

rable with the chemical compounds with which we are familiar in common inorganic chemistry; or (3) definite chemical compounds of a metal with a metalloid, such as the iron carbide ( $\text{Fe}_3\text{C}$ ) called *cementite*, which plays a very important part in the metallography of iron and steel; *etc., etc.* One aim of microscopic examination is to ascertain whether the alloy is of this porphyritic type and consists of different distinct crystals of definite chemical composition, or whether it is of the obsidian type consisting solely of a solid solution; or whether it contains both definite minerals and also solid solutions. The further aim is to distinguish the shape, size and the properties both physical and chemical of these various components.

The first step in general is to polish the metallic mass so that a large field may be visible under high magnification. The second is to subject it to an attack, either chemical or mechanical, which will affect the different constituents in different ways, and thus enable us not only to distinguish one from another but also to determine the shape, habit and properties of each. Of these methods five deserve mention here. Of these the first three are chemical, the fourth mechanical, and the fifth partly chemical and partly mechanical. They are as follows:

(a) *Simple attack* by some solvent such as nitric acid, iodine or licorice, a method which we owe to Sorby.\* Such a method may dissolve away one component more than another, or color one component differently from another, or it may simply eat away the joints between adjacent grains of crystals, and thus disclose their shape when they are later examined under the microscope.

(b) *Weyl's Method*, which has received great development in the hands of Charpy, is to attack by means of a solvent under the influence of a very gentle electric current. Charpy uses as the two poles (1) the alloy which is under examination and (2) at times platinum and at times another alloy of a composition so nearly similar to the first that the electro-motive force shall be very feeble, and therefore that the attack shall be extremely gentle. This gentleness is needed in all our methods. The particles which we wish to recognize and identify are so extremely minute, and often so feebly held in place, that we must use the

\* *Journal Iron and Steel Institute*, 1887, I, p. 256.

utmost gentleness, whether in dissolving or in mechanically separating one from the other, lest we remove mechanically those components which we seek to leave untouched.

(c) *Heat-Tinting*. The different constituents may be differently colored by gently heating the polished surface, so that the more oxidizable ones become covered with oxide tints. This method has been used by Guillemin, and later by Stead,\* with most valuable results.

(d) *Relief Polishing*. Beyond these we have the mechanical methods, of which Osmond's "relief-polishing" is very important. By prolonged very gentle polishing, the softer constituents of a conglomerate alloy are worn away, leaving the harder ones standing in relief.†

(e) *Osmond's "attack-polishing"* combines the chemical and mechanical methods happily. He polishes the surface while it is exposed to a reagent which attacks or colors the different constituents differently, so that disintegration by the reagent and removal by the rubbing go hand in hand.

## CHAPTER II.—COOLING CURVES

10. PHYSICAL PROPERTIES OF INDIVIDUAL ALLOYS. COOLING CURVES. — If we were studying the alloys of two metals, such as the alloys of silver with gold taken as a group, or those of lead with tin taken as a group, we should of course examine many of these alloys individually, in order to see to what degree it had the property toward which our study was particularly directed, be it hardness, tensile strength, conductivity, or whatever. But besides this, in order to learn the constitution of that individual alloy, we should in particular determine with great care its "cooling curve." Let an example explain what a cooling curve is. If we place a thermometer in a flask of pure water, and place that water in a freezing-mixture, and follow carefully the fall of

\* *Journal Iron and Steel Inst.*, 1900, II, p. 137.

† F. Osmond, "Méthode Générale Pour L'Analyse Micrographique des Aciers au Carbone," *Bulletin de la Société d'Encouragement*, May, 1895. See preferably the reprint in the "Contribution à l'Étude des Alliages," 1896-1900, p. 277.



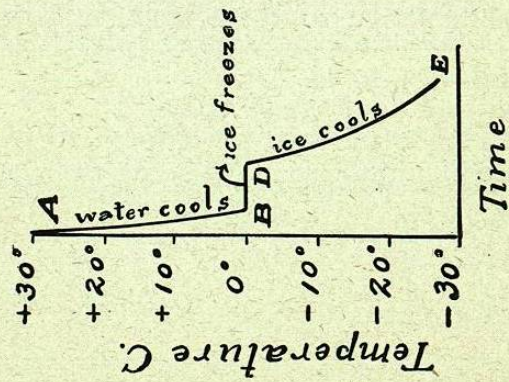


Fig. 7.  
Cooling Curve of  
Pure Water.

