperature curve, nor differed from it in any consistent way. Taken altogether, therefore, the data indicate that there is another agent or agents constantly in operation whose effects are a large fraction of those obtained from temperature. These effects are overlaid upon that due to temperature and the sum of these is all that the measurements can show. The continual action of these agents is illustrated by the following data:

Time.	Potential Difference.
10:30	+ .945
10:40	+ .923 Inner cylinder of zinc.
10:52	+ .928 Both cylinders at room temperature.
11:21	+ .948
11:38	+ .946

The first rapid lowering is the effect previously mentioned, that obtained when the inner cylinder is first brought out after standing in the outer for some time. This effect was found in all metals used and was sometimes as large as .065 volt in magnitude. That it was the result of standing inside the outer cylinder is evident because at any time while the potential was diminishing, the decrease could be checked or even reversed by letting the inner cylinder remain in the outer one for ten or fifteen minutes. After standing outside for some time the potential would reach a minimum and then go through some such variations as are given above, without any apparent regularity and from no evident cause. The cylinder merely stood in the air of a closed room illuminated by daylight and was not even approached.

It would seem then that the only way to get at the effect due to temperature alone would be to consider these extraneous effects as following the law of probability. The most nearly true value of the temperature effect would accordingly be reached by averaging. All observations on the variation of potential difference at constant temperature would tend to justify this method of interpretation, and it will accordingly be used. The curves appended give the results from most of the data obtained but certain effects peculiar to each metal will be mentioned here.

Copper.—Erskine-Murray found that copper if heated above 80° seemed to begin oxidizing or at least this was the action supposed to take place. It must be understood that it does not alter the appearance of the surface

in any noticeable way but the change is evidenced only by the fact that on cooling to room temperature the potential falls far below its value at the beginning. To assume that a slight oxidation has taken place seems the most reasonable explanation as oxidation of the surface will produce, a similar but larger effect. To locate the temperature at which this takes place in copper is somewhat difficult as in passing that point either when heating or cooling no marked change is to be noticed. It is determined only by the fact that if copper is heated above 80° its potential when cooled to room temperature again will be far below the value at the beginning, while if not heated to quite that temperature it will return practically to the original condition. The following data illustrate this action.

Potential Diff.	Temperature.	Potential Diff.	Temperature.
+.078	17.1	+.134	91.3
+.078	27.2	+.084	79.2
+.082	38.0	+.086	67.9
+.084	48.2	+.068	55.2
+.095	58.7	+.051	42.9
+.109	68.7	+.045	33.8
+.127	77.8	+.049	23.1
+.127	84.7		

Numerous trials located this oxidation point at closely 80° , the same as found by Erskine-Murray. The maximum temperature used in determining the true temperature effect is then always below 80° .

Zinc.—Zinc shows the same oxidation effect at 65° as copper does at 80° but it is much easier to locate the temperature at which the action begins. This is because at that point the potential begins to fall and increased temperature only increases the rate of fall. That this is not a change in the sign of the temperature coefficient is shown by the fact that in cooling the potential decreases continually and does not return through the values obtained in heating. In copper, it is evident that the temperature coefficient is greater than the effect of the oxidation and masks it so that the oxidation point can only be determined as described above. This point for zinc can be found from one measurement because of the sharp fall of potential when this temperature is exceeded. The following data will illustrate this action and also how the change is a permanent one.

The rapid decrease shown in Part I. of these data is due to the oxidation effect minus the temperature effect and not to the sum of the two because Part II. shows that after the potential has been greatly decreased by overheating, the coefficient is still positive as for a normal zinc surface.

Erskine-Murray did not find this oxidation point because the maximum temperature he used with zinc was only 60°.

Potential Diff.	Temp.	Potential Diff.	Temp.
Part I. +.912	18.5	+.834	23.0
+.933	26.6	Part II. +.830	23.0
+.944	35.2	+.833	30.3
+.957	43.6	+.838	36.0
+.964	51.2	+.845	41.5
+.988	58.5	+.847	46.3
+.984	66.0	+.847	50.8
+.972	71.8	+.852	55.3
+.945	88.1	+.846	48.9
+.901	74.2	+.844	42.7
+.894	61.9	+.834	34.6
+.872	42.3	+.826	20.5
+.848	29.3		

For nickel, aluminum, and tin no temperature of oxidation was found up to the maximum used, 100°. Some of the observations on aluminum and tin might indicate otherwise but the lower potentials reached in these cases by cooling were only temporary effects. After standing for

