NOTES ON THE TABLE OF PHYSICAL CONSTANTS OF METALS.

The atomic weights given are those approved by the International Congress for the year 1910 (see *Proc. Chem. Soc.*, vol. xxv., No. 362, p. 255). The atomic volumes have been calculated from the latest figures for atomic weights and specific gravities. The specific heats given are the mean specific heats between 100° and 15° in most cases. Great care has been taken to obtain the latest and most trustworthy figures for the melting-points. The thermal conductivities are given in calories, centimetre-seconds; when multiplied by 100, the figures obtained are practically the same as when silver is taken as the standard with a conductivity of 100. The electrical conductivities are given in absolute units measured in mhos. Mhos are the reciprocals of ohms, and the mho-conductivity is obtained by dividing 10^9 by the volume resistivity in c.g.s. units.

CHAPTER III.

ALLOYS.

Early Investigations.—Many valuable mechanical properties are conferred upon metals by associating them with each other—this fact was discovered at a very early period of metallurgical history, and it seldom happens that metals are used in a state of purity when they are intended for industrial purposes. The word "alloy" originally comes, in all probability, from the Latin *adligo* (alligo), "to bind to," and not, as Sir John Pettus thought, from the Teutonic *linderen*, "to lessen," suggestive as it is of the fact that a precious metal is lessened in value by the addition of a base one.

The distinguished chemist Dumas eloquently pleaded, many years ago, against leaving alloys in the oblivion to which modern chemists consigned them. Until quite recently the extent and complexity of the subject was not realised, and Lupton,[1] in 1888, directed attention to the number of alloys which then awaited examination. He said:—"Hatchett recommended that a systematic examination of all possible alloys of all the metals should be undertaken. He forgot to remind anyone who should attempt to follow his advice that if only one proportion of each of the thirty common metals were considered, the number of binary alloys would be 435, of ternary 4060, and of the quaternary 27,405. If four multiples of each of the thirty metals be taken, the binary compounds are 5655, ternary 247,660, and quaternary 1,013,985."

Nevertheless, if the properties of many alloys have yet to be investigated, the study of alloys generally has not been neglected. The modern bibliography relating to them is much more extensive than it is usually supposed to be, and the older writings are very full, and contain the results of far more accurate observation than they are credited with. In the early days of chemistry, as its history abundantly proves, alloys received much attention; and

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[1] *Nature*, vol. xxxvii., Jan. 5, 1888, p. 238.

although the early chemists often failed to distinguish alloys from simple metals, or used them in unsuitable ways, they left an experimental record, the value of which is sadly unappreciated. From this record it is, incidentally, evident that the development of the art of separating metals from their ores, and from each other, was quickly followed by the acquisition of the knowledge that metals possess peculiar properties when reunited in certain proportions, and are thereby rendered more useful than they were in the pure state.

In early times some metals were used unalloyed, although at the present day they have little industrial application except in union with other metals. Antimony, for instance, now only employed as a constituent of certain alloys, was formerly cast and fashioned into ornaments, as is proved by the analyses of Virchow, and by a fragment of a very ancient Chaldean vase, which fragment, when examined by Berthelot, proved to be of pure antimony.[1] The implements and ornaments discovered by Schliemann abundantly show that the early Greeks were familiar with alloys of silver and gold, copper and tin, lead and silver, and with many others, all artificially prepared. Throughout the Middle Ages there seems to have been a belief that the action of metals on gold and silver was, on the whole, corrupting; and Biringuccio, in 1540, possibly seeing that this was the prevailing view, carefully defined such alloys as being "nothing but amicable associations of metals with each other"; and he further pointed out that metals must be mixed by weight, and not at random.

Views as to the Constitution of Alloys.—Passing from the sixteenth to the eighteenth century, we find four writers whose names deserve to be specially mentioned, because they seem to have been the first to indicate the direction in which modern investigation has been conducted. These are Réaumur, Gellert, Musschenbroek, and Achard, who respectively studied — 1st (Réaumur), molecular change produced in a metal by heat; 2nd (Gellert), the relation of fluid metals to each other considered as solvents; 3rd (Musschenbroek), the cohesion of alloys as shown by certain mechanical properties; and 4th (Achard), the electrical behaviour of metals and alloys. It is interesting to trace the connection between the older work and the new. Réaumur,[2] in explaining the hardening of steel by rapid cooling from an elevated temperature, comes very near the modern view that a metal may, under certain conditions, pass from one allotropic state to another, for he distinctly contemplates the possibility of molecular change produced by the expulsion by heat of "sulphurs and salts" from the molecules into interstitial spaces between them. He speaks of "molecules and elementary parts

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[1] *Ann. de Chim. et de Phys.*, vol. xii., 1887, p. 135.

