

THE PHYSICAL REVIEW.

THE TEMPERATURE COEFFICIENT OF RESISTANCE OF METALS AT CONSTANT VOLUME AND ITS BEARING ON THE THEORY OF METALLIC CONDUCTION.¹

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IT is a well established fact that, excepting at very low temperatures, the resistance of pure metals increases very nearly as a linear function of the temperature.² If we grant the postulate that the electric current consists in a transfer of electricity in the form of discrete charges, it obviously follows that a change in resistance must be due either to a change in the number of carriers or to a change in their speed. In the theoretical treatment of the problem of metallic conduction it is usually assumed or implied that the number of carriers in a metal is independent of the temperature. This assumption greatly simplifies the treatment of the problem, but, as will be shown below, such an assumption is not always justified.

If the current in metals is carried by the negative electrons, then some manner of equilibrium must exist between the negative electrons, the positively charged residuals, and the neutral molecules. To what extent the metal atoms are dissociated is still an open question. Unless the dissociation is very high, the influence of temperature on the dissociation process must make itself felt; but whether the dissociation increases or decreases with increasing temperature is a question that can not be answered *a priori* either in the affirmative or negative. On the one hand, as in the case of many homogeneous equilibria with which we are familiar, the dissociation may increase with increasing temperature,

¹ Contributions from the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, No. 99.

² There are numerous cases where the resistance-temperature curve passes through a minimum instead of approaching a zero value as the temperature approaches the absolute zero. This abnormal course of the curve is doubtless due to the presence of impurities. The nature of the phenomenon underlying the action of impurities on the resistance is as yet unknown.

while, on the other hand, metallic systems may behave analogous to electrolytic solutions, in which case the dissociation as a rule decreases with increasing temperature. It is to be borne in mind that the metals constitute highly condensed systems and that therefore a very small change in physical condition may have a large influence on the equilibrium in question. Thus, for example, temperature change is accompanied by change in density and it will be shown below that the change in the resistance of metals with temperature is in a large measure a consequence of the accompanying density change.

If the conduction of the current is due to electrons having a considerable freedom of motion in the body of the metal, then, other factors remaining equal, the resistance should increase with increasing temperature, since the frequency of collision increases with temperature according to the kinetic theory. The general form of the resistance-temperature curve of metals is therefore in harmony with the usual theory of metallic conduction. The fact should not be overlooked, however, that the observed resistance change is a resultant effect of all factors concerned among which are included effects due to volume change.

It is evident that with decreasing volume, the number of collisions per unit of time will increase and that the resistance will therefore increase. On the other hand, in most cases, it is found that the resistance actually decreases. The number of carriers under these conditions must therefore increase by an amount more than enough to compensate the decrease in resistance due to the increase in the number of collisions.

In determining the influence of volume change on the number of carriers present in a metal the obvious course is to determine the resistance of the metal at different temperatures keeping the volume constant. Without going into a detailed discussion, it is evident that with increasing density of a metal the number of carriers may be expected to increase. For example, in the case of mercury we know that the vapor is a non-conductor. If we were able to pass mercury through the critical state, we would doubtless find a continuous gradation of conducting power all the way from that of metallic liquid mercury to non-conducting mercury vapor. Similarly, when a metal is dissolved in a non-metallic solvent, we have a continuous gradation of conductance from that of a highly conducting metal to that of a poorly conducting solution.¹ So also, metals which melt with decrease of density increase in resistance on melting, while metals which melt with increase of density decrease in resistance on melting.

¹ In this case, however, the condition approached as the metal becomes highly attenuated is materially modified by the presence of the solvent medium in which the metal is imbedded. Kraus, *Trans. Am. Electroch. Soc.* 27, 119 (1912).

Data are available for calculating the resistance-temperature coefficient at constant volume for a number of metals. With the exception of mercury, all are solids. Taking into account the crystalline structure of solid metals, the influence of pressure on their resistance can not be interpreted with certainty. In the case of mercury, however, we have a metallic system of very simple molecular structure the results with which may be interpreted unambiguously if our kinetic conceptions regarding metals have any foundation in fact.