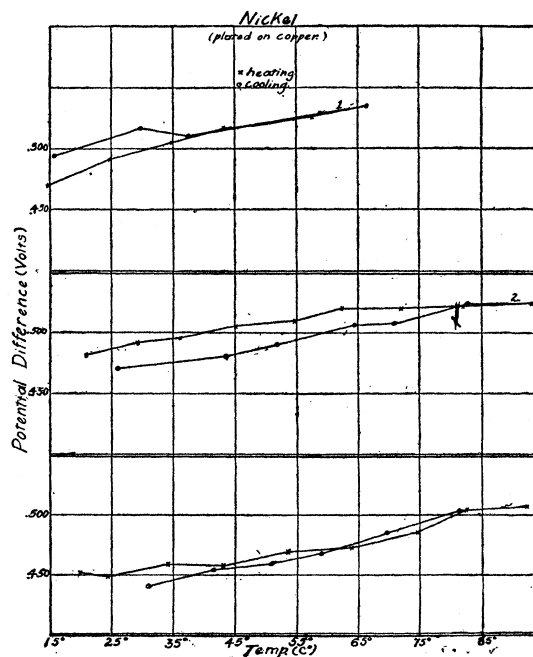


Fig. 3.

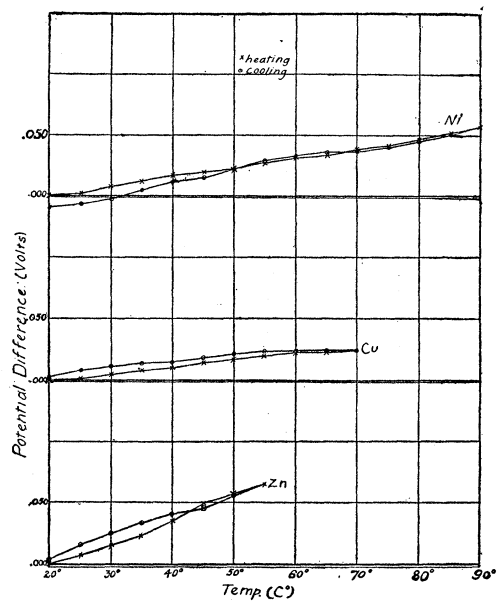


Fig. 4.

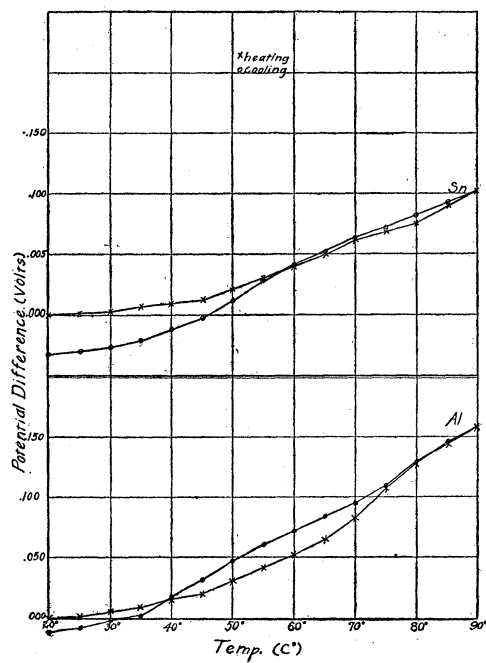


Fig. 5.

an hour or so the potential in each of these cases rose to, or nearly to, the value before heating. This rise in potential was not a change due to temperature because the final temperature of an experiment was usually so nearly that of the room that the hour or more standing did not change it by more than one or two tenths of a degree.

It is to be noted here that Erskine-Murray is undoubtedly mistaken in the value he gives for the coefficient of tin as he found it to be negative while the data here given show tin to have one of the largest positive values.

Curves.—Fig. 3 contains the curves showing three sets of observations on nickel. These are given as being typical in every way of the observation curves for all the metals investigated. It was curves similar to these that were used in obtaining the average curves of Figs. 4 and 5. These figures show the average change in potential with temperature without any reference to the absolute value of the potential. The average curve for nickel (Fig. 4) was obtained by taking from curve 3, Fig. 3, the potential for every 5° from 20° up to the multiple of 5° nearest to the maximum temperature used for nickel. All these values of the potential were subtracted from the value at the highest temperature and the differences tabulated. Tabulations were made in the same way from curves 1 and 2 (Fig. 3). The three differences of potential for each temperature when heating were averaged and the three when cooling separately. The value of the potential on any curve that stopped short of this highest temperature used with nickel was obtained by extrapolation except where this would exceed 5°. Finally the zero of the plot was shifted to coincide with the potential on the average heating curve at 20° temperature. This procedure amounted to shifting vertically all the observation curves for nickel until the upper extremities coincided and then getting the average of the curves so placed, with attention given only to the change in potential. A similar process was carried out for each metal giving the curves of Figs. 4 and 5. No curve of these plates is the average of less than three observation curves.

