pounds of metals with non-metals which occur as definite constituents of alloys:—

$Co_2 Si$
$Co_3 Si_2$
$Co Si$
$Co Si_2$
$Co Si_3$

$Cu_3 P$
$Cu_3 Si$, and others
$Cu_2 O$

$Fe_3 C$
$Fe O$

$Fe_2 P$, $Fe_3 P$
$Fe_2 Si$, $Fe Si$

$Mg_2 Si$
$Mn_2 Si$, $Mn Si$
$Mn_5 P_2$ and another.

$Ni_3 P$, $Ni_5 P_2$, $Ni_2 P$
$Ni_3 Si$, $Ni_2 Si$, $Ni_3 Si_2$, $Ni Si$, $Ni_2 Si_3$

$Sn_3 P_2$

5. **Eutectic Mixtures.**—By this term is meant a eutectic after solidification and separation into its constituent parts which remain in micro-juxtaposition in the alloy, thus forming a constituent. The term *eutectic* was first used by Guthrie in 1875 to indicate solidified mother liquor. A eutectic is that alloy of a series or portion of a series which has the *lowest melting-point.*

It is often advisable to prepare the eutectics in as pure a state as possible in order to carry out the various methods of investigation on them. The following are among the methods which have been devised for this purpose:—

(*a*) *Guthrie's Method.*—In this method the metals under examination were melted together; then the metal which was in excess over the eutectic ratio was allowed to crystallise out, and when the greater part had become solid, the residual alloy which still remained fluid was poured off and allowed to set. This crude eutectic was remelted and allowed to partially solidify, and the mother metal again poured off. This treatment was repeated until the mother metal invariably yielded an alloy of the same composition.

(*b*) *Roberts-Austen's Method.*—In this case a steel cylinder fitted with two loose steel plungers is used. The alloy under examination is placed in the cylinder between the plungers and suitable pressure applied to these. The cylinder is heated up, and when the temperature at which the eutectic melts is reached, it will be forced out between the plungers and the cylinder. The eutectic alloy first obtained may be re-treated. The temperature at which the eutectic is obtained may be ascertained by the insertion of a thermo-couple.

(*c*) *Stead's Method* for small quantities of low melting-point alloys. A portion of the molten alloy is poured on to a sheet of asbestos, and when the mass has solidified to a thick paste, a second sheet of asbestos is placed on top, and a wooden roller is rolled over the surface. The eutectic runs as a fluid drop in front of the roller, and may thus be separated and re-treated if desired.

(*d*) *Synthetical Method.*—As a general rule, the best method for making a quantity of pure eutectic is to first ascertain the correct composition by thermal and microscopical methods, and then make up the alloy to this composition.

The following is a list of the most important properties, etc., of a eutectic alloy:—

(*a*) A single melting and solidifying point.

(*b*) A melting and solidifying point lower than that of the mean of its constituents.

(*c*) A composition which is constant and independent of the initial composition of the alloy.

(*d*) A composition not necessarily in simple atomic proportions.

(*e*) It must be the most fusible alloy in a given series or portion of a series, for some series of alloys have more than one eutectic.

(*d*) It consists of a conglomerate of distinct particles of the components, mechanically mixed.

(*e*) It may consist of two or more metals which do not unite chemically, or two solid solutions.

(*f*) It may consist of a free metal or a solid solution, and a compound.

(*g*) It may consist of two or more compounds.

(*h*) It may be formed in the solid alloy, that is, at a temperature lower than that at which freezing is completed. The most important example of this is pearlite, which forms in the solid in carbon-steels, and is generally known by the term "eutectoid."

(*i*) It may possibly consist of two eutectics, one formed during solidification, and the second after solidification is complete.

The exact microscopic structure of eutectics is found to vary in different alloy-series, and the following types may be considered as the most important.

Curviplanal, in which the constituents consist of curved plates in juxtaposition. Examples of this are found in the alloys of silver and copper, lead and tin, slowly cooled steels, etc.

Honeycombed or Cellular.—This is a very common eutectic structure, and is found in bismuth-tin, gold-lead, iron-phosphorus series, etc.

Spherulitic.—This is frequently met with, especially when the eutectics have been cooled down rapidly. The constituents commence to separate and solidify from nuclei, and grow from these; found in alloys of lead and antimony, lead and gold, etc.

Geometric crystalline forms are occasionally found in eutectics allowed to solidify very slowly; for example, the antimony-lead eutectic yields hexagonal prisms built up of alternate laminæ of lead and antimony; the gold-lead eutectic yields cuboidal forms.