[2] *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 321.

of molecules," like a modern writer, and tries to show that when hot steel is rapidly cooled, "sulphurs and salts" cannot return into the molecules, but remain in the interstitial spaces; and that, therefore, the physical properties of hard steel become quite different from those of soft. If it should be urged that the analogy between carburised iron and alloys is overstrained, it may be pointed out that, in 1867, Matthiessen said, after appealing to the fact that in certain alloys the constituent metals are present in allotropic states, "I have always made a comparison between iron and steel (and alloys). This has been done to show that the carbon iron alloys behave in an analogous manner to other alloys, which cannot be looked upon as chemical combinations."[1]

Gellert makes the analogy of certain alloys to solutions very clear, and in his *Metallurgic Chemistry* he gives a table showing the relative solubilities of metals in each other, while in the observations which accompany it[2] he says, to cite one of the cases he takes as an illustration, "Since copper and silver and copper and gold dissolve one another very readily, the copper cannot be parted from gold or silver by means of iron," probably having in mind a reaction which enables silver to be parted from gold by the action of sulphur and iron. He further clearly shows that, with regard to the solution of metals in a triple alloy, he understood the possibility of a division of a metal between two other metals acting as solvents.

The mechanical properties of alloys were investigated by Musschenbroek, who, working in the early part of the eighteenth century, made some experiments on the tensile strength of metals and alloys. He writes of "the absolute cohesion by which a body resists fracture when acted upon by force drawing according to its length," and gives the tenacity of several metals, and the alloys, brass and pewter.[3] He shows the importance of such work so clearly that it is remarkable how slowly the mechanical testing of metals has developed since his time.

Achard, whose researches were published in 1784, made a very extended series of experiments on multiple alloys, as well as those of simple metals. He pointed out that the relative conductivities of substances for heat and for electricity are closely related.[4] He devised an appliance for the experimental verification of this fact, and, as he included alloys in his researches, it may fairly be claimed that he led the way for the important generalisation that alloys may be ranged in the same order as regards their power of

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[1] *Journ. Chem. Soc.*, 1867, p. 220.

[2] English translation of his work, London, 1776, p. 186.

[3] *Elements of Philosophy*, translated by John Colson, F.R.S., vol. i., 1744, p. 237.

[4] *Sammlung physikalischer und chemischer Abhandlungen*, Berlin, 1784, vol. i.

conducting heat and electricity which was made by Wiedemann and Franz in 1853–9.

The necessity of metals being pure when added to each other was hardly recognised until the eighteenth century; and Duhamel, who contributed the article on alloys to the *Encyclopédie Méthodique* in 1792, appears to have been the first writer to insist on the necessity for making exact experiments upon alloys with metals which possess a high degree of purity, and on effecting their union by heat in closed vessels. He further pointed out that up to his time no chemist had taken these precautions, and it is certain that in conducting some modern experiments they have been neglected.

In the early part of the nineteenth century researches on alloys became more numerous; they were mainly directed to ascertaining the effect on the density of metals produced by alloying them, and to determining the effects of slow cooling on alloys with low melting-points. Of such a nature was the work of Ermann in 1827 and of Rudberg (1830–1). Ermann called attention to the peculiar behaviour of alloys of lead and tin when solid. Rudberg studied anomalies in these alloys when in the liquid state.

Regnault showed that the specific heats of certain fusible alloys were greater near 100° than the mean specific heat of their constituents; and this fact appears, as Spring has shown,[1] to have induced Person to undertake researches on the latent heat of alloys and on these specific heats.

Undoubtedly, one of the greatest works on alloys of the present century was that of Matthiessen, who studied the electrical resistance of metals and alloys, and was led to the conclusion that in many cases metals are present as allotropic modifications—that is, in totally different forms from those in which we ordinarily know them.

It is by no means easy to investigate the molecular constitution of alloys, but evidence may be gathered in the following ways:—

1. By comparing the properties of an alloy with those of its constituent metals.
2. By studying the behaviour of alloys in passing from the liquid to the solid state, and conversely in passing from the solid to the liquid.
3. By determining the physical constants of solid alloys, such as the melting-point, specific gravity, specific heat, electrical resistance, electromotive force, and their mechanical properties, such as tenacity and extensibility.
4. By examining with the microscope, suitably prepared surfaces of alloys, after various thermal and mechanical treatments.

First we must consider the methods of producing alloys, for the union of metals may be effected in three ways:—

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[1] *Bull. de l'Académie Royale de Belgique*, 1886 (3), vol. xi. p. 355.

1. By fusion—that is, by causing metals to unite by melting them together.
2. By compression of the powders of the constituent metals.
3. By electro-deposition.

Union of Metals by Fusion.—The first method, by fusion, is naturally the method ordinarily adopted. One of the metals is melted, and the other is added to it, sometimes in the fluid state, but often in the solid. The product—the alloy—will have very different properties from those possessed by either of the constituent metals. Every metal has, of course, a definite melting-point, but, apart from the heat initially required to melt a metal, we find that the union of metals is sometimes attended with an evolution and sometimes with an absorption of heat.

The following metals evolve heat when they are united:—aluminium and copper, platinum and tin, arsenic and antimony, bismuth and lead, gold and just-melted tin; while, on the other hand, lead and tin absorb heat when their union takes place. There are many other cases.

In the case of many metals these effects can only be demonstrated by the aid of delicate instruments. There is, however, a simple case in which the union of metals is attended with a considerable diminution of temperature; it is an experiment we owe to Mohr, and its explanation is a very complicated one.

