

the surface of the alloy, leaving a coating of almost pure silver. This is a point which has to be considered by the assayer in taking an average sample of the metal. A change of composition in the surface layer of an alloy may also be produced by the ancient process of cementation. This process, which is still used in the hardening of steel, consists in heating the alloy, in the presence of a substance with which it is capable of alloying, at a temperature below its melting-point. Thus steel is superficially hardened by packing it in charcoal, and maintaining it at a high temperature for some time. The steel gradually alloys with the carbon, with the result that the surface is much harder than the interior. A similar result is obtained by heating copper alloys in zinc dust, or even in zinc vapour, which alloys with the copper. A similar method is employed in the production of what is known as malleable cast iron; in this case the result aimed at is not the addition of a new element, but its extraction. Cast iron is heated with oxide of iron, which decarburises the iron and renders castings softer and less brittle.

CHAPTER II.

PROPERTIES OF ALLOYS.

Density.—The density of an alloy is influenced (1) by the purity of the metals of which it is composed; (2) the mechanical treatment it has undergone; (3) the temperature at which it has been cast; and (4) the rate of cooling. These facts may to a great extent account for the disagreements shown in the work of Mallet, Calvert and Johnson, Matthiessen and Riche. Their work shows, however, that the density of an alloy is seldom the mean of the densities of its constituent metals, sometimes being greater and sometimes less than the mean. The mean density of an alloy may be calculated from the formula

$$M = \frac{(W + w)Dd}{Dw + dW},$$

where M is the mean density, W and w the weights of the constituent metals, and D and d their respective densities. The following alloys have frequently been given as examples of cases in which the densities are respectively greater and less than the mean:—

Alloys whose Density is less than the Mean of their Constituents.

Au and Zn
 Au ,, Sn
 Au ,, Bi
 Au ,, Sb
 Au ,, Co
 Ag ,, Zn
 Ag ,, Sn
 Ag ,, Bi
 Ag ,, Sb
 Cu ,, Zn
 Cu ,, Sn
 Cu ,, Pd
 Cu ,, Bi
 Pb ,, Sb
 Pt ,, Mo
 Pd ,, Bi

Alloys whose Density is greater than the Mean of their Constituents.

Au and Ag
 Au ,, Fe
 Au ,, Pb
 Au ,, Cu
 Au ,, Ir
 Au ,, Ni
 Ag ,, Cu
 Fe ,, Bi
 Fe ,, Sb
 Fe ,, Pb
 Sn ,, Pb
 Sn ,, Pd
 Sn ,, Sb
 Ni ,, As
 Zn ,, Sb

Matthiessen also states that some of the alloys of tin and gold have a greater and some a less density than the mean of their constituents, and the same is true of the alloys of bismuth and silver, and also of the alloys of some other metals.

Very little recent work has been done on the subject, and it appears that the study of the densities of alloys has been considered a barren field of investigation.

Colour of Alloys.—Of the well-known metals, only two—copper and gold—may be said to have any very decided colour; hence it might, at first sight, be supposed that the range of colour of alloys would be strictly limited. This, however, is not the case, and the colours produced in alloys are in many cases very remarkable and well worth a little consideration.

In the first place it is well known that the metals vary in their decolorising power, and Ledebur has arranged the principal metals in the following order:—Tin, nickel, aluminium, manganese, iron, copper, zinc, lead, platinum, silver and gold. Each metal in this series has a greater decolorising action than the metal following it. For example, it requires nearly 50 per cent. of silver added to gold to produce a white alloy; whereas the addition of only 10 per cent. of aluminium is quite sufficient to completely destroy the colour of the gold. Again, an alloy of 75 per cent. of copper and 25 per cent. of zinc has the well-known colour of brass; but if the zinc is replaced by the same quantity of nickel, we get the perfectly white alloy so largely used for the Continental nickel coinage.

In addition to this property of destroying the colour of metals we have cases in which by the simple fusion of two metals the most unexpected colours are obtained. Thus an alloy of copper and antimony containing 51 per cent. of copper and 49 per cent. of antimony has a beautiful violet colour, and even more interesting is the case of the violet alloy of Roberts-Austen, produced by melting 78 parts of gold with 22 of aluminium.

In these cases we start with one coloured constituent, but it is possible to obtain coloured alloys even from two white metals. The alloy of platinum and aluminium, for example, containing 75 per cent. of platinum and 25 per cent. of aluminium, is distinctly yellow, and resembles gold containing a small percentage of silver. Another yellow alloy is obtained by the fusion of 33 per cent. of aluminium and 66 per cent. of cobalt.

Heycock and Neville have drawn attention to the alloy in the silver-zinc series corresponding to the formula AgZn , which is capable of assuming a red colour when heated to about 300° and suddenly chilled; and it has also been shown that the corresponding cadmium alloy AgCd has a distinct and very beautiful pink colour.

