

tion series of alloys. And in the case of copper-antimony alloys he would similarly, from the mere inspection of the freezing-point curve, infer the general plan of constitution described in § 126, p. 148. In the first and the third case the direction of the V-shaped branches would indicate approximately the composition of the eutectic or eutectics, and in the third case the composition of the definite compound. Here then are the critical points indicated approximately by a very few and very easy observations. The investigator is in a position to "throw himself on the hinge," and examine immediately the alloys at and near these critical points, for these are the ones which are likely to have the maxima or minima of the various useful properties.

CHAPTER VII.—VARIATIONS IN ELECTRIC CONDUCTIVITY AND OTHER PROPERTIES OF SERIES OF ALLOYS

129. ELECTRIC CONDUCTIVITY. — While the manner in which the other properties, for instance, the electric conductivity, of a series of alloys, vary from one end of this series to the other at the room-temperature, in short the electric-conductivity-composition curve, also may throw light on the constitution of the alloys of that series, yet its indications are far less instructive than those of the cooling and freezing-point curves, *i. e.*, of our thermal study. These latter tell us the history of each individual alloy as it traverses a long range of temperature, and record each birth and transformation within it; while the electric-conductivity-composition curve for given temperature gives simply the conductivity of the cold alloy, (giving if this is composite the average conductivity of its constituents) with no suggestion of the genesis of those constituents.

But were our study of electric conductivity parallel with our thermal study, it should give indications of great value. Le Chatelier has already used this method.* Let me explain my meaning. Instead of determining simply the conductivity in the cold of several different alloys of a given series, let us fol-

* Le Chatelier, "Sur la Résistance Électrique des Alliages" (*Contribution à l'Étude des Alliages, Commission des Alliages, 1896-1900, p. 413*).

low for each of those alloys the variations in conductivity which occur as it cools from the molten state downwards to the cold. With a pair of autographic galvanometers, one recording time and temperature, *i. e.*, the cooling curve, and the other recording simultaneously time and conductivity, we should have two records of the genesis of each constituent of the alloy, one the thermal effect of that genesis, the other the variation in electric conductivity which the birth of the little stranger introduces. Then from these two sets of curves we should plot a general diagram on the principle of the freezing-point curve, with temperature as ordinate and composition as abscissa, drawing on this, as on our freezing-point curve, the loci of the critical points in the temperature-conductivity curves.

The principle of such an autographic arrangement is extremely simple. The beam of light from the galvanometer mirror moves to the right and left in a horizontal plane, following, if the galvanometer indicates temperature, the varying thermo-electric power, *etc.* To obtain an autographic record of these deflections of the galvanometer it is simply necessary to focus the beam of light upon a photographic film moving in the vertical plane. This film may be rolled on a cylinder, the axis of which is at right angles with the beam of light; or, as is in my opinion better, it may be on a photographic glass plate, the surface of which is normal to the beam of light, or more accurately, to the beam in its position of mid-travel. The plate of glass moves vertically, and the resultant of this vertical motion together with the horizontal motion of the beam of light is a curve, for instance a cooling curve, every inflection of which indicates a variation in the thermo-electric current passed through the galvanometer, due in turn to a variation in the rate of cooling of the substance under observation.

In order that the value of our results should approach that of our thermal study, the range of temperature covered by our conductivity determinations should start from a point above the freezing-point of the alloy, and should include the whole range of freezing in addition to the range between this and the room-temperature, because it is in the freezing-range that most of the constituents of our alloys come into existence. To determine the conductivity of molten and of solidifying alloys would not be easy; but the difficulties are not insuperable.

130. THERMO-ELECTRIC POWER. — This same method should apply with great ease to the study of thermo-electric power. Here as before, with two autographic galvanometers we should get at the same time (1) cooling curves, telling us of the thermal effect of each transformation, and (2) thermo-electric-power-time curves; and from these we should construct thermo-electric-power-temperature curves, telling us how the products of the several transformations differ in thermo-electric power. Then as before, constructing a diagram with temperature as ordinate and composition as abscissa, and drawing on it the loci of the critical points for thermo-electric power, we should have a reinforcement of the teachings of the freezing-point curve.