The following series of alloys serve as examples in which eutectics are important constituents:—

Pb–Sb; Cd–Zn and AuTl, which contain eutectics practically throughout; Sn–Pb; Pb–Ag; Sn–Ag; Sn–Bi; Sn–Zn; Cu–Au; Cu–Ag; Al–Zn, etc., which contain eutectics only within certain limits of composition; and Pb–Mg; Sn–Mg; Sn–Ni; Zn–Sb; Te–Bi; Na–Sn; Fe–Si; Au–Sn, etc., which yield two or more distinct eutectics, each one occurring within a certain range of composition only.

6. **Solid Solutions of Definite Compounds in excess of Metal.**—It has already been shown that chemical compounds form an important constituent of many series of alloys, and it will be readily understood that many of these compounds form solid solutions with excess of either or both of the elements of which they are composed, thus forming a new constituent. In a few cases the compound and each metal are completely soluble in each other, the best example of this being the magnesium-cadmium series; in other cases the compound and component metals are only partially soluble in each other, as in the copper-antimony series.

In commercial alloys the most important instances of solid solutions of compounds are found in the copper-tin and copper-zinc alloys, and very important solid solutions of compounds, containing a non-metal, are met with in the case of iron, in which, under suitable conditions, solid solutions may be formed with the compounds Fe_3C, Fe_2P, and FeO.

7. **Allotropic Modifications.**—It is recognised that many metals are capable of existing in two or more allotropic conditions, each modification being stable only within certain limits of temperature; this phenomenon is also exhibited in the alloys of these metals containing only a certain amount of a second metal, but in a less marked manner.

Certain definite compounds of metal also exhibit similar polymorphic changes. Any change in the nature of the structural constituents of solid alloys takes place with difficulty unless the material is cooled extremely slowly, and may be prevented almost entirely by rapid cooling in the neighbourhood of the transition temperature. The velocity of transformation varies considerably at different temperatures, being greater the higher the temperature, and the farther this temperature is removed from the transition point. Above the temperature of the transition point both these conditions act in the same direction, and the velocity of transformation is increased indefinitely as the temperature is raised. Below the transition point, however, these two conditions act in opposite directions, the velocity being decreased by lowering the temperature, but increased by withdrawing farther from the transition temperature; it will thus be seen that there must be a certain temperature at which the transformation will take place with a maximum velocity. Below this temperature the velocity of transformation decreases with comparative rapidity, and may possibly become zero, showing how it becomes possible to maintain certain metals in an unstable allotropic state at ordinary temperatures.

A simple illustration of allotropic change is found in the gold-thallium alloys;[1] pure thallium possesses a transition point at 225° C., and an arrest is found at this temperature in all the alloys containing primary precipitated thallium; in an equilibrium diagram this change appears as a straight horizontal line. Similar allotropic changes are found in many of the alloys containing nickel, cobalt, etc., corresponding to the temperature at which magnetic transformations take place. The allotropic changes which take place during the cooling of iron and iron-carbon alloys have already been mentioned. Rosenhain[2] has recently described a similar change in lead-tin alloys containing between 8 and 63 per cent. of tin; the change takes place at a constant temperature of 149° C. for the alloys containing above 18 per cent. of tin, and at lower temperatures for alloys of lower tin-content. This change involves the rejection of tin from the solid solution, the form stable at low temperatures possessing a smaller solubility for tin than the form stable above 149° C. As examples of similar changes taking place in metallic compounds, mention may be made of the compound Na_4Sn_3 occurring in the sodium-tin series;[3] this compound changes with an increase of volume at a temperature below solidification. The compound $AuPb_2$ also exhibits allotropic change after solidification, as do also the compounds Co_5As_2, Co_2As, Co_3As_2, besides many more.

Classification of Binary Alloys. — Undoubtedly the best method of classification for alloys of two metals is based on the type of equilibrium curve obtained. The subject is far too extensive for full treatment in this book, and will be given in outline only; for a fuller description the student is referred to Gulliver's *Metallic Alloys.* In the following groups, however, are included the most important types of freezing-point curves.

Group I. Alloys.—These are obtained by alloying any two metals which are completely mutually soluble in the liquid state, and completely insoluble in the solid state. In these alloys a eutectic is found at a certain composition, and intermediate alloys between the pure metals and the eutectic consist of two constituents, viz. crystals of the pure metal which happens to be in excess over the eutectic ratio, and the eutectic itself.

An example of this group of alloys is found in the lead-antimony series, the equilibrium diagram of which is given in fig. 118, after Roland Gosselin.[4] It will be seen that the eutectic point occurs with a composition of 13 per cent. of antimony and 87 per cent. of lead, and that the eutectic temperature is 228° C. All the alloys between pure lead and that one containing 13 per

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[1] Levin, *Zeit. anorg. Chem.*, 1905, xlv. p. 31.

[2] *Phil. Trans.*, 1908, Series A, vol. ccix. pp. 89-122.