All these alloys are formed by the union of definite atomic proportions of their constituents, and must be regarded rather as chemical compounds than as simple metallic mixtures. They are perfectly homogeneous, brittle alloys, breaking with a conchoidal fracture; properties which render them practically useless to the art-metal worker. There are, however, a large number of useful, if less brilliantly coloured, alloys for the metal worker to choose from, and an excellent example may be found in the numerous gold alloys employed by jewellers and goldsmiths. Some of these, with their percentage compositions, are shown in the following table:—

Colour.	Composition.				
	Gold.	Silver.	Copper.	Iron.	Cadmium.
Deep yellow . . .	90	...	10
" " . . .	53	25	22
Red " . . .	75	...	25
Dark red . . .	50	...	50
" " . . .	25	...	75
Pale yellow . . .	91.6	8.3
" " . . .	91.6	8.3	...
Green " . . .	75	25
" " . . .	75	16.6	8.4
" " . . .	74.6	11.4	9.7	...	4.3
" " . . .	75	12.5	12.5
Grey " . . .	85.7	8.6	...	5.7	...
" " . . .	83.3	16.7	...
Blue " . . .	75	25	...
" " . . .	66.7	33.3	...

The coloured alloys used by the Japanese in their famous art-metal work have been described by Roberts-Austen and others, but a brief description of them may be of interest. The most important of these alloys are known as *shaku-do* and *shibu-ichi*, and both of them are, within certain limits, very variable in

composition. Two samples of *shaku-do*, for example, gave the following analysis:—

Copper	94.50	95.77
Silver	1.55	0.08
Gold	3.73	4.16
Lead	0.11	...
Iron and arsenic	Traces	...

Other samples have been found to contain as little as 1.5 per cent. of gold, but the precious metal is an essential constituent of the alloy and enables the metal to assume a beautiful surface colouring, or "patina," when treated with suitable pickling solutions.

Shibu-ichi is a copper-silver alloy, and is fairly represented by the following analysis:—

Copper	67.31	51.10
Silver	32.07	48.93
Gold	Traces	0.12
Iron	0.52	...

In addition to these alloys and their various combinations one with another there are varieties of impure copper, all of which are capable of assuming different colours on pickling. The pickling solutions most commonly used are made up of the following ingredients, and are used boiling:—

	I.	II.	III.
Verdigris	438 grains	87 grains	220 grains
Sulphate of copper	292 "	437 "	540 "
Nitre	87 "	...
Common salt	146 "	...
Sulphur	233 "	...
Vinegar	1 gallon	5 drachms
Water	1 gallon	...	1 gallon

Examples of the different colours obtained by pickling may be seen at the Victoria and Albert Museum, South Kensington, where there is a collection of fifty-seven plaques illustrating the different sorts of bronze used in Japan. Another excellent collection, consisting of twenty-four plates, is to be found in the Museum of Practical Geology in Jermyn Street.

In connection with the use of coloured alloys in art-metal work a brief reference to the Japanese *mokumé* ("wood grain") and *mizu-nagashi* may not be out of place. An effect closely resembling the grain in wood is produced by taking thin sheets of various metals and alloys, such as gold, silver, *shaku-do*, *shibu-ichi*, etc., soldering them to-

gether, and then either cutting a device into them and hammering the whole until flat, or else hammering from behind and then filing down the prominences. The methods are sufficiently well shown in the two illustrations (figs. 1 and 2). Fig. 2 shows the effect of these banded alloys in a bead which is only three-quarters of an inch in diameter.

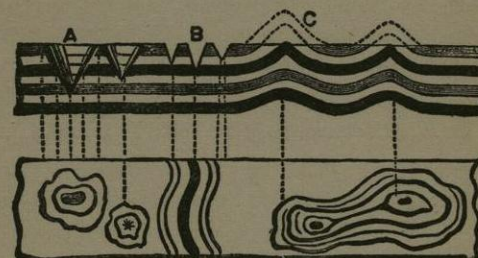


FIG. 1.—Japanese Art-Metal Work.



FIG. 2.—Japanese Art-Metal Bead.

Specific Heat.—The most important determinations of the specific heats of alloys were made by Regnault in 1841. For the purpose of his investigations he divided alloys into two classes: those having a fusing-point considerably above 100° C., and those fusing at or near 100° C. In the case of the first class he concluded that the specific heat was an additive property, and agreed closely with the calculated specific heat obtained by multiplying the specific heat of each constituent metal by the percentage amount of the metal contained in the alloy and dividing the sum of the products by 100. This led him to announce that

"the specific heat of the alloys at temperatures considerably removed from their fusing-points is exactly the mean of the specific heats of the metals which compose them." He further discovered that in the case of these alloys the product of the

specific heat of the alloy into its atomic weight is approximately constant. In the whole series examined by him this number only varied from 40.76 to 42.05. On examining the second class of alloys, those which fuse at or near 100° C., Regnault discovered that they did not obey his law, and that the specific heats were in all cases higher than those obtained by calculation from the specific heats of the constituents. Moreover, he found that the product of the specific heats into the atomic weights varied from 45.83 to 72.97.

