CHAPTER VI.—COOLING CURVES AND FREEZING-POINT CURVES OF SERIES CONTAINING DEFINITE CHEMICAL COMPOUNDS

126. SERIES OF WHICH ONE ALLOY IS A DEFINITE CHEMICAL COMPOUND.—The copper and antimony alloys, Fig. 51, p. 150, lead us a step farther. These two metals form a definite chemical compound, antimonide of copper (Cu_8Sb_3?), represented by the ordinate PA'; so that the series of their alloys really consists of two parts, those in which copper is in excess over this ratio and those in which antimony is in excess over this ratio. If copper is in excess, as in the left-hand part of Fig. 51, we have in effect alloys of copper with antimonide of copper. If, as in the right-hand part of that figure, antimony is in excess, we have in effect alloys of antimony with antimonide of copper. We naturally expect a critical point in the freezing-point curve at the composition of this antimonide of copper, and indeed in the corresponding curves for the various physical properties, because a given addition of copper to copper-antimonide should produce an effect different from that which a like addition of antimony to the copper antimonide should cause. It so happens that each of the two series of alloys, copper plus copper-antimonide and antimony plus copper-antimonide, is eutectiferous, so that each series has its own eutectic. Thus taking the series of copper-antimony alloys as a whole it presents two eutectics, one rich in copper,

in the act of freezing. It is the composition of these latter layers thus removed out of the molten mother-metal which determines the rapidity of its enrichment. And, while it is quite true that the frozen layers, made homogeneous through diffusion, reach saturation at the time when the mother-metal reaches the eutectic composition and freezing-point; it is also true, as shown in Fig. 49, that the composition of the layers in the act of freezing, which must necessarily be intermediate between that of the already frozen mass and that of the mother-metal, must cross the saturation-point line Daa' before the mother-metal reaches B.

Indeed, it is because I have actually found that both these fallacies confused even intelligent post-graduate students, that it has seemed worth while to write the present section.

These fallacies show us how dangerous is the convenience of such graphical illustrations as that of the temperature-composition curves of the frozen layers made homogeneous. The student readily loses sight of the assumption on which alone these curves are true.

B, the other rich in antimony, B'. In any given alloy of course only one of these eutectics could be present. The eutectiferous alloys rich in copper, represented by the region aBc, contain the eutectic B rich in copper; while the eutectiferous alloys rich in antimony, represented by the range $a'B'c'$, contain the eutectic B' rich in antimony. (As usual, equilibrium is here assumed to exist.)

Taking four typical alloys at random, those containing 20, 38, 60 and 80 per cent of antimony respectively, their constitution would be as follows:*

PER CENT ANTIMONY	EUTECTIC	EXCESS-METAL
20	B, Copper and copper-antimonide	Copper (containing antimonide dissolved in it)
38	B, Copper and copper-antimonide	Copper-antimonide (containing copper dissolved in it)
60	B', Antimony and copper-antimonide	Copper-antimonide (containing antimony dissolved in it)
80	B', Antimony and copper-antimonide	Antimony (containing copper-antimonide dissolved in it)

127. SERIES OF WHICH SEVERAL MEMBERS ARE DEFINITE CHEMICAL COMPOUNDS. — The case of gold-aluminium alloys is still more complicated, for there is evidence tending to show that gold and aluminium form no less than five different definite chemical compounds. Hence the complexity of their freezing-point curve, Fig. 52. These alloys are of special interest from the fact that one of them, $AuAl_2$ (H), a purple alloy discovered by Sir William Roberts-Austen, is not only much more infusible than the mean of gold and aluminium, but has a melting-point very close to that of gold.†

* Roberts-Austen and Stansfield, *Rapports Présentés au Congrès International de Physique, Réuni à Paris en 1900*, I, p. 394, Fig. 19. A. Stansfield, private communication, January 31, 1902.

The matter is complicated still farther by the fact that some of the alloys rich in copper undergo after solidification the transformations represented by the line c_2c_4, a complication which, to simplify our present study, we may leave out of consideration.