The value of this method for thermo-electric-power study is of course limited by the fact that it must stop short of the temperature at which the alloy studied reacts chemically on the metal used as the other member of the thermo-electric couple. How serious this limitation would be remains to be seen. Where it confines us to temperatures below the lower freezing-point, the limitation would be very serious, because it would exclude us from a most important critical range. But for the study of transformations which, like those of iron and steel, occur within the solid metal well below the freezing-point, the method should be of very great value.

Each of these methods promises a rich and easily won harvest.

The same is true of the coefficient of dilatation, in the study of which Le Chatelier has already reached important results.*

131. ELECTRIC CONDUCTIVITY AT THE COMMON TEMPERATURE. — Returning to the electric conductivity of the cold alloys, a word may not be amiss as to the way in which it varies throughout different classes of series of alloys. This subject will be treated in §§ 132 to 135, pp. 154 to 159.

132. SOLID SOLUTIONS. — If all the alloys of the series, say of gold with silver, were to consist of solid solutions, of silver in gold or gold in silver, then since the properties of our familiar liquid solutions in general vary progressively and without abrupt

* Le Chatelier, "Sur les Propriétés des Alliages" (*Contribution à l'Étude des Alliages, Commission des Alliages, 1896-1900, p. 387*).

changes or critical points as the degree of concentration increases, *i. e.*, as we pass from one end of the series to the other; so here we should expect the electric-conductivity curve to be a smooth one throughout, without inflections or critical points; and this Matthiessen found to be the case. (Fig. 54.)

133. SERIES EUTECTIFEROUS THROUGHOUT. — But what shape of electric-conductivity curve should we expect in case two metals are absolutely insoluble in each other? Let us for the moment assume that this is true of lead and tin; then every alloy of these two metals would when cold consist of a eutectic plus crystals of pure lead or pure tin, according to which of

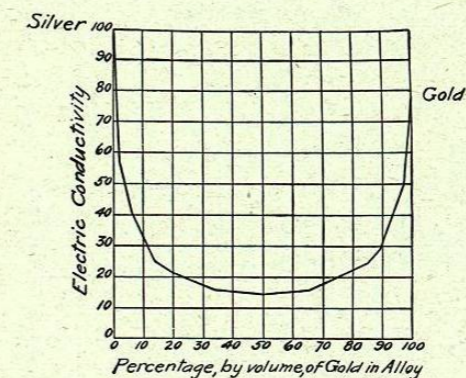


Fig. 54. Electric Conductivity Curve of the Silver-gold Alloys. Matthiessen, *Rept. British Assoc.*, XXXIII, p. 46, Pl. V, 1863.

these two metals was in excess over the eutectic ratio; and the eutectic itself would consist of interstratified plates of pure lead and pure tin. The current in crossing such an alloy would have to cross in effect simply a mechanical mixture of the crystals of pure lead and pure tin, and were there no breaks of continuity the conductivity of the whole should be the mean of that of pure lead and pure tin. This inference should not be affected in the least by the fact that certain of these crystals are grouped together in the form of the eutectic, which for our present purpose is simply a special form of mechanical mixture. In short, the electric-conductivity curve should be a straight line, and this Matthiessen found it to be for the lead-tin and for several other groups of alloys. (Fig. 55.)

But unless we were quite sure that the conductivity curve was really a perfectly straight line, it would not tell us whether the alloys were solid solutions or mechanical mixtures, because the electric conductivity of the solid solutions of two metals in each other might differ only very slightly from the mean conductivity of those metals, and indeed might be exactly that mean; in other words, the smooth electric-conductivity curve of a solid-solution series of alloys might deviate only very slightly from a straight line, and conceivably could be exactly a straight line. Here then the teaching is inconclusive.