Malleability has been described as the property which enables metals to be permanently extended in all directions, without rupture, by pressure produced by slow stress or by impact. The degree of malleability of a metal is measured by the ease with which its shape or form can be modified by rolling or hammering. The order of malleability of the common metals is as follows:—Gold, silver, copper, tin, platinum, lead, zinc, iron and nickel. Some metals are less malleable when hot than when cold and are described as *red short*, while those that are more malleable when hot are called *cold short*. Alloys are less malleable than pure metals, and the most malleable alloys are those whose structure most closely resembles that of pure metals.

Ductility is the property which enables metals to be permanently elongated, *i.e.* to be drawn into wire. The order of ductility of the common metals is as follows:—Gold, silver, platinum, iron, nickel, copper, zinc, tin, lead. Alloys are less ductile than pure metals, and, as in the case of malleability, the most ductile alloys are those possessing structures resembling pure metals.

The **hardness** of metals is measured in several ways. Bottone measured the hardness of metals by determining the time necessary to produce a cut of definite depth. Taking the diamond as 3010, the relative hardness of a number of metals was determined as follows:—

Carbon	3010		
Manganese	1456	Gold	979
Cobalt	1450	Aluminium	821
Nickel	1410	Cadmium	760
Iron	1375	Magnesium	726
Copper	1360	Tin	651
Palladium	1200	Lead	570
Platinum	1107	Thallium	565
Zinc	1077	Calcium	405
Silver	990	Sodium	400
Iridium	984	Potassium	230

Brinell measures the hardness of metals by determining the depth of the indentation produced by a hard sphere of known dimensions under a definite pressure. This method is the one generally adopted in engineering practice.

Alloys are nearly always harder than the metals of which they are composed.

Thermal Conductivity.—The power of alloys to conduct heat has been examined by several experimenters; but it was not until 1858 that the subject was thoroughly dealt with by Calvert and Johnson, who made a large number of determinations, using alloys prepared from pure metals. The apparatus employed consisted of a box containing a known volume of water; to this box one end of the bar to be tested was secured. The other end of the bar was maintained at a temperature of 90° C., and the relative conductivity of the bar determined by noting the rise in temperature in a given time of the known volume of water in the box. The conductivity of silver, which is the best conductor, was taken as 1000.

Calvert and Johnson state that in some cases the conductivity of an alloy is the mean of the conductivities of its constituent metals; but in many cases there appears to be no relation between the two. For example, the conductivity of silver was taken as 1000 and that of gold 981, but the conductivity of gold containing 1 per cent. of silver was found to be only 840.

These experimenters divide alloys into three classes according to their conductivity:—

1. Alloys which conduct heat in ratio with the relative equivalents of the metals composing them: alloys of tin and zinc, and of tin and lead.

2. Alloys in which there is an excess of equivalents of the worse conducting metal over the number of equivalents of the better conductor, such as alloys composed of one equivalent of copper and two of tin, or one of copper and three of tin, and which possess the remarkable property of conducting heat as if they contained none of the better conductor. The conducting power of these alloys is the same as if the bar were composed entirely of the worse conductor. Similarly in the case of the bismuth-lead alloys, those containing two equivalents of bismuth and one of lead, three of bismuth and one of lead, and four of bismuth and

one of lead, all conduct alike, the decrease in the quantity of lead having no influence on the conductivity.

3. Alloys composed of the same metals as the last class, but in which the number of equivalents of the better conducting metal is greater than the number of equivalents of the worse conductor. In these alloys the conductivity tends towards the better conductor.

Matthiessen gives it as his opinion that the conductivity of an alloy furnishes no evidence of whether an alloy is a chemical compound or a mixture.

Electrical Conductivity.—The study of the electrical conductivity of alloys may be said to have begun with the publication, in 1860, of the results of Matthiessen's famous research. With regard to the conducting power for electricity he divides the metals into two classes:—

Class A.—Those metals which, when alloyed with one another, conduct electricity in the ratio of their relative volumes.

Class B.—Those metals which, when alloyed with one of the metals belonging to Class A, or with one another, do *not* conduct electricity in the ratio of their relative volumes, but always in a lower degree than the mean of their volumes. To Class A belong lead, tin, zinc, and cadmium. To Class B belong bismuth, mercury, antimony, platinum, palladium, iron, aluminium, gold, copper, silver, and “in all probability most of the other metals.”