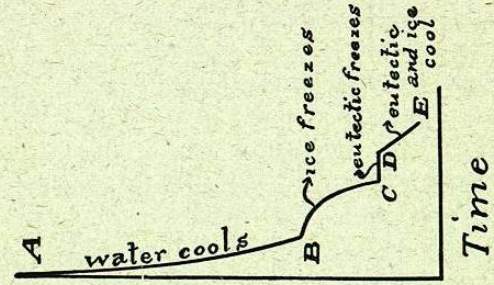


Fig. 8.  
Cooling Curve of a 15 per  
cent Salt Solution.

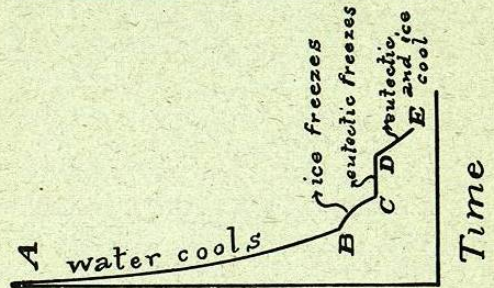


Fig. 9.  
Cooling Curve of a 20 per  
cent Salt Solution.

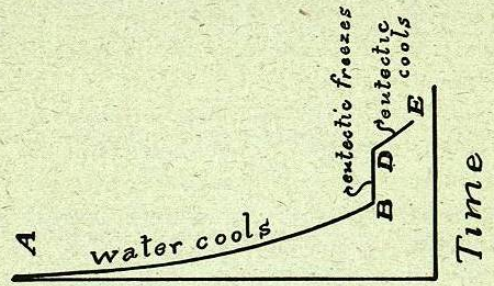


Fig. 10.  
Cooling Curve of a 23.6 per  
cent Salt Solution.

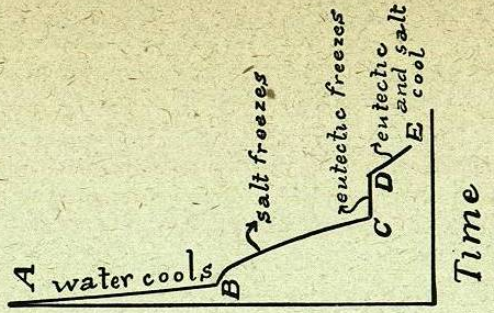


Fig. 11.  
Cooling Curve of a 26.2 per  
cent Salt Solution.

temperature, plotting each degree of temperature as ordinate and time as abscissa, we should get a curve like that in Fig. 7.

As the temperature of the water progressively falling approaches that of the freezing-mixture, the fall of temperature will be slower and slower, and the curve will progressively become flatter and flatter (*AB*), but it will be smooth, *i. e.*, free from inflections and critical points until the temperature falls to  $0^{\circ}$  C. At this point the water will begin to freeze, and the temperature will remain stationary until the whole of the water has frozen, so that the curve will here become a horizontal line or jog *BD*. As soon as all the water has frozen the temperature of the resultant ice will again fall toward that of the surrounding freezing-mixture, and this part of our cooling would give us the part *DE* of our curve.

The reason why the jog occurs is that the freezing of a considerable mass of water occupies a considerable time, and until the whole has frozen the still unfrozen water or "mother-liquor" will still be at its freezing-point, *i. e.*, it will remain at constant temperature. To look at the same thing in another way, in the passage from the liquid to the solid state heat is liberated, and this arrests the fall of temperature.

In the parts *AB* and *DE* of the curve there is no change, chemical or physical, occurring within the water or the ice; hence the smoothness of the curve in these parts.

#### 11. DEFINITION OF MOTHER-LIQUOR AND MOTHER-METAL.

— At any given instant during the freezing of a liquid or molten mass, the part which is still liquid or molten, *i. e.*, the part which has not yet frozen, is called the "mother-liquor" in case of aqueous liquids, and "mother-metal" in case of molten metals.