If tin, lead, and bismuth, as finely divided as possible, be intimately and rapidly mixed in equivalent proportions, with eight equivalents of mercury, under conditions in which heat is not transmitted to the mixture from the walls of the containing vessel, it will be found that the temperature falls from the ordinary temperature of the room + 17° C. to − 10° C., so that if a vessel containing water be placed in the mixture the water will be frozen. The experiment proves that by the union of metals, using mercury as a solvent, a freezing mixture may be produced.

Union of Metals by Compression.—For many years the labours of Prof. Walthère Spring, of the University of Liége, were largely devoted to the study of the effect of compression on various bodies.[1]

The particles of a metallic powder left to itself at the ordinary atmospheric pressure will not unite, but by augmenting the points of contact in a powder the result may be very different. Spring's experiments were made with the aid of a compression apparatus, the general form of the appliance employed being shown in the diagram, fig. 23. The metallic powder is placed under a short cylinder of steel, A, in a cavity in a steel block divided vertically, held together by a collar, and placed in a chamber of gun-metal,

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[1] *Bull. de l'Académie Royale de Belgique* (2), vol. xlv. (1878), No. 6; (2), vol. xlix. (1880), No. 5. See also subsequent papers in the same publication, in the *Bull. Soc. Chim.*, Paris, and in the *Berichte der Deutsch. Chem. Gesellschaft* (Bildung von Legirungen durch Druck), vol. xv. p. 595.

which may be rendered vacuous. The pressure is applied to a cylindrical rod passing through the stuffing-box. Under a pressure of 2000 atmospheres on the piston, or 13 tons on the square inch, lead, in the form of filings, becomes compressed into a solid block, in which it is impossible to detect the slightest vestige of the original grains, while under a pressure of 5000 atmospheres lead no longer resists the pressure, but flows, as if it were liquid, through all the cracks of the apparatus, and the piston of the compressor descends to the base of the cylindrical hole, driving the lead before it. The more interesting results were obtained by Spring with crystalline metals. Bismuth, as is well known, is crystalline and brittle, yet fine powder of bismuth unites, under a pressure of 6000 atmospheres, into a block very similar to that obtained by fusion, having a crystalline fracture. Tin when compressed in powder unites; and if it is made to flow through a hole in the base of the compression apparatus, the wire so formed sometimes, though not always, emits the peculiar "cry" of tin when bent. The following table shows the amount of pressure required to unite the powders of the respective metals:—

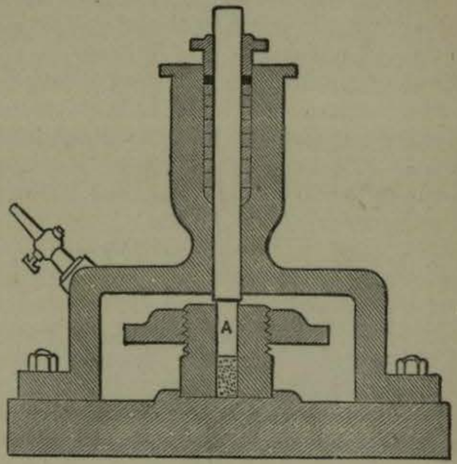

Fig. 23.

		Tons per Square Inch.
Lead	unites at	13
Tin	,,	19
Zinc	,,	38
Antimony	,,	38
Aluminium	,,	38
Bismuth	,,	38
Copper	,,	33
Lead	flows at	33
Tin	,,	47

We know that combinations are produced when certain bodies in solution are submitted to each other's action. But do solids combine? Is the alchemical aphorism "That bodies do not react unless they are in solution" true? Experiment proves that such solution is not necessary. Take, for example, two anhydrous salts—iodide of potassium and corrosive sublimate—both in a dry condition. When they are mixed in a mortar they unite, as is shown by the vermilion-coloured iodide of mercury which is produced. But do solid metals combine, in the sense in which chemical combination is possible between metals, when submitted to each other's action under the conditions which prevail when their powders are compressed? Mohr has pointed out[1] that cohesion is a form of chemical affinity; and the experiment cited of freezing water by the cold produced by amalgamation, affords valuable evidence in support of his view. It occurred to M. Spring that if there be true union between the particles of a metallic powder when submitted to great pressure in the appliance shown in fig. 23, it ought to be possible to build up alloys by compressing the powders of the constituent metals, and he urged that the formation of alloys by pressure would afford the most conclusive proof that there is a true union between the particles of metals in the cold when they are brought into intimate contact. Experiment proved that this reasoning is correct, for by compressing in a finely divided state fifteen parts of bismuth, eight parts of lead, four parts of tin, and three parts of cadmium, an alloy is produced which fuses at 100° C. It is necessary, however, to compress the mixed powder twice, crushing and filling up the block obtained by the first compression, because the mechanical mixture of the constituent metals is not sufficiently intimate to enable a uniform alloy to be obtained by a single compression. The alloy produced fuses in boiling water actually at 98° C., although the melting-point of the most fusible of its constituents, the tin, is 232° C. It may be urged that by compressing these powders heat is evolved, and that this heat may be sufficient to produce incipient fusion of the metallic powders, or, at all events, may exert a material influence on the result obtained. This objection has been experimentally anticipated by Prof. Spring. First the compression is effected with extreme slowness, and therefore there can be no question as to the sudden evolution of heat, as would be the case if the powders were compressed by impact instead of by slow squeeze; and, to sum the matter up briefly, Spring calculates an extreme case—that if it be granted that all the work done in compressing the powders were actually translated into heat, it would only serve to heat a cylinder of iron 10 mm. in height and 8 mm. in diameter (the dimensions of cylinder A, fig. 23, used in his apparatus) 40·64° C.