Matthiessen showed that the electrical conductivity of any series of alloys composed of two simple metals may be represented graphically by one or other of three typical curves which are respectively straight lines, L-shaped, or U-shaped. The metals of Class A produce alloys whose conductivity is represented by straight lines; those of Class A with Class B by L-shaped curves; and those of Class B with one another by U-shaped curves (see p. 263).

At the conclusion of a research which Roberts-Austen has justly described as classical, Matthiessen considers the nature of alloys and sums up his arguments in the following manner:—

“The question now arises, What are alloys? Are they chemical combinations, or a solution of one metal in another, or mechanical mixtures? And to what is the rapid decrement in the conducting power in many cases due? To the first of these questions I think we may answer, that most alloys are merely a solution of one metal in the other; that only in a few cases may we assume

chemical combination—for example, in some of the gold-tin and gold-lead alloys; and we may regard as mechanical mixtures some of the silver-copper and bismuth-zinc alloys. The reasons for the foregoing assumptions are the following:—

“1. That if we had to deal with chemical combinations we should not find in the conducting power of alloys that regularity in the curves which certainly exists; for on looking at those belonging to the different classes we see at a glance that each class of alloys has a curve of a distinct and separate form. Thus, for the first, we have nearly a straight line; for the second the conducting power always decreases rapidly on the side of the metal belonging to Class B, and then, turning, goes almost in a straight line to the side of the metal belonging to Class A. For the third group, we find a rapid decrement on both sides of the curve, and the turning-points united by almost a straight line.

“If we now examine the part of the curve where the rapid decrement takes place we find that in the lead and tin alloys it generally requires twice as much of the former as it does of the latter to reduce a metal belonging to Class B to a certain conducting power; for instance, to reduce that of silver to 67 it would require 0.9 vol. per cent. of lead, or about 0.5 vol. per cent. of tin; to reduce it to 47.6 there would be required 1.4 vol. per cent. of lead, or about 0.7 vol. per cent. of tin. Again, to reduce bismuth to 0.261 there is required 1.4 vol. per cent. of lead, or 0.62 vol. per cent. of tin; and to reduce it to the minimum point of the curve, which is when alloyed with lead 0.255, and 0.245 when alloyed with tin, it requires 1.76 vol. per cent. of lead and 0.85 vol. per cent. of tin.

“2. We cannot explain the reason of the decrement of the conducting powers by assuming that the turning-points of the curves are chemical combinations, for it is not at all probable that there are such as contain only 0.6 per cent. of tin and 99.4 per cent. of bismuth; or 2 per cent. of lead and 98 per cent. of bismuth; or 2.6 per cent. of tin and 97.4 per cent. of silver.

“3. That the alloys at these turning-points have their calculated specific gravities.

“From the similarity of the curves of alloys, where we may assume, from their chemical behaviour, that we have only a solution of one metal in another, we may always draw approxi-

mately the curve of the alloys of any two metals, if we know to which class they belong. Thus, before a single copper-gold alloy had been determined, the curve was almost correctly drawn, and agreed with that which was afterwards found by experiment."

"That some alloys are chemical combinations," he adds, "may be deduced from the following facts:—

"1. At the turning-points of the curve we generally find the alloys contract or expand.

"2. There is no regular form of curve (gold-tin, gold-lead, and silver-copper), so that it cannot be *a priori* even approximately represented.

"3. At the turning-points the alloys contain large percentages of each other.

"4. At the turning-points of the curves the alloys are different from each other in appearance (crystalline form, etc.)."

To the second question, "To what is the rapid decrement of the conductivity due?" Matthiessen says, "The only answer which I can at present give to this question is that most of the other physical properties of the metal are altered in a like manner."

In a later research Matthiessen determined the electrical conductivity of a large number of alloys and established formulæ by which the conductivity of an alloy at any temperature might be calculated.

More recently Le Chatelier, working with greater ranges of temperature, has shown that in the case of metals which do not undergo any molecular change at temperatures below their melting-points the increase of electrical resistance is proportional to the temperature. Many metals, however, such as iron, exhibit irregularities in the resistances which occur at definite temperatures, and are evidently due to molecular or allotropic changes in the metal. Similar changes are also shown in the case of alloys.

The electrical resistance of metals and alloys at very low temperatures has been studied by Dewar and Fleming, who have shown that in the case of pure metals the resistance decreases with the fall in temperature, and the evidence tends to show that at the absolute zero all the metals would be practically perfect conductors. In the case of alloys, however, the results are entirely different. The resistance decreases only slightly as the temperature falls, and in many cases the resistance at -200° is almost as great as at 100° . The figures obtained by Dewar and Fleming for a number of alloys and metals are given in the following tables:—

ALLOYS.
Arranged according to Decreasing Resistance.