134. SERIES OF LIMITED MUTUAL SOLUBILITY: BISMUTH-TIN TYPE, PARTLY EUTECTIFEROUS. — We have seen in § 60, p. 68, and Fig. 49, p. 136, that these series, while eutectiferous in

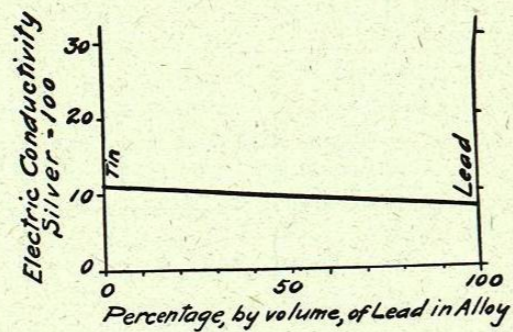


Fig. 55. Electric Conductivity Curve of the Lead-tin Alloys. Matthiessen, *Rept. British Assoc.*, XXXIII, p. 46, Pl. V, 1863.

the middle, are solid solutions at their ends. The copper-silver alloys belong to this general class, but the solid solution part of the range is very short. Apparently all argentiferous copper containing more than about 1 per cent of silver and all cupriferous silver containing more than about 1 per cent of copper are eutectiferous. The electric-conductivity curve of this series, Fig. 56, appears to reflect the solid-solution part of the series by the smooth curve or nearly straight line at either end of the diagram. Moreover, Fig. 31, p. 76, shows us that in the eutectiferous part of the diagram, the successive layers of such alloys, taken at the moment of their deposition, consist of (1) an unsaturated solid solution progressively approach- ing sat-

uration, so that each layer in it contains a larger proportion of the dissolved metal than the preceding layers (part BB'), plus (2) a saturated solid solution, the composition of which should vary slightly from layer to layer as, with the fall of temperature, the saturation-point gradually shifts (part $B'C$), plus (3) the eutectic (part CD). And, if part of each of these three divisions persists, *i. e.*, if diffusion has failed to efface this initial heterogeneity but has left part of it, then the electric-conductivity curve, even in the eutectiferous region of the diagram, need not be a straight line, but might have a critical point at the eutectic composition. For as we pass to the left of this point we have

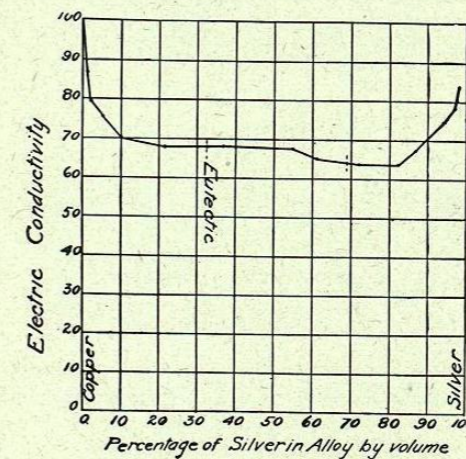


Fig. 56. Electric Conductivity Curve of Silver-copper Alloys. Matthiessen, *Phil. Trans. Royal Soc.*, CL, p. 170, 1860.

the eutectic plus (1) a saturated and (2) a progressively varying solid solution of copper in silver, for which, at the right of the eutectic, like solutions of silver in copper are substituted. Thus we have two excess-substances at either end, if diffusion has not effaced the initial heterogeneity. Now clearly the progressively increasing quantities of these solutions of copper in silver on the left should affect the electric conductivity differently from like quantities of like solutions of silver in copper on the right; hence the lines at right and left of the eutectic should be differently inclined; hence in short, at the eutectic composition there should be a critical point.