In order that direct experimental evidence might not be want-

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[1] *Liebig's Ann.*, vol. cxcvi. (1879), p. 183.

ing, Spring took the organic body, phorone, a hard, crystalline substance which melts at 28° C., and compressed it exactly as in the case of the metallic powders.[1] He took the precaution to place a shot of lead on the top of the powder before submitting it to compression. Only imperfect union of the particles of phorone resulted. The conclusion of the experiment proved that the shot remained where it had been placed at the top of the column, and therefore the 28° necessary to melt the substance had not been evolved, for if it had, the shot must have fallen through the fluid mass. It is, then, absolutely safe to conclude that, in the compression of bismuth for instance, there can be no question of the evolution of the heat necessary for the fusion of the metal.

It appears to be also quite safe to conclude that it is proven that *solid* metals possess the power of reacting on each other and forming alloys, provided their particles are really in contact.

Union of Metals by Electro-Deposition.—The formation of alloys by the electrolytic deposition of the constituent metals is a subject of great importance; and although the union of metals is usually effected by fusion, fire is not the only agent which can be employed for this purpose. Two or more metals can be deposited side by side by the aid of the electric battery. Copper and zinc may be deposited by electrolysis so as to form brass, and many of the beautiful bronzes and alloys of the Japanese can be obtained electrolytically; and, further, by suitable admixture of gold, silver, and copper, red gold, rose-coloured gold, or green gold may be deposited, so that the electro-metallurgist has at his command the varied palette of the decorative artist.

Liquation and Segegration.—It is now necessary to examine more closely the mutual relations of the metals when united. Metals may be mixed in the fused state, but it by no means follows that they will remain in admixture if they are allowed to cool slowly, or sometimes even rapidly. In fact, a cooling mass of mixed metals often behaves much as water containing suspended matter does in freezing, when the ice first formed rejects the foreign matter, and, as has been shown by the classical researches of Levol,[2] the portion of the alloy which first solidifies rejects certain other portions of the constituent metals. This action is called **liquation.** The term is also applied in a somewhat wider sense to the actual isolation of the components of ores or of alloys from each other. For instance, when an ore or mixture of metals is exposed to a degree of heat sufficient only to melt the most fusible member or constituent present in the mass, it flows away from the unmelted residue. In the case of alloys the importance of liquation has been fully recognised. If lead and zinc be thoroughly mixed in the fused state, and slowly cooled in a deep mould, the separation will be almost complete, and it will also be seen that it is easy to break off one corner at the side where the zinc has separated itself, and to flatten out another one, which shows it to be nearly pure lead. Take, again, the case of what was a triple admixture of lead, antimony, and copper, thoroughly mixed when fluid, and cooled in a cylindrical mould. The copper and the antimony unite, but they reject much of the lead, and drive it to the centre of the mass, so that the solidified cylinder, when broken across, presents a ring of the purple copper-antimony alloy surrounding a malleable core. Silver and copper alloys behave in a similar manner, but in any mixture of fused silver and copper, one particular alloy of these metals is formed, which is driven outward or inward in the cooling mass according to whether silver or copper is in excess in the bath. In all these cases the separation is never complete; the lead retains some 1·6 per cent. of zinc, and the zinc about 1·2 per cent. of lead. The copper and antimony retain a small amount of lead, and the lead a small amount of copper and antimony, as is shown by some very careful experiments of Dr E. J. Ball, to which reference has already been made. The solid mass in all these cases is a mixture of solidified solutions of the metals in each other.

Dr Guthrie investigated this side of the problem at some length.[3] It is difficult to give a brief account of his work, but his conclusions may be stated as follows: He considers that certain alloys in cooling behave as a cooling mass of granite would: clear molten granite would throw off, in cooling, "atomically definite" bodies, leaving behind a fluid mass, which is not definite in composition, as the quartz and the felspar undergo solidification before the mica. In alloys much the same thing happens, for when a molten mass of lead and bismuth or bismuth and tin cools, a certain alloy of the metals falls out, just as the quartz and felspar did, and ultimately the most fusible alloy of the series is left, which Dr Guthrie calls the eutectic alloy. It is the most fusible alloy of the series, but the proportions between the constituent metals are not atomic proportions, and Guthrie says 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"; but he adds "that certain metals may and do unite with one another in the small multiples of their combining weight may be conceded; 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 the less definite."

Guthrie dealt only with alloys of low melting-points, such as the fusible metals, but the facts are the same in the case of alloys

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[1] *Bull. Soc. Chim.*, vol. xli. (1884), p. 488.

[2] *Ann. de Chim. et de Phys.*, vol. xxxvi. (1852), p. 193; vol. xxxix. (1853), p. 163.