Alloy.	Specific Resistance in Microhms per c.c.			Temperature Coefficient at 18° C.
	At Boiling Water Temperature, 100° C.	At Normal Temperature, 18° C.	At Liquid Air Temperature, -182° C.	
Manganese steel	75.29	68.52	55.41	0.00127
Manganin	47.53	47.64	45.82	0.0000
Platinoid	42.88	41.94	39.19	0.00031
Nickel steel	35.18	30.40	19.47	0.00201
Platinum, Iridium	33.27	31.30	26.03	0.000822
Platinum, Silver	32.30	31.73	30.17	0.000243
German silver	30.73	30.11	28.32	0.000273
Platinum, Rhodium	23.94	21.63	15.13	0.00143
Copper, Nickel, Aluminium	15.78	15.07	13.05	0.000645
Copper, Aluminium	9.57	8.99	7.33	0.000897
Gold, Silver	7.00	6.42	4.82	0.00124
Aluminium, Silver	5.69	4.82	2.48	0.00238
Titanium, Aluminium	4.94	4.08	1.66	0.00290
Aluminium, Copper	3.97	3.09	0.72	0.00381
Silver	2.61	2.17	0.91	0.00285
Mn 12%				
Mn 12%, Ni 4%, Cu 84%				
Ni 4.35%				
Pt 80%, Ir 20%				
Pt 33%, Ag 66%				
Pt 90%, Rd 10%				
Cu 87%, Ni 6.5%, Al 6.5%				
Cu 97%, Al 3%				
Au 90%, Ag 10%				
Al 94%, Ag 6%				
Al 94%, Cu 6%				
Ni 17%, Cu 77%, Co 2%, Zn 2%, Fe 2%				

METALS.

Arranged according to Decreasing Resistance.

Metal.	Specific Resistance in Microhms per c.c.			Temperature Coefficient at 18° C.
	At Boiling Water Temperature, 100° C.	At Normal Temperature, 18° C.	At Liquid Air Temperature, -182° C.	
Lead	27.97	21.96	6.03	0.00411
Thallium	24.66	18.75	4.89	0.00398
Nickel	19.42	14.65	1.91	0.00622
Tin	18.30	14.14	3.40	0.00440
"A" Iron (Armstrong's)	15.73	11.50	2.34	0.00544
Platinum	14.81	11.65	3.34	0.003529
"H.W." Iron (Hopkins and Williams)	14.63	10.01	1.22	...
Cadmium	13.84	10.98	2.95	0.00419
Palladium	13.79	10.88	2.78	0.00354
Zinc	7.91	6.21	1.50	0.00406
Magnesium	5.99	4.65	1.00	0.00381
Aluminium	3.57	2.77	0.56	0.00423
Gold	2.94	2.34	0.68	0.00377
Copper	2.22	1.68	0.29	0.00428
Silver	2.06	1.57	0.39	0.00400

Lord Rayleigh suggests a possible explanation for the remarkable difference in the behaviour of alloys and pure metals, with regard to their electrical resistance, on the assumption of the heterogeneity of the alloys. According to this view, when a current is passed through an alloy, it sets up between the particles of the different metals a series of Peltier effects proportional to the current, and these create an opposing electromotive force also proportional to the current and indistinguishable, as far as experiments are concerned, from a resistance. If the alloy were a true chemical compound this opposing force would not exist.

This explanation is undoubtedly of great service in considering heterogeneous alloys; but it must be remembered that, in the case of the most perfectly homogeneous alloys known, namely, those of gold and silver, the alloy containing atomic proportions of the two metals and corresponding to the formula AuAg has the highest resistance of the series, a fact which could only be explained by assuming, as has been suggested, that the Peltier effects occurred between the molecules themselves.

The variations in the electrical resistance of amalgams at

different temperatures have been investigated by Mr R. S. Willows. The amalgams experimented upon include those of tin, zinc, cadmium, and magnesium; but the most interesting of these is the amalgam with zinc. For a given amalgam two curves could be obtained which differed entirely in certain important characteristics. Thus, for example, if, after determining the resistance, the amalgam was heated and allowed to cool and the resistance again determined, it was found that it was greater after heating than before. This could be repeated several times, the increase in the resistance becoming less and less, until after heating about six times it was found that a further heating did not increase the resistance. When this condition was reached the resistances at various temperatures were determined and the results plotted in the form of a curve. The amalgam was then allowed to stand at the temperature of the room for several weeks, its resistance being measured every morning at the same temperature. It was found that the resistance gradually fell slowly for the first three days, most rapidly about the seventh, and then again more slowly. In some cases it took six weeks for the resistance to become steady. A second series of determinations were then made, when it was found that the curve so obtained differed entirely from the first.