The temperature coefficient of resistance of a metal at constant volume is given by the equation:

$$\frac{\partial R/R}{\partial T} = \frac{dR/R}{dT} - \frac{\partial R/R}{\partial p} \cdot \frac{\partial v/v}{\partial T} \bigg/ \frac{\partial v/v}{\partial p}.$$

The values of the last four coefficients have previously been measured and found to be as follows for liquid mercury at 20° and at one atmosphere pressure:

$$\begin{aligned} \frac{dR/R}{dT} &= 8.9 \times 10^{-4}; & \frac{\partial R/R}{\partial p} &= -3.3 \times 10^{-5}; & \frac{\partial v/v}{\partial T} &= 1.82 \times 10^{-4}; \\ & & \frac{\partial v/v}{\partial p} &= -3.8 \times 10^{-6}. \end{aligned}$$

From these we find by calculation

$$\frac{\partial R/R}{\partial T} = -6.9 \times 10^{-4}.$$

This result shows that when liquid mercury at 20° is heated at constant volume its resistance *decreases* by 0.069 per cent. per degree, whereas when heated at constant pressure its resistance increases 0.089 per cent. per degree.

The result obtained above for the resistance-temperature coefficient of liquid mercury at constant volume is very significant and admits of only one interpretation, namely: *the increase in resistance of liquid mercury with increasing temperature is due to its decrease in density.* The total resistance change due to density change is 0.156 per cent. per degree.

Since the influence of increasing temperature, according to kinetic conceptions, is to increase the resistance of a metal, owing to reduction of the mean free path, and since at constant volume the resistance of liquid mercury decreases with increasing temperature, it follows that *at constant volume the number of carriers in liquid mercury increases with the temperature.*

If carriers are present in metals at all, they must be in some manner of equilibrium with each other and with the neutral molecules from which

they are derived. This equilibrium is controlled by two main factors, namely: density and temperature, and these two factors influence the equilibrium in opposite directions. The dependence of the equilibrium on temperature and density is in entire conformity with our knowledge of equilibria in general and in particular with electrolytic equilibria. For example, the enormous decrease in the dissociation of electrolyte with increasing temperatures is in very considerable measure due to the decrease in the density of the solvent with increasing temperature. This is well illustrated by solutions of potassium iodide in methyl alcohol beyond the critical point where, for constant concentration of the electrolytes, the conductance increases enormously with increasing density of the solvent.¹

The magnitude of the effect of density on the conductance of mercury has a very important bearing on the question as to the number of carriers present in liquid mercury. In many cases there has been a tendency to assume that the number of electrons present in a metal is of the order of the number of atoms present. From the foregoing data, we see that on heating liquid mercury at constant volume the number of carriers increases at least 0.07 per cent. per degree.² Such an increase in the number of carriers could not result if the metallic atoms were even approximately completely ionized. We must therefore conclude that *only a small fraction of the atoms of liquid mercury are ionized and furnish carriers for the current.*

The foregoing considerations would appear to demonstrate the necessity for considering the equilibrium between the charged carriers in a metal and the neutral atoms in any theory of metallic conduction which is founded on kinetic considerations. To do this, however, presents great difficulties. It need only be recalled that the corresponding problem is as yet only very incompletely solved in the case of ordinary electrolytes, where the conditions apparently are much simpler than in metals. The whole question of equilibria in systems of charged particles requires fundamental study and there is little hope that the problem of metallic conduction will be solved from a theoretical standpoint until such studies are forthcoming. The lack of tangible results in the problem of metallic conduction and of the metallic state in general is ample proof of the inadequacy of present day conceptions respecting this subject.

BOSTON, March, 1914.

¹ Kraus, this Journal, 18, 101 (1904.)

² If we assume that the decrease in translatory speed is proportional to the square root of the absolute temperature, the resistance decrease per degree due to this cause is 0.18 per cent. per degree. The increase in the number of carriers on this basis would therefore be 0.25 per cent. per degree.