[3] *Phil. Mag.*, vol. xvii. (1884), p. 462.

with higher melting-points, as shown by later experiments. The silver-copper alloys, for instance, which melt below 940° C., afford a striking instance. For further information upon this point we must wait for the development of Mendeléef's theory of solution. He regarded solutions as strictly definite, atomic, chemical combinations at temperatures higher than their dissociation temperatures. Definite chemical substances may be either formed or decomposed at temperatures above those at which dissociation commences; the same phenomenon occurs in solution; at ordinary temperatures they can either be formed or decomposed.

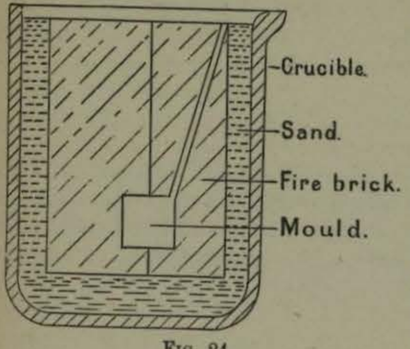

FIG. 24.

Liquation is very marked in the case of copper-silver alloys, and it is well known in Mints that when molten alloys of certain metals are cooled, groups of the constituent metals, or even the constituent metals themselves, separate, and thus occasion irregularity in the composition of the solidified mass. The phenomenon has been carefully studied by, amongst others, Lazarus Ercker and Jars, whilst in more modern times the researches of D'Arcet in 1824, of Mercklein in 1834, of Levol in 1854, have shown that ingots of silver and copper are not homogeneous throughout. Levol cast the alloy to be examined either in a cubical iron mould of 45 mm. side, or in a sphere 50 mm. in diameter. He concluded that the only homogeneous copper-silver alloy was that containing 71·89 per cent. of silver, and he considered this to be a definite combination of the two metals, with the formula Ag_3Cu_4 (or Ag_3Cu_2 if 63·57 be taken as the atomic weight of copper). All other alloys of silver and copper he viewed as mixtures of this definite alloy with excess of either of the metals. In 1875 the author[1] repeated many of Levol's experiments, and gave evidence for modifying his view that the only homogeneous alloy of silver and copper is that which contains 71·89 per cent. of silver. The uniformity in composition of the series of copper-silver alloys depends greatly on the method of cooling. By slow cooling, many alloys, other than the one mentioned above, may be made as uniform as it, its peculiarity consisting in the fact that its composition is uniform whether it is cooled slowly or rapidly. In order to ascertain whether liquation is modified if the cooling be greatly protracted, cubical moulds, about 4 to 5 millimetres in side, of firebrick (fig. 24), were employed. These could easily be heated to bright

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[1] *Proc. Roy. Soc.*, vol. xxiii. (1875).

redness, and slowly and uniformly cooled. The following results show that the maximum difference in the composition of an alloy containing 925 parts of silver and 75 parts of copper was only 1·40 per thousand when the alloy was slowly cooled, while it was as much as 13 parts per thousand when the alloy was rapidly cooled:—

Vertical Plane	*a.*	925·7	Horizontal Plane	1.	924·8
	b.	925·0		2.	925·0
	c.	925·0		3.	924·9
	d.	925·0		4.	924·9
	e.	925·4		5.	925·0
	f.	924·3		6.	925·1
	g.	925·0		7.	925·1
	h.	925·3		8.	925·1
	i.	925·3		9.	925·0
	j.	925·3		10.	925·0
	k.	924·3			
	l.	925·3	Corners	α.	924·1
	m.	925·3		β.	924·1
	n.	924·4		γ.	924·1
	o.	925·0		δ.	924·4
	p.	924·3		ε.	924·0
	q.	925·0		ζ.	924·2
	r.	925·3		η.	924·2
	s.	925·0		θ.	924·9
	t.	924·9			
	u.	924·3			
	v.	924·7			
	w.	924·9			
	x.	924·9			
	y.	925·3			

"Dip Assay," 924·9.

Maximum difference [between the centre and the corners], 1·40 per thousand.

The diagram (fig. 25) shows the position in the cube corresponding to the letters and figures given above.

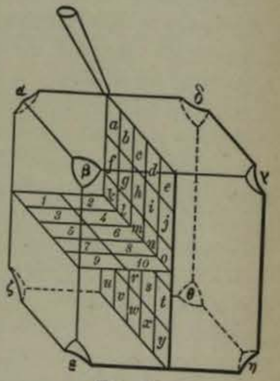

FIG. 25.

Levol also showed that in solidifying alloys of lead with the precious metals, if the latter are present in small quantity, they are driven towards the centre of the solidifying mass. Gowland and Koga[1] have shown that when 984·37 parts of silver and 14·80 parts of bismuth are melted and cast into an open ingot mould so as to give an ingot weighing about 1000 troy oz., the portions of the ingot which remain longest fluid are richer in silver than the others. The entire question was reviewed in 1889 by Peligot,[2] who endeavoured to ascertain, by assaying various parts of an ingot of gold weighing 13 lbs., whether he could detect the

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[1] *Journ. Chem. Soc.*, vol. li. (1887), p. 410.