Many attempts have been made to trace analogies between metallic conduction and the electrolytic dissociation of salt solutions, but so far without success. In 1861 Gérardin conducted some experiments on sodium amalgam, from which he concluded that the metals might be separated by means of an electric current; but Dr Obach, who repeated his experiments with great care, was unable to obtain any evidence of dissociation of the amalgam. In 1887 the question was again investigated by Roberts-Austen at the request of the Electrolysis Committee of the British Association. He experimented upon alloys of gold and lead and silver and lead placed in cavities cut in a fire-brick and maintained in a molten state, but was unable to detect any separation with currents of 300 amperes. It must be remembered, however, that at the high temperatures employed in these experiments the diffusion must have been very rapid, and would probably be more than sufficient to counterbalance any separation of the metals due to the electric current. With reference to

these experiments it has been suggested by Professor Lodge that there must be a group of bodies on the borderland between alloys proper and electrolytes, in which some gradual change from wholly metallic to wholly electrolytic conduction might be expected.

Diffusion.—It has long been known that gases which do not act chemically upon one another are capable of mixing uniformly or diffusing into one another, even if the vessels containing them are only connected by a narrow tube, and if the vessel containing the lighter gas is placed above that containing the heavier gas. The same property of diffusion is observed in liquids, and becomes an important factor in the manufacture of alloys. It is evident, for example, that mere mechanical mixing could hardly produce the uniformity which is found in the alloy of gold and copper used for purposes of coinage. In this case 1200 ozs. of the alloy, containing 1100 ozs. of gold and 100 ozs. of copper, are melted at one time and cast into bars, when it is found that an assay of the last bar is practically identical with that of the first.

The question of the diffusion of metals was taken up by Roberts-Austen as a continuation of the work of Graham on gases and liquids, and in 1896 he communicated to the Royal Society the results of his investigations on the diffusion of gold and platinum in lead. In these experiments the molten metal was contained in tubes placed in an air bath, which was maintained at definite temperatures. The extent to which diffusion had taken place was determined by allowing the metal in the tube to solidify after a given time and analysing sections cut from the bar. The linear diffusion is expressed, in accordance with Fick's law, by the equation

$$\frac{dv}{dt} = k \frac{d^2v}{dx^2},$$

where x is the distance in the direction in which diffusion takes place, v is the degree of concentration of the diffusing metal, and t is the time. k is the diffusion constant, and is the quantity of metal in grams diffusing through unit area (one sq. cm.) in unit time (one day), when unit difference of concentration (in grams per c.c.) is maintained between the two sides of a layer 1 cm. thick.

Fig. 3 is the diagram given by Roberts-Austen to show the relative diffusion of gold and platinum taking place in a period of twenty-four hours in molten lead at a temperature of 500° C. The columns AB represent the actual length and diameter of

columns of fluid lead, and the spheres represent the sizes of the buttons of gold and platinum extracted from the sections of the columns as shown. The curves are plotted with distances of diffusion as ordinates, and concentrations as abscissæ.

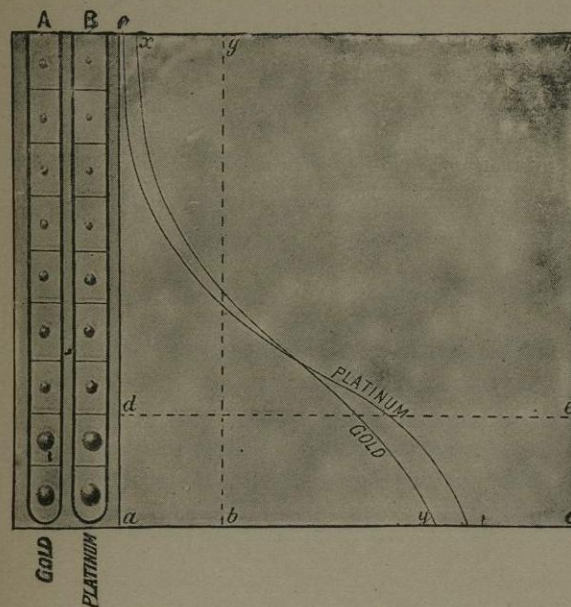


FIG. 3.—Diffusion of Gold and Platinum in Lead.

The determinations of k for a few metals are given in the following table:—

Diffusing Metal.	Solvent.	Temperature.	k in square centimetres.	
			Per day.	Per second.
Gold . . .	Lead . . .	492°	3·00	$3·47 \times 10^{-5}$
" . . .	" . . .	492	3·07	$3·55 \times "$
Platinum . . .	" . . .	492	1·69	$1·96 \times "$
" . . .	" . . .	492	1·69	$1·96 \times "$
Gold . . .	" . . .	555	3·19	$3·69 \times "$
" . . .	Bismuth . . .	555	4·52	$5·23 \times "$
" . . .	Tin . . .	555	4·65	$5·38 \times "$
Silver . . .	" . . .	555	4·14	$4·79 \times "$
Lead . . .	" . . .	555	3·18	$3·68 \times "$
Gold . . .	Lead . . .	550	3·18	$3·69 \times "$
Rhodium . . .	" . . .	550	3·03	$3·51 \times "$

By way of comparison with these figures the results of some determinations of the diffusion of metals in mercury published by Dr Guthrie in 1883 have been calculated by the same method and give the following values of k in sq. cms. per day:—

Tin in mercury at about 15°	·	·	·	1·22
Lead	”	”	·	1·00
Zinc	”	”	·	1·00
Sodium	”	”	·	0·45
Potassium	”	”	·	0·40

These results have since been practically confirmed by Humphreys.