12. OTHER INFLECTIONS IN COOLING CURVES. — Just as the heat evolved in the freezing of the water arrests the fall of temperature, so every change, chemical or physical, which occurs within any cooling mass (be it an aqueous solution, an alloy, or a rock-mass) as it passes any particular temperature or range of temperature, will in general cause either an evolution or an absorption of heat, in short will be accompanied by some thermal action, and this will affect the progress of the cooling and thus will record itself automatically on the cooling curve. For instance the ideal cooling curve of a pure metal is of the same



general family as that of Fig. 7, because the ideal metal undergoes no change in cooling, except that it freezes. If, however, the metal in its cooling should undergo any other change, that change will be recorded in the cooling curve.

A striking case of such changes is afforded by the cooling curve of pure iron. This, as shown in Fig. 12, has no less than ten inflections. The interpretation of these inflections is not always easy. In addition to the jog which occurs as the iron freezes from the molten state, two of these inflections, that of  $895^{\circ}$  and that just below  $766^{\circ}$  C., appear to represent allotropic changes in the metal itself, and these inflections are known as  $Ar_3$  and  $Ar_2$ . The latter of these coincides with the recovery of the magnetic properties: *i. e.*, at temperatures above  $Ar_2$  iron is not magnetic, but on cooling past  $Ar_2$  it again becomes magnetic. (See §§ 162, 192, pp. 193, 215.)

13. DISTORTIONS OF COOLING CURVES. — The cooling curves given in Figs. 7 to 11 must be taken as types only. To bring out their features clearly the inflections are exaggerated, and certain irregularities are suppressed. Two causes of irregularity may here be mentioned for illustration.

14. SURFUSION. — It sometimes happens that the freezing of a liquid or molten body, instead of beginning accurately at the true freezing-point of the substance, is deferred through a sort of molecular inertia until the temperature has fallen considerably below this point. This phenomenon is called surfusion. Once freezing sets in, however, the heat which it evolves raises the temperature towards, and more often quite to, the true freezing-point, where it remains during the remainder of the freezing. (Compare § 30, p. 35.)

15. MALOBSERVATION. — The curves here given are supposed to represent the cooling of the mother-mass, the part which freezes last of all, *i. e.*, the part which, at any given moment during freezing, still remains unfrozen; in case of an aqueous solution it is the mother-liquor, in case of a molten alloy it is the mother-metal. But, while these curves are supposed to represent the mother-mass itself, yet they cannot do so accurately towards the end of the freezing, for the reason that we cannot then determine the temperature of the mother-mass accurately. If a mercury thermometer, or any instrument as large as that, were used, it is clear that only part of the bulb could be in the mother-mass

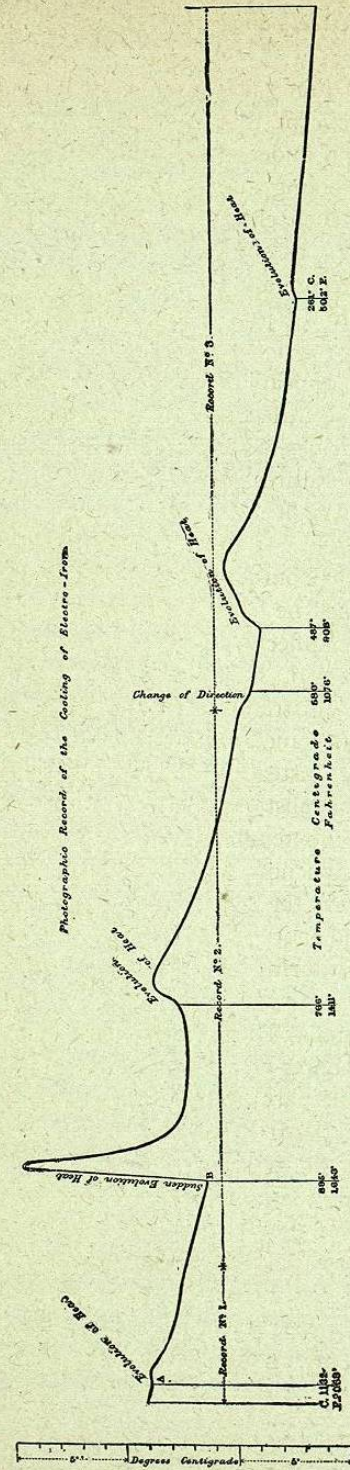


Fig. 12. Differential Cooling Curve of Electrolytic Iron.