† There is a prevalent belief that the melting-point of an alloy is always below the mean of the melting-points of the constituent metals. This, however, is not necessarily true. Indeed some alloys have a melting-

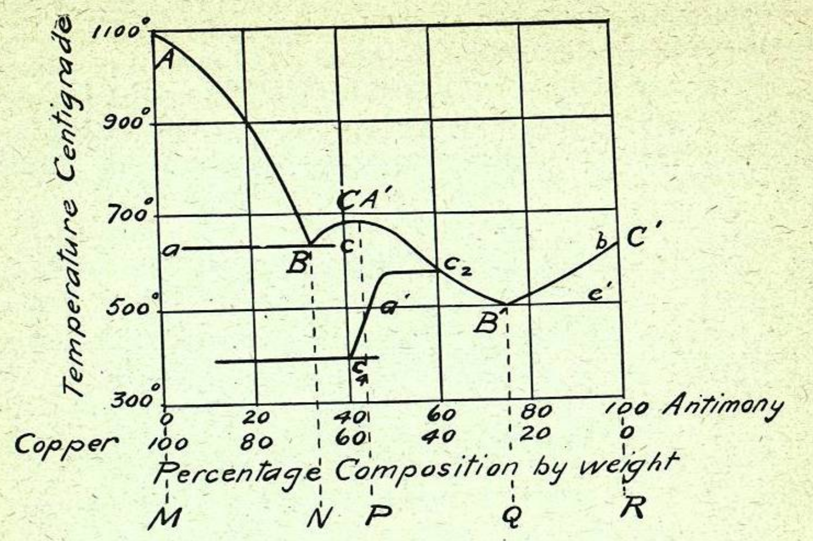

Fig. 51. Freezing-point Curve of Copper-antimony Alloys.
Roberts-Austen and Stansfield, *Rapports Présentés au Congrès International de Physique Réuni à Paris en 1900*, I, p. 394, Fig. 19.

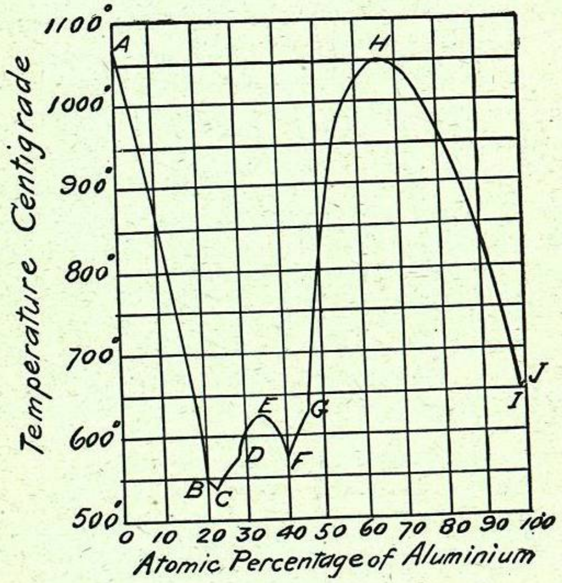

Fig. 52. Freezing-point Curve of the Gold-aluminium Alloys.
Heycock and Neville, *Phil. Trans.*, 194 A, p. 201, 1900.

In still other cases, the definite chemical compound which two metals form may itself form a eutectiferous series with one of those metals, but a non-eutectiferous or solid-solution series with the other. The freezing-point curve of the former series, occupying one end of the diagram, should be of the familiar underscored V-shape, while that of the latter covering the other end of the diagram should be smooth; so that the diagram as a whole should have the general shape shown in Fig. 53.

128. Meaning of Superior Analysis. — We can now see what is meant by saying that the study of the constitution of alloys, for instance by means of their freezing-point curves, gives us a method of superior analysis. For instance, if one

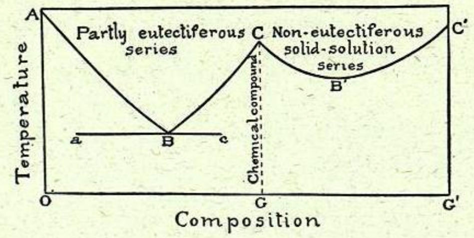

Fig. 53. Suppositious Freezing-point Curve of a Series Containing a Definite Chemical Compound and Eutectiferous at One End but not at the Other.

should determine the cooling curves of pure lead, pure tin and the lead-tin alloys with say 20, 50, 70, and 90 per cent of tin, and should plot from their freezing-points the freezing-point curve of the series, he would find that it was of the family of Fig. 24, and he would at once have ground to believe that they formed a single series, eutectiferous through at least most of its length, and free from any definite chemical compound. Examining a similar series of gold-silver alloys he would have ground to believe that they formed throughout a solid-solu-

point higher than that of either of the constituent metals. Thus C. R. Alder Wright reported in 1892 that, in case of the alloys of antimony and aluminium, "with certain proportions alloys are formed exhibiting melting-points much above those of either antimony or aluminium." (*Jour. Soc. Chem. Indus.*, XI, 493, 1892.)

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 follow 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.

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

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.