This shifting to have the maximum points coincide instead of the initial points, or some others, was done because the heating and cooling curves, of necessity, coincide at this point but do not at any other. With this choice both the average heating and the average cooling curves for a metal could be referred to the one reference point and they would coincide at that point and would appear as the curves from a single set of observations. In a case such as shown for nickel where curve 1, Fig. 3, has a much shorter range than curves 2 and 3, the mean of these two was taken down to the highest temperature on curve 1. This curve was

then shifted until its extremity coincided with the mean of 2 and 3 at the same temperature. The average of the three curves was then used for the remaining lower temperatures.

Each curve of Fig. 6 is the average of the heating and cooling curves for each metal from Figs. 4 and 5. Then they are so shifted that the initial points of each resulting curve coincide with the potential which is the average of all the observed values of the difference in potential between each metal and the copper base.

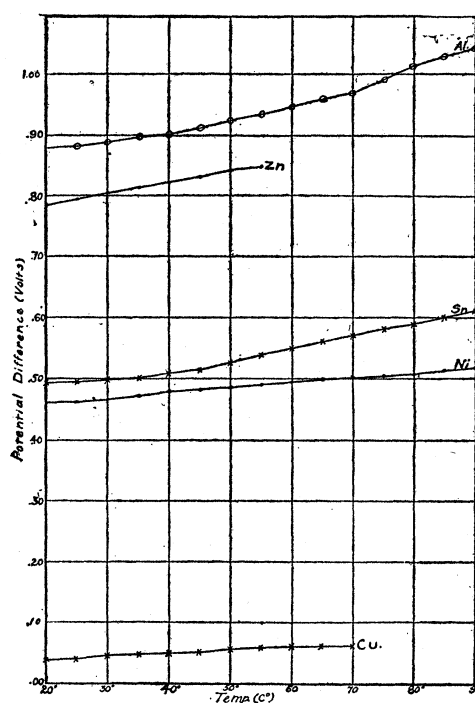


Fig. 6.

It appears that the curves for zinc, nickel, and copper are closely straight lines but those for tin and aluminum appear nearer an exponential form. The temperature coefficient for zinc, nickel, and copper is then constant over the whole range of temperature used, but for tin and aluminum it can be considered constant only for a limited range, as the numerical values below indicate.

Of course, only where the coefficient is constant would extrapolation be reasonable. Applying it to nickel, copper, and zinc, it was found that nickel and zinc would come to the same potential at -242° (C.),

copper and zinc at -371° (C.), and copper and nickel at -1200° (C.). Erskine-Murray states that the curves he has given would intersect at about the absolute zero if extended, though how rough an approximation this is he does not mention. The above results do not agree with his statements, that is, they do not in the least indicate that all metals would come to the same potential at the absolute zero.

Metal.	Temp. Range.	Coefficient (Volts per Degree).
Copper.....	20° to 70°	.00050
Nickel.....	20° to 90°	.00086
Zinc.....	20° to 55°	.0024
Tin.....	20° to 45°	.00096
Tin.....	45° to 90°	.0020
Aluminum.....	20° to 40°	.0011
Aluminum.....	40° to 70°	.0023
Aluminum.....	70° to 90°	.0036

It might be presumed that all the above procedure of averaging was hardly permissible considering the wide divergence of the original data, but it was done on the assumption of one or more uncertain, extraneous effects being present. If, then, these follow the law of probability, that is, that the errors they introduce are as great and as often positive as negative, then the method of obtaining the results given is justified. It is recognized that the amount of data on some of the metals was rather meager to be handled in this way, but if the assumption of extraneous effects is correct, this method would give the most probable values of the measured quantities, no matter how few the observations. It is believed that the most reasonable method of consideration was used and that the data here presented offer some dependable values of the change of contact potential difference with temperature.

It is hoped later to give further data on other metals and perhaps with a wider range of temperature and also some other aspects of the subject may be considered at that time. In conclusion I wish to thank Professor Sanford and Professor Rogers for their interest in the problem and their timely advice throughout the experimental work.