For like reasons there might be critical points between the non-eutectiferous end-parts of the curve, and the eutectiferous range; and this latter range might itself be curved, and indeed a complex curvature may be expected, since each of the two excess-substances, the saturated and the unsaturated solid solutions at either end, may be of variable composition and quantity.

In view of this complexity it is small wonder that the conductivity curve, Fig. 56, tallies poorly with the constitution as we have actually learned it by means of the microscope, and that the teachings of conductivity in general in the cold are of little value compared with the story which the microscope and the cooling and freezing-point curves tell.

135. SERIES OF WHICH ONE MEMBER IS A DEFINITE CHEMICAL COMPOUND. — As pointed out in § 126, p. 148, such a series

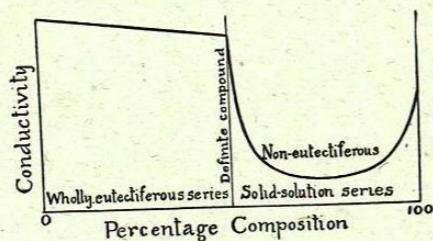


Fig. 57. General Shape of Electric Conductivity Curve of a Series of Alloys of two Metals, of which series one member is a definite chemical compound, which in turn forms with one metal a wholly eutectiferous series of alloys, and with the other metal a solid-solution series.

as a whole really consists of two distinct series, (1) metal *A* plus this definite compound and (2) metal *B* plus this compound. Each of these series should have its own distinct diagram, the shape of which should be governed by the principles just explained; and there should be a critical point at the composition of the definite compound, *i. e.*, at the junction of the two diagrams. Thus, if both series are eutectiferous from end to end, each diagram should be a straight line, and the diagram of the whole should be two straight lines meeting at a critical point, the composition of the definite compound. If both are solid solutions, each should have a smooth curve, and as before these curves should meet at a critical point, the composition of the definite compound. If one series consisted of solid solutions

and if the other series was eutectiferous throughout, the curve should be of the shape shown in Fig. 57; *etc., etc.*

We have now seen (§§ 131 to 135, pp. 154 to 159) the several different families of composition-conductivity curves which should accompany the different types of constitution.

Conversely, on finding the shape of the conductivity curve of a new series of alloys, we may apply like reasoning, and deduce the probable constitution of the series; which we then proceed to verify with the microscope. How close correspondence will actually be found remains to be shown.

136. OTHER PROPERTIES. — It requires little reflection to see that what has been said as to the curves of electric conductivity may be expected to apply to those of thermal conductivity, hardness, density, dilatation and many other properties.

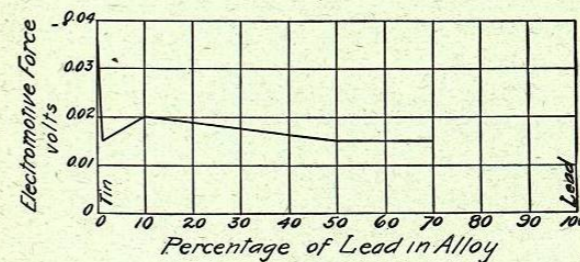


Fig. 58. Electromotive Force of the Lead-tin Alloys. Laurie, *Journ. Chem. Soc.*, LV, p. 677, 1889.

137. ELECTROMOTIVE FORCE. — For the same reasons as in the case of the other physical properties, the electromotive-force curve should be a smooth one if the two metals form a solid-solution series of alloys with each other. But if the solid alloys are eutectiferous there is an obvious reason why the curve should be of a very different family.