Diffusion of Solid Metals.—It has long been known that solid bodies are capable of diffusing into one another, and the old processes of cementation are based upon this fact; but it is only within comparatively recent years that the subject has received serious attention from a theoretical point of view. In 1820 Faraday and Stodart, while experimenting on the alloys of iron, observed that steel and platinum in the form of bundles of wire could be readily welded at a temperature considerably below that at which either of the metals alone would be affected. They further observed that on etching the welded mass with acid the iron appeared to be alloyed with the platinum. More than half a century later (in 1877) Chernoff drew attention to the fact that if two surfaces of iron are heated to about 650° in intimate contact with one another they will unite. From this date the publication of researches on the diffusion of solids became more frequent. In 1882 Spring demonstrated that alloys may be produced by compression of their constituent metals in a fine state of division, while Hallock in 1888 showed that similar results could be obtained without the aid of pressure, but at somewhat higher temperatures. In 1894 Spring showed that two carefully prepared surfaces of two metals pressed together and maintained at temperatures of from 180° to 400° for eight hours would interpenetrate and form alloys at the junction of the two metals. The first actual measurements of the rate of diffusion of solids are, however, due to Roberts-Austen,* who extended his researches on diffusion from the fluid to the solid state, and in 1896 published the results of what is now justly considered one of the classical

researches on alloys. He determined the rate of diffusion, k , of gold in solid lead at various temperatures, and his results are given below, with the rate of diffusion of gold in fluid lead at 550° for the sake of comparison:—

				K	
Diffusivity of gold in fluid lead at 550°	·	·	·	3·19	
”	”	solid lead	251°	·	0·03
”	”	”	200°	·	0·007
”	”	”	165°	·	0·004
”	”	”	100°	·	0·00002

In order to determine the rate of diffusion of gold in lead at the ordinary temperature, discs of pure gold were clamped to the ends of cylinders of lead 0·88 cm. in diameter, and these were kept at the ordinary temperature of the atmosphere for a period of four years. At the end of this time it was found that the discs of gold adhered to the lead cylinders and that diffusion had taken place. Slices were cut off the cylinders, the first 0·75 mm. thick, and succeeding layers 2·3 mm. thick, and these were then assayed. The first layer was found to contain as much as 1 oz. 6 dwts. of gold per ton, while the fourth layer was estimated to contain 1½ dwt. per ton. From these results Roberts-Austen calculated that the amount of gold which would diffuse in solid lead at the ordinary temperature in one thousand years would be almost the same as that which would diffuse in molten lead in one day.

Liquation.—When two or more metals are melted together and allowed to cool it seldom happens that the resulting alloy solidifies, or freezes, as a whole and at a definite temperature. Usually one portion freezes first, rejecting another portion of different composition, which then solidifies at a lower temperature. This property is known as *liquation*, and has been made use of in the well-known Pattinson process for the separation of silver from lead. In this process it will be remembered that the lead containing silver is melted and allowed to cool slowly, the almost pure lead being ladled off as it solidifies, leaving a still molten alloy comparatively rich in silver.

The property of liquation has been long known, but it is to Dr Guthrie that we owe the first systematic investigation of the problem. He considers that the solidification of a molten alloy is analogous to the solidification of a mass of molten rock in which the quartz and felspar solidify before the mica. So, in the case

of alloys, a certain metal or alloy solidifies first and eventually leaves behind the most fusible alloy of the series. This alloy Dr Guthrie calls the *eutectic* alloy. The constituent metals in the eutectic alloy do not occur in atomic proportions, and he remarks that "the preconceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportions, that it must be a chemical compound, seems to have misled previous investigators." He admits the existence of compounds, but declares that "the constitution of eutectic alloys is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties less definite."

The phenomenon of liquation has been long known in the case of the copper-silver alloys, and, owing to the importance of these alloys for coining purposes, they have received considerable attention. D'Arcet in 1824 and Mercklein in 1834 both pointed out that the alloys of silver and copper are not homogeneous; and Levol, in 1854, as the result of a very careful investigation conducted on these alloys cast in both cubical and spherical moulds, came to the conclusion that the only homogeneous alloy of the series was that containing 71.89 per cent. of silver, which he considered to be a definite combination of the two metals corresponding to the formula Ag_3Cu_2 .