[3] Mathewson, *Zeit. anorg. Chem.*, 1905, xlvi. p. 94.

[4] *Contribution à l'étude des Alliages*, 1901, p. 93.

cent. of antimony will commence to freeze at some temperature indicated on the line Pb.E., and at this temperature crystals of pure lead will be deposited; as the temperature falls, lead crystals will continue to be thrown out of solution until a temperature of 228° is reached, when the still liquid portion will contain 87 per cent. of lead, no matter what the initial composition of the alloy was, and this liquid portion of eutectic composition will solidify as a conglomerate of crystals of pure lead and pure antimony. If an alloy consisting of 13 per cent. of antimony be taken, no crystallisation will take place during cooling until the eutectic temperature 228° is reached, when the alloy will solidify as a whole at this definite temperature. Alloys containing more than 13 per cent. of antimony will resemble the alloys containing less than 13 per cent. of antimony in the mode of solidifying, except that the first crystals to fall out of solution will consist of pure antimony instead of pure lead.

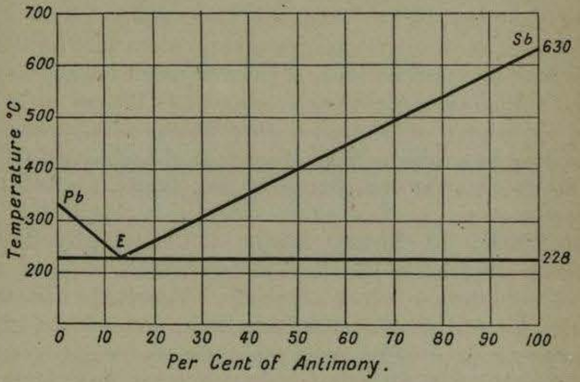

FIG. 118.

Thus all alloys between the eutectic composition E and pure antimony will commence to solidify at some temperature on the line E.Sb, and the crystals formed will consist of pure antimony; as the temperature falls, antimony will continue to be deposited until the portion remaining liquid contains only 13 per cent. of antimony; as before, this state of affairs will be reached at a temperature of 228°, at which temperature solidification will be completed. It should be remembered that the micro-structure of these alloys is closely connected with the deductions drawn from the freezing-point curve, and resembles the micro-structure of the silver-copper alloys (see page 223).

Group II. Alloys.—These are obtained by alloying any two metals which are completely mutually soluble in the liquid state and partially soluble in the solid state. In these alloys the general form of the freezing-point curve resembles that of the Group I. curves, except that the eutectic line does not extend throughout the series. A eutectic is found at a certain composition as before, and in alloys of any other composition the excess metal crystallises out as a solid solution, the amount of the second metal held dissolved varying with the metals under consideration.

An example of this important group of alloys is found in the aluminium-zinc series, the equilibrium diagram of which is given in fig. 119, after Shepherd.[1] The conclusions drawn from this diagram, which are confirmed by microscopic analysis, are that above the line ZnEAl the alloys consist of homogeneous fluids. In the region ZnE*a*, primary crystals of zinc holding a certain amount of aluminium in solution (the amount dissolved being indicated by line Zn *a*) are in equilibrium with a still molten portion of the alloy; similarly, in the region EAl *b*, crystals of aluminium holding an amount of zinc, indicated by Al *b*, exist in equilibrium with a still molten portion of the alloy. At the temperature of the straight line *a* E *b*, the eutectic solidifies and is made up of two solid solutions, one having composition *a* and the other of composition *b*. In this series, alloys containing up to 4 per cent. and also those containing more than 45 per cent. of aluminium are homogeneous in structure, and only the alloys between these limits consist of two constituents. The fact that the lines *a d* and *b c* are not vertical indicates that the mutual solubility of these metals varies with the temperature; for example, solid aluminium at 200° is capable of holding in solid solution more zinc (*f c*) than at a temperature of 300° C.

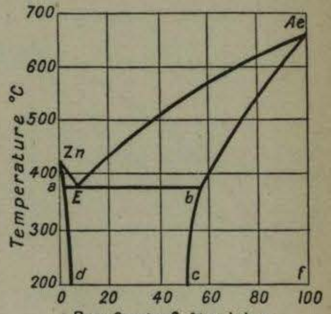

FIG. 119.

Group III. Alloys.—These are obtained by alloying any two metals which are completely soluble in each other, both in the liquid and in the solid state. When absolute equilibrium is attained in these alloys they possess a homogeneous structure, but in the ordinary course of freezing the first crystals to separate are invariably richer in that metal having the higher melting-point, and the last portions to crystallise are correspondingly richer in the metal with the lower melting-point. Distinct differences can generally be seen in the appearance of the individual crystals after polishing and etching, owing to the gradual variation in composition from the centre to the outside.