The lead-tin alloys, for instance, may be regarded as mechanical mixtures of sheetlets of lead and of tin, in the form of the eutectic plus sheetlets of the excess-metal (see § 48, p. 62). If now we determine the electromotive force of these alloys in a slightly acid stannous chloride solution, using a sheet of the alloy as one pole and a sheet of lead coated with lead chloride as the other pole, then, since only the sheetlets of tin in the alloy should cause electromotive force, and since the sheetlets of lead should be inert, the electromotive force should be the same whether the

lead electrode, and not on the extent of surface offered by those alloy contained much or little tin, since it depends on the difference of potential between the tin sheetlets in the alloy and the sheetlets. And such is the electromotive-force curve of these alloys found by Laurie (Fig. 58).*

CHAPTER VIII.—THE METALLOGRAPHY OF IRON AND STEEL

138. INTRODUCTION.—Let us first survey in a general way the different classes of iron and steel, their constitution, and their properties. Let us next consider the genesis of that constitution, and in Chapter IX the correspondence between the changes in that constitution, *i. e.*, the transformation in the solid metal, and the prominent methods of heat-treatment.

139. GENERAL SURVEY.—What are the iron and steel of commerce and industry? Examined under the microscope they prove to be composite or granitic substances, intimate mechanical mixtures or conglomerates of microscopic particles of certain quite distinct, well defined, simple substances, in widely varying proportions. The structure of these conglomerates is of the type shown in Fig. 1, p. 3.

The chief of these substances are,

(1) pure (or nearly pure) metallic iron called *ferrite*, soft, weak, very ductile, with high electric conductivity, and in general like *copper* in its qualities, color excepted,

(2) a definite iron carbide, Fe_3C , called *cementite*, which is harder than *glass* and nearly as brittle, but probably very strong under gradually and axially applied stress.

* We may regard these alloys as mixtures not of chemically pure lead and tin, but of sheets of slightly plumbiferous tin and of slightly stanniferous lead. From the drop of electromotive force as we pass from pure tin to tin containing one per cent of lead, and the substantial horizontality of the curve to the right of this (for the deviation appears to be well within the limits of experimental error), it appears that one per cent (or perhaps even less) of lead suffices to saturate tin; so that the composition and hence electromotive force of the sheetlets of tin is independent of the total quantity of lead present provided this reaches one per cent, or the perhaps smaller quantity needed to saturate the tin.

Take immediately as the most important fact, the most essential part of the skeleton about which the various phenomena are to be grouped, that the great classes of iron and steel of chief value to the engineer and probably to the world at large, are essentially intimate mixtures or conglomerates of these two strikingly different microscopic constituents, ferrite extremely soft and ductile, cementite extremely hard and brittle, the former like copper, the latter like glass. The properties of several of the classes may indeed be influenced, and very profoundly, by thermal and mechanical treatment, and by the presence in certain of them of slag or of graphite; but the fact on which our attention should be concentrated at first is this, that the difference in properties between the different industrial classes of iron and steel are due chiefly to differences in the ratio which the ferrite bears to the cementite.

What has just been said does not apply, it is true, to what is called "hardened steel," which consists not of ferrite and cementite but essentially of austenite, as will be explained shortly; but it does apply to the great industrial classes of wrought iron and of steel such as ship, rivet, fencing-wire, tube, rail and tin-plate steel, and indeed all structural steels whether for plates, beams, eye-bars, angle-irons or any like object.

The steels which are especially soft and ductile, *e. g.*, the rivet and boiler-plate steels, consist chiefly of the soft, ductile, copper-like ferrite, as do those with very high electric conductivity, such as telegraph and telephone wires. In these steels the proportion of cementite may not exceed one per cent of the whole, the rest consisting almost wholly of ferrite.

The harder steels like rail steels, which are called upon to resist abrasion, *e. g.*, the grinding action of the car-wheels intensified by the presence of sand between wheel and rail, have a much larger proportion of cementite. About 93 per cent of their total mass is made up of ferrite and the remaining 7 per cent consists of cementite. This quantity of cementite suffices to increase greatly the resistance to abrasion, while the loss of ductility which it causes, though very marked, is not dangerously great.

Naturally, as the proportion of cementite in steel increases and that of ferrite decreases, the ductility diminishes continuously and the hardness increases continuously; the tensile strength.