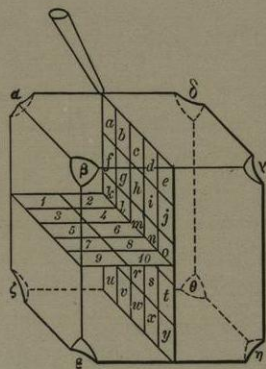


FIG. 4.—Cube showing liquation of Silver and Copper Alloys.

In 1875 the question was taken up by Roberts-Austen, who repeated Levol's experiments. He drew attention to the influence

of the rate of cooling on liquation, and showed that in the case of an alloy containing 925 parts of silver and 75 parts of copper very slowly cooled in a cubical mould 45 mm. in side, the maximum difference in composition was only 1.4 per thousand, but as much as 13 per thousand when rapidly cooled. His figures are given below, together with a diagram (fig. 4, p. 36), showing the position in the cube corresponding with the assays:—

	a	925.7		
	b	925.0		
	c	925.0		
	d	925.0		
	e	925.4		
	f	924.3		
	g	925.0	Horizontal Plane	1. 924.8
	h	925.3		2. 925.0
	i	925.3		3. 924.9
	j	925.3		4. 924.9
	k	924.3		5. 925.0
	l	925.3		6. 925.1
	m	925.3		7. 925.1
	n	924.4		8. 925.1
	o	925.0		9. 925.0
	p	924.3		10. 925.0
Vertical Plane	q	925.0		
	r	925.3		
	s	925.0		
	t	924.9		
	u	924.3	Corners	a 924.1
	v	924.7		β 924.1
	w	924.9		γ 924.1
	x	924.9		δ 924.4
	y	925.3		ε 924.0
				ζ 924.2
		η 924.2		
		θ 923.9		

Dip assay, 924.9. Maximum difference (between the centre and the corners) 1.40 per thousand.

Some years later Roberts-Austen returned to the subject, and by means of cooling curves taken with the recording pyrometer showed that Levol's alloy was the only one which solidified at a definite temperature. Heycock and Neville, and Osmond have also shown that Levol's alloy is the true eutectic of the series.

Mr E. Matthey has investigated the liquation of alloys of gold and silver containing lead and zinc as obtained in the extraction of gold by the cyanide process, and his results are extremely important. An ingot of this type weighing 120 ozs. was found to contain 662 parts of gold per thousand at the bottom corner and only 439 at the top. Another ingot weighing 400 ozs. and containing 16.4 per cent. of lead and 9.5 per cent. of zinc was found, on separating the whole of the precious metals, to contain

gold 514.0 parts per thousand, and silver 75.8 parts per thousand, and its value was reckoned at £1028. The value, however, as calculated from the mean of fourteen assays on the ingot was only £965. In the case of gold and zinc Matthey found that the gold tends to liquate towards the centre of the mass, but only slightly.

An alloy containing 900 parts of gold and 100 of zinc in the form of a sphere 3 in. in diameter was found to be only 1 to $2\frac{1}{2}$ parts per thousand richer in the centre than at the outside. Lead behaves in a similar manner; but the liquation is more marked, the centre of a sphere containing 30 per cent. of lead being 29 parts per thousand richer than the outside. When both lead and zinc are present the liquation is still more marked, and in the case of an alloy containing 15 per cent. of lead and 10 per cent. of zinc the sphere contained 657 parts per thousand at the top, 785 in the centre, and 790 at the bottom. In connection with these alloys it is a curious fact that if the quantity of silver present is not less than two-thirds that of the lead and zinc together, they show very little tendency to liquate, and an alloy containing 55 per cent. gold, 7 per cent. zinc, 18 per cent. lead, and 20 per cent. silver, was found to be practically homogeneous.

CHAPTER III.

METHODS OF INVESTIGATION.

THE experimental difficulties encountered in any attempt to inquire into the nature and constitution of metals and alloys are by no means inconsiderable, and until comparatively recently the subject has been one for speculation and hypothesis rather than for any positive knowledge. These difficulties, however, have been largely overcome by the improved methods of modern research, and before dealing with the constitution of alloys it may be well to consider the various methods which have been employed in their investigation.

These have been conveniently classified by Roberts-Austen and Stansfield under the following heads:—

1. The Chemical Grouping of the Metals in a Solid Alloy.
2. The Separation of the Constituents during Solidification.

The first of these includes the following methods of investigation:—

- a.* The specific gravity of alloys.
- b.* The electrical resistance of alloys.
- c.* Diffusion of metals in alloys.
- d.* Electrolytic conduction.
- e.* Thermo-electric power.
- f.* The heat of combination of metals to form alloys.
- g.* The electromotive force of solution of metals and alloys.
- h.* Isolation of the constituents of alloys by chemical methods.
- i.* Microscopical examination of alloys.

The second group deals with those methods involving a study of the separation of the constituents of an alloy on solidification, and includes—