[2] *Bull. Soc. d'Encouragement*, vol. iv. (1889), p. 171.

effects of liquation. The ingot contained 900 parts of gold in 1000, the alloying metal being principally copper, and he concluded that, within the limits of the errors of observation, there was no evidence of liquation. As this is a question of much industrial importance in relation to the precious metals, the author has made further investigations into the subject, and, in view of the difficulty of obtaining more precise evidence on the point, the following experiment was made: A gold ingot of a fineness of 984·7, the alloying metal being silver, was melted and poured into a spherical mould of iron. The temperature of the molten metal was much higher than that of the mould, and probably in this case the position of the metal which solidified last would be situated somewhere above the geometrical centre of the mass. From the sphere of solid gold, which was 3 in. in diameter and weighed 140 oz., a disc, $\frac{3}{8}$ in. in thickness, and of the full diameter of the sphere, was cut in a vertical plane. This disc, which weighed 31 oz., was rolled in two directions, at right angles to each other, to a convenient thickness for cutting with shears, and assay pieces were cut from points distributed over its entire surface. The results of eighty-two assays afforded no clear evidence of systematic rearrangement, for although there appeared to be an enrichment towards the upper part to the extent of $\frac{8}{100000}$ths, such small differences as existed in the assays made on metal taken from the same horizontal planes could not be regarded as being due to any definite redistribution of the metal. It will thus be evident that gold of high standard alloyed with silver does not show any marked tendency to reject on solidification the silver with which it is associated. It is well known, however, that there is a development of crystallisation, and that other remarkable changes are produced in the structure of pure gold by the addition of minute quantities of lead, bismuth, and certain other metals. Ample evidence has been obtained by Dr T. K. Rose and the author[1] to show that gold alloyed with copper and properly mixed in the molten state is not homogeneous when solid. The importance of this fact is revealed by the opinion which has been expressed[2] that standard trial plates of gold alloyed with copper should no longer be used in testing the accuracy of the coinage.

Mr E. Matthey[3] has, moreover, shown that by casting an alloy of gold and platinum containing 900 parts of gold and 100 parts of platinum in the identical mould above described, there is a concentration of platinum towards the centre of the mass, the gold and platinum being as 900 gold to 98 platinum on the

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[1] Rose, *Chem. Soc. Journ.*, vol. lxvii., 1895, p. 552. Roberts-Austen and Rose, *Proc. Roy. Soc.*, vol. lxvii., 1900, p. 105.

[2] *Annual Mint Report*, 1900.

[3] *Phil. Trans.*, [A] vol. clxxxiii. (1892), p. 629; *Proc. Roy. Soc.*, vol. xlvii. (1890), p. 180.

exterior, against 845 gold and 146 platinum at the centre of the mass. Consequently, it is evident that gold on solidifying does tend to free itself from associated platinum.

It is, however, in relation to the metallurgy of iron and steel that the question of liquation and segregation is of primary importance. There can be no doubt that when an ingot of steel slowly cools, phosphorus, sulphur, and carbon, and to a less degree manganese and silicon, tend to separate from the mass and to become concentrated in that portion of the ingot which solidifies last. The fact that segregation takes place in steel ingots appears to have been discovered by Stubbs,[1] who mentioned it, whilst discussing a paper by Parry, at the spring meeting of the Iron and Steel Institute, 1881. The subject was then taken up by Snelus,[2] who published his results in the same year, completely confirming Stubbs' earlier observations. Since then the subject has received attention from Eccles, Stead, Howe, Talbot, and others.

Talbot[3] made an exhaustive examination of segregation in acid and basic steel ingots, with and without the addition of aluminium. He concluded that in ingots to which no aluminium has been added, excessive segregation occurs down the central portion of the ingot, from about 6 inches from the top to half-way down, that sulphur tends to segregate most, phosphorus next, then carbon, and finally manganese, the segregation of which is so slight as to be almost negligible. The effect of the addition of 4 ounces of aluminium per ton was to immediately reduce the amount of segregation, as will be seen from the figures in the table on the next page, taken from analyses of borings from the centre and outside of acid steel ingots.

The borings were taken from top to bottom at distances of 6 inches, and the ingots measured 18 in. × 22 in. × 67 in.

The average analysis of all the drillings taken from the ingot to which no aluminium had been added was S ·059 P ·055 C ·41; and the average analysis of all the drillings from the ingots to which aluminium had been added was S ·060 P ·052 C ·39. There can be no doubt, therefore, that constituents whose presence is injurious to the mechanical properties of steel find their way towards the top centre of the ingot. In steel ingots destined for the manufacture of guns it is usual to cut off the tops, which are unsound as well as impure, and in some cases to bore out the centre of the ingot. For similar reasons, it is now customary to cut off the "crop" ends of steel rails. The importance of this procedure has been widely recognised,[4] and the effect of segrega-

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[1] *Journ Iron and Steel Inst.*, 1881, i. p. 200.

[2] *Ibid.*, 1881, ii. p. 379.

[3] *Ibid.*, 1905, ii. p. 204.