(Roberts-Austen, *Fifth Report Alloys Research Committee*, Plate 2, 1899, also *The Metallographist*, II, p. 194.)

Abscissæ are actual temperatures, and ordinates are the differences, at each temperature, between the temperature of the electrolytic iron and a mass of platinum cooling under identical external conditions. This delicate method reveals even slight evolutions and absorptions of heat.



towards the end of the freezing, when the quantity of mother-mass has grown very small.

Much greater accuracy of course can be had by the use of thermo-electric measurement. In this method we determine the temperature of the mother-mass by placing in it a thermo-junction, which consists simply of the ends of two wires of unlike metals, welded or even merely twisted together. These wires extend outside of the mass, and indeed are carried to a convenient distance, and their further ends are twisted together and kept at known temperature, say that of the room. Because of the difference between the temperature of the thermo-junction, *i. e.*, the end which is in the mother-mass, and the cold junction, *i. e.*, the other end at room-temperature, a current of electricity flows through the pair of wires; and this current is a function of this difference of temperature. By measuring this current by means of a delicate galvanometer we determine the difference in temperature between the two ends, and knowing the temperature of the cold junction, by simple addition we get the temperature of the thermo-junction. As the thermo-junction may be made of very fine wires, and as the current is due only to the temperature-difference between the final points of parting of the two wires in the thermo-junction and the cold junction respectively, the indications of the instrument clearly refer only to a very small space in the mother-mass under observation, and not to the whole of that mass, nor even to the relatively large space to which the indication of a mercurial thermometer must necessarily refer, a space necessarily at least as large as the thermometer bulb.

But even with this more delicate mode of measurement, serious causes of malobservation exist. First, while this method will give us the temperature of the mother-mass accurately so long as there is a large quantity of this mass, yet when the freezing is nearly complete and only a small bead of mother-mass still remains unfrozen, the temperature of the couple will be below that of the mother-mass. For the temperature of the already frozen mass will be below that of the still unfrozen mother-mass, not appreciably so to be sure at its very contact with the mother-mass, but decidedly so at its outer layers through which the heat is escaping, and to an intermediate degree in the region between; and the difference in temperature will be the greater the lower is the thermal conductivity of the metal. Now the lead wires of

the thermo-electric couple will conduct heat away from the couple itself towards this outer cooler region, and so tend to depress the temperature of the couple itself below that of the mother-mass in which it is immersed. This effect will be the more pronounced the smaller the quantity of mother-mass remaining.

Again, since the shape of the successively deposited layers is not mathematically concentric, so that the last freezing particles of the mother-mass are not situated in the very centre of the mass, but more or less excentrically, we cannot expect that our couple will, through the last part of the freezing, be in the mother-mass; it is far more likely to find itself in some layer which has frozen an appreciable time before the last of the mother-mass, a layer which consequently is appreciably cooler than the mother-mass. By operating on large masses, and by cooling extremely slowly, we can lessen the error from these sources, but hardly efface it.

To take a single example of the distortion of these curves, the outer corner of the jog, *D*, while theoretically sharp in case of a pure substance as given in Fig. 7, when actually observed is usually more or less rounded as at *D* in Fig. 14, partly because the point at which we determine the temperature is not likely, towards the end of the freezing, to be in the mother-mass or last freezing part. Another probable reason is the escape of dissolved gases during the end of the solidification, so that the mother-mass, even the residual water in case of distilled water, would not in general be pure water, but water containing more or less atmospheric oxygen and nitrogen in solution. The volatilization of this gas in itself absorbs heat and so distorts the cooling curve.

16. EASE OF THERMAL STUDIES.—The cooling curve gives us a very delicate method of detecting all changes which take place within a cooling mass, and of determining accurately the temperature at which they occur. Moreover, the method is not only very delicate but very easy and rapid, much more so than most of our common methods of investigation. For instance, if we are to determine the tensile properties of an alloy, its tensile strength, elastic limit, *etc.*, we must prepare test pieces of considerable size, and these must be throughout their length free from mechanical defects such as blowholes, seams, *etc.* Moreover, the tensile strength which we observe will simply be that of the



section of least resistance of our metal; it gives us no direct indication as to the constitution of the mass as a whole.