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[1] *Journ. Phil. Chem.*, 1905, ix. p. 504.

As an example of this series of alloys, those of antimony-bismuth may be taken, the freezing-point curve of which is shown in fig. 120, after Gautier.[1] The full line BiASb indicates the temperature of the commencement of solidification, and the dotted line BiCSb indicates the temperature at which solidification is complete; this part of the diagram, however, has not yet been determined with accuracy. To illustrate the mode of procedure of the freezing in this case, suppose an alloy of 50 per cent. Sb and 50 per cent. Bi be cooled down from some temperature above 600°. The molten alloy will merely cool down until a temperature of 500° is reached (A), at which solidification will commence, the first crystals to be deposited being of composition B, that is, containing about 75 per cent. Sb. From 500° downwards crystallisation will proceed, the crystals being deposited becoming poorer and poorer in Sb, and correspondingly richer in Bi, until a temperature of about 400° is reached, when the whole mass will be solid, the last portion to solidify having a composition D, or about 25 per cent. Sb.

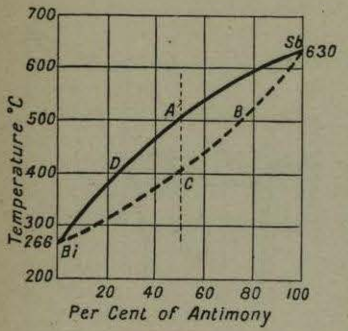

FIG. 120.

By keeping the alloy at a temperature just below solidification for a long time diffusion is assisted, and continues until the whole mass is homogeneous in composition. To this group belong the series Au–Ag, Au–Pt, Mn–Fe, Ni–Co, Pd–Ag, Pd–Au, etc.

Group IV. Alloys.—These are obtained by alloying metals which form chemical compounds.

It will be readily seen that this group may be subdivided according to whether the compound or compounds are completely soluble, partially soluble, or completely insoluble in the other constituents of the alloy. As an example, the tin-magnesium series may be taken, the equilibrium diagram of which is given in fig. 121 after Grube. It will be noticed that at C a maximum point is obtained; this is found in the alloy containing 71 per cent. of tin, and corresponds to the compound $SnMg_2$, which has a freezing-point of 783° C.

If this type of diagram be divided vertically through C (the compound) two diagrams will be obtained, each similar to the diagrams given by Group I. Alloys, the compound taking the place of one of the pure metals. The composition of the various portions is clearly indicated on the diagram, both for temperatures at which crystallisation has commenced and for temperatures at which the alloys are completely solid.

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[1] *Bull. de la Soc. d'Enc. p. l'Ind. nationale*, 1896.

For a complete consideration of the Phase Rule and its application to the study of alloys, which is of very great value, the student is referred to the books already mentioned, and to the original papers given in the following bibliography. The consideration of the equilibrium curves of the very important series of alloys copper-zinc, copper-tin, copper-aluminium, and iron-carbon is omitted, as being complex and beyond the scope of this work. These important classes of industrial alloys have received a large amount of attention from metallographists, and comprehensive accounts of their constitution and properties are fairly accessible.

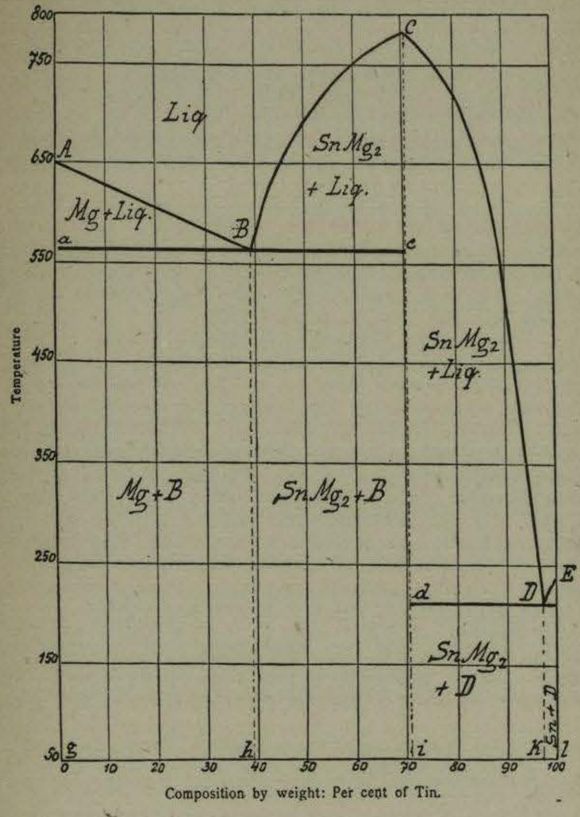

FIG. 121.—Group IV. Alloys.

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