[4] Maitland, *Min. Proc. Inst. C.E.*, vol. lxxxix. (1887), p. 127. See also Eccles, *Journ. Iron and Steel Inst.*, No. 1 (1888), p. 70, and the discussion on Greenwood's paper on the "Treatment of Steel by Hydraulic Pressure," *Min. Proc. Inst. C.E.*, vol. xcviii., 1889.

tion must be carefully considered in making large castings and forgings.

ANALYSES TAKEN FROM CENTRE AND OUTSIDE OF TWO INGOTS, FROM TOP TO BOTTOM, AT DISTANCES OF 6 INCHES APART.

No.	Without Aluminium.						With Aluminium.					
	Centre.			Outside.			Centre.			Outside.		
	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.	Carbon.
Top. 1	·053	·051	·41	·035	·047	·33	·038	·035	·32	·067	·054	·39
2	·049	·052	·39	·031	·034	·32	·042	·040	·35	·066	·057	·39
3	·267	·197	·95	·018	·030	·31	·078	·061	·48	·065	·056	·39
4	·141	·109	·59	·027	·036	·32	·086	·063	·43	·066	·055	·40
5	·097	·083	·47	·034	·040	·35	·081	·049	·34	·068	·067	·41
6	·081	·065	·46	·036	·046	·37	·059	·054	·38	·066	·058	·42
7	·056	·061	·46	·040	·048	·38	·067	·052	·38	·064	·057	·41
8	·056	·053	·38	·041	·046	·38	·057	·049	·36	·058	·052	·41
9	·043	·045	·35	·039	·044	·36	·053	·049	·36	·058	·056	·40
10	·048	·047	·35	·044	·046	·38	·056	·050	·36	·056	·056	·38
11	·047	·045	·34	·048	·048	·41	·057	·047	·37	·060	·053	·38
12 Bottom.	·051	·050	·39	·053	·054	·43	·056	·049	·38	·065	·054	·39

Various methods have been introduced for compressing steel ingots while still in the fluid state, with a view of preventing segregation and lessening the amount of blowholes produced during the solidification. Casting under pressure was first attempted by Bessemer in 1856, but was reintroduced and rendered practicable by Whitworth in 1865;[1] more recently the Harmet[2] process of compressing steel ingots during solidification in vertical taper moulds, and the Robinson and Rodger[3] method of horizontal compression, have been introduced with considerable success, and both methods are successfully employed in various steelworks. All these methods very largely produce the desired results, giving greater homogeneity and freedom from blowholes, and greatly reducing the amount of cropping necessary.

In the case of pig-iron it is possible to isolate products of liquation, as has been shown by M. Lencauchez,[4] who heated fragments of iron to a temperature of 940° for 100 hours. At the end of this time a number of spherical grains sweated out from the surface of the fragments. Analysis of these exudations showed that they contained from 4 to 6 per cent. of phosphorus, from 0·6 to

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[1] Patent No. 3018, 1865.

[2] *Journ. Iron and Steel Inst.*, 1902, ii. p. 146.

[3] Capron, *Journ. Iron and Steel Inst.*, 1906, i. p. 28.

[4] *Mém. Soc. Ing. Civils*, 1887.

0·8 per cent. of silicon, from a trace to 1·5 per cent. of graphite carbon, and from 0 to 1·24 per cent of combined carbon. The original pig-iron contained about 3·5 per cent. of total carbon, 2·6 of silicon, and 1·9 of phosphorus. The composition of these exudations, therefore, is that of pig-iron impoverished in carbon and silicon, but considerably enriched in phosphorus. The question of the modes of existence of phosphorus in iron has been exhaustively studied and described by Stead.[1]

If lead, tin, and zinc are melted together, and left at rest in a fused condition, no separation takes place if the proportion of tin exceeds a certain amount; but if the quantity of tin is less than this, the alloy separates into two layers, each layer consisting of a ternary alloy of the three metals. Dr C. R. A. Wright and Mr C. Thompson[2] have examined the nature of this separation, and the composition of the alloys under different conditions. The heavier alloy, they found, consists of a saturated solution of zinc in lead containing tin, whilst the lighter consists of lead in zinc containing tin. The two alloys always correspond with two conjugate points on the solubility curves of zinc in lead-tin, and of lead in zinc-tin. The tin is not distributed equally in the two alloys, except when present in a particular proportion, which varies with the ratio of zinc to lead. With less tin than this, the lighter alloy takes up the excess of tin; with more, the heavier takes up the excess.

Solution of Metals in Metals in the Fluid Condition.—Many researches of late years have been made on this important and interesting subject, and the late Dr Alder Wright, F.R.S., originally prepared for this book the following account of his work in this direction.[3]

He stated that in the course of a series of experiments lasting over several years the following results were arrived at.

Of the 36 pairs which it is possible to form with the 9 metals Pb, Bi, Al, Zn, Sn, Ag, Sb, Cd, Cu, the great majority have been found to possess the property of *completely blending with one another so as to form a homogeneous fluid* stable for many hours when they are heated to such a temperature that the whole mass remains liquid. On cooling, segregation occurs in many cases during solidification. Five pairs, however, are exceptional when the components lie within the under-mentioned limits; when well intermixed by stirring, and then allowed to stand molten for some hours at an equable temperature (preferably by pouring the fluid mass into clay test-tubes heated to the required temperatures in a bath of molten lead), two alloys separate from one another; the denser consists mainly of the heavier metal, A, containing in solution a small quantity of the lighter metal, B, the amount

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[1] *Journ. Iron and Steel Inst.*, 1900, ii. p. 60.