So determinations of electric conductivity, dilatation and many other important properties, while they require great care and expense in preparing specimens, yet when applied to a single specimen, throw little light on its constitution. The cooling-curve method, however, not only gives us much light on this question, but can be applied to small and cheaply prepared specimens, and, if carried out with autographic apparatus, is extremely rapid and relatively easy, as well as delicate and accurate.

17. SELECTIVE FREEZING. — The cooling curve in Fig. 8 differs from that in Fig. 7 having a rounded part *BC* between its first part *AB* and its horizontal step or jog *CD*. This is the general shape of the cooling curve of a solution of say 15 per cent of common salt in water, and the rounded part *BC* represents the fact that the salt water in freezing does not freeze to a homogeneous ice as pure water does, but splits up in freezing into crystals of relatively pure water and crystals of relatively pure salt.

In certain cases the salt which thus freezes out is hydrated; but in order to simplify the discussion this fact is left out of consideration throughout this work.

18. DEFINITION OF SELECTIVE FREEZING. — By this I mean that the particles which freeze out of a molten or liquid mass have not, at any given instant, the same composition as the mother-mass out of which they freeze; but that freezing proceeds by selecting from the mother-mass certain elements or compounds either alone, or in greater proportion than that in which they exist in the mother-mass. For instance, in our present case of the freezing of salt water, the fact that what freezes out first is salt ice nearly pure, *i. e.*, having much less salt than the original liquor, is an instance of selective freezing.

Many of us no doubt were surprised on reading Nansen's travels to see that, although he was travelling over a salt ocean and on ice which should have been salt, nevertheless he appears to have very little difficulty in obtaining fresh drinking water. While this is no doubt to be referred in large part to his finding pools of melted snow, yet there is this other cause, that when salt water begins freezing, its freezing is selective. The ice which forms first is relatively free from salt, *i. e.*, the salt which had been dissolved in it is rejected in freezing, and accumulates in the

still unfrozen water beneath, so that a crust of relatively pure ice forms on the top of the salt ocean. When some of the upper layers of this crust remelt under the heat of the sun and again freeze, a second expulsion of salt and purification of the ice occurs, and by this repeated crystallization drinkable water may be had.

In a direct experiment with artificial sea water the author found that, after two freezings, the resultant water was potable, and though saltish to the taste left no after-taste in the mouth: that the outer surface of the ice resulting from the third freezing was quite tasteless, and that the water formed from the melting of this third ice was agreeable, about like Apollinaris water when flat.\*

19. OTHER FEATURES OF COOLING CURVES. — Several features of the curve in Fig. 8 demand attention. First, the point *B* at which freezing begins is not at the normal freezing-point of water,  $0^{\circ}$  C., but at  $-11^{\circ}$ . We say that the dissolved salt lowers the freezing-point, and, within limits, the more salt a solution contains the lower is its freezing-point.

So when plumbiferous tin (Fig. 28 F, p. 60) is cooled, the freezing of the tin does not begin until the temperature has fallen considerably below the freezing-point of pure tin. In other words, although the freezing-point of pure lead ( $326^{\circ}$ ) is higher than that of pure tin ( $231^{\circ}$ ), yet by the presence of this lead the tin is

\* The numerical results were as follows:

	SP. GR.	TASTE
(1) Original liquor, artificial seawater	1.0205	
(2) 1st ice, crust formed on partly freezing No. 1.		
(3) 1st remelted liquor, resulting from completely remelting No. 2,	1.0150	
(4) 2nd ice crust, formed on partly freezing No. 3.		
(5) 2nd remelted liquor resulting from wholly remelting No. 4	1.0060	potable, taste saltish, but no taste remains in mouth.
(6) 3rd ice crust formed on partly freezing No. 5.		upper part tasteless.
(7) 3rd remelted liquor, resulting from wholly melting No. 6,	1.0031	agreeable, about like Apollinaris when flat.