Relationship between the Atomic Volume of an Element added to a Metal and the Effect produced by this Addition.—In studying this question, it must be borne in mind that any relationship between the atomic volume of an added element and the effect produced by its addition can only hold good in those cases in which solid solutions are formed. There are many instances in which an added element, even in small quantities, causes the formation of a eutectic, which, in turn, greatly reduces the strength of the metal to which it is added, and in these cases there is absolutely no connection between the properties and the atomic volume. Since 1826, when Gmelin called attention to the relation between the atomic weights of elements which have similar properties, chemists have been actively engaged in establishing analogies between the properties of the elements and in arranging them systematically, and the result has been (mainly through the labours of Newlands, Mendeléeff, and Lothar Meyer) the promulgation of the Periodic law. This law states that the properties of the elements are a periodic function of their atomic weights. Lothar Meyer has gone further, and has shown that a remarkable relation exists between the atomic volumes of the elements. Now, however tiny the atoms may be, they must possess volume, and the atomic volume of each element will be peculiar to itself. The space occupied by one atom cannot yet be measured absolutely, but relative measurements may be obtained "by taking such quantities of the elements as are proportional to their atomic weights, and comparing the space occupied by these quantities." The relative atomic volumes of the elements are found by dividing the atomic weights by their specific gravities in the solid state. The atomic weight of gold is $197{\cdot}2$; $\frac{197{\cdot}2}{19{\cdot}3}=10{\cdot}2$ the atomic volume, or, expressed in the metric system, 197·2 grammes of gold would occupy a space of 10·2 cubic centimetres. Lead, on the other hand, would have the large atomic volume of 18·2, and potassium that of 45·5. The question now arises—Does the power to produce fragility, which we have seen certain elements to possess, correspond to any other of their properties by which they may be classified? The facts represented in the Periodic law were, in 1869, graphically represented by Lothar Meyer in his well-known curve of the elements. By adopting atomic weights and atomic volumes as co-ordinates he showed that the elements can be arranged in a curve representing a series of loops, the highest points of which are occupied by cæsium, rubidium, potassium, sodium, and lithium, whilst the metals which are most useful for industrial purposes occupy the lower portions of the several loops.

An examination of some results the author[1] obtained shows that not a single metal or metalloid which occupies a position at the base of either of the loops of Lothar Meyer's curve diminishes the tenacity of gold. On the other hand, the fact is clearly brought out that metals which render gold fragile all occupy high positions on the curve. This would appear to show that there is some relation between the influence exerted by the metallic and other impurities and either their atomic weights or their atomic volumes. It seems hardly probable that it is due to atomic weight, because copper, with an atomic weight of 63·6, has nearly the same influence on the tenacity of pure gold as rhodium, with an atomic weight of 103.

Several of the elements, the action of which was examined, occupy abnormal positions, and one reason for this is that solid solutions are not formed in these cases. It is difficult to offer any mechanical theory to account for the action of the elements, but it may perhaps be well to give a rough indication of what may take place. If five spheres, representing atoms of a certain volume, are arranged in one plane so as to touch each other, then the addition of an element with a small atomic volume may improve the tenacity by filling up the central space which would otherwise remain void; with such an arrangement of five atoms the addition of an element with the same atomic volume as themselves will tend to drive them slightly further asunder, and should, therefore, act prejudicially in a five-atom group, although it would exactly fill the space between a six-atom group, but in either case the insertion of a larger atomic volume than that of each member of the group must tend to drive the members of either the five- or six-atom group further asunder, and by so doing would diminish the cohesion of the mass.

It is, however, inadvisable