[2] *Proc. Roy. Soc.*, vol. xlv. (1889), p. 461.

[3] *Proc. Roy. Soc.*, 1889-1893.

dissolved increasing with the temperature; whilst the lighter alloy consists, conversely, mainly of B, with a little A. Using the nomenclature proposed by Sir G. G. Stokes, these pairs of metals form *real* alloys only when employed outside of the limits stated, while within these limits they form *ideal* alloys only.

It must be remembered that the word *ideal* is used in the sense of imaginary or *unreal*, as the alloys probably do not actually exist; they give rise to mixtures that are incapable of permanently remaining homogeneous, being analogous to intimate emulsions of oil and water, or ether and water, rather than to true mutual solutions of alcohol and water. The term "stable" and "unstable" alloys may also be conveniently used to distinguish the two classes respectively.

I. *Mean Values of Limits for Lead and Zinc* (*Average of numerous Determinations*).

At about 650° C. .	Between	Pb = 98·76 Zn = 1·24	and	Pb = 1·14 Zn = 98·86
,, 800° C. .	,,	Pb = 98·70 Zn = 1·30	,,	Pb = 1·57 Zn = 98·43

II. *Bismuth and Zinc.*

At about 650° C. .	Between	Bi = 85·72 Zn = 14·28	and	Bi = 2·32 Zn = 97·68
,, 750° C. .	,,	Bi = 84·82 Zn = 15·18	,,	Bi = 2·47 Zn = 97·53
,, 800° C. .	,,	Bi = 84·17 Zn = 15·83	,,	Bi = 2·52 Zn = 97·48

III. *Lead and Aluminium.*

At about 800° C. .	Between	Pb = 99·93 Al = 0·07	and	Pb = 1·91 Al = 98·09

IV. *Bismuth and Aluminium.*

At about 800° C. .	Between	Bi = 99·72 Al = 0·28	and	Bi = 2·02 Al = 97·98

V. *Cadmium and Aluminium.*

At about 750° C. .	Between	Cd = 99·78 Al = 0·22	and	Cd = 3·39 Al = 96·61

Out of the above-mentioned 9 metals, 84 different combinations can be formed, taking them 3 at a time. Of these, 55 combinations invariably form *real* alloys when heated so that the whole mass remains liquid, whilst 29 give rise to *ideal* ternary alloys when the proportions in which the materials are used lie within certain limits. These limits are delineated graphically by a method due to Sir G. G. Stokes (see p. 86). A triangle (preferably equilateral) is drawn, at the three corners of which weights are supposed to be placed in the ratio of the relative quantities of the 3 metals respectively present in a given mixture of them; then this mixture is denoted by a point within the triangle representing the centre of gravity of the 3 weights of the metals An *ideal* alloy gives rise to two "conjugate points," representing the heavier and lighter alloys respectively into which the mass divides itself; the line joining the points is referred to as a "tie-line" or "tie." With a sufficiently extended series of observations at a constant temperature, T°, with the metals in suitably varying proportions, the various pairs of conjugate points deduced map out an area inside the triangle corresponding with the limits of composition within which *ideal* alloys result, and outside of which *real* alloys are formed at the temperature T°. The loci of the two series of points represent curves, conveniently designated "critical curves," indicating the boundary of this limiting area.

The 29 possible kinds of ideal ternary alloys above mentioned are divisible into two classes characterised by entirely different kinds of critical curves, and differently shaped areas enclosed by them.

In the first class (23 in number), calling the 3 metals respectively A, B, and C, 3 pairs can be taken, respectively AB, AC, and BC. Of these, one pair, AB, is "immiscible"—*i.e.* is one of the 5 binary combinations furnishing ideal alloys when mixed within the limits above stated; or, in other words, A will mix in all proportions with C, as also will B with C; but A will not mix in all proportions with B. The third metal, C, which will mix in all proportions with either A or B, is conveniently designated the "solvent" metal. The 23 combinations of this kind are—

A.		B.	C = "Solvent."	
Pb	... ...	Zn	either Sn, Ag, Sb, Cu, or Cd	= 10
Bi	... ...	Zn		
Pb	... ...	Al	either Sn, Ag, Sb, or Cu	= 8
Bi	... ...	Al		
Cd	... ...	Al	either Sn, Ag, Sb, Cu, or Zn	+ 5
				23

The critical curves deduced at certain definite temperatures for the majority of these combinations have been recorded in various papers communicated to the Royal Society. In all cases, when the triangular delineation is effected with the immiscible metals A and B at the base, and the solvent metal C at the apex of the triangle, the two series of points respectively representing the heavier and lighter conjugate alloys formed in a series of experiments with gradually increasing proportions of solvent metal form two branches or portions of a single curve, rising upwards from the base line to a maximum elevation, and then descending again to the base; so that the area enclosed by the critical curve is roughly a segment of an ellipse. The point where the two branches meet and merge into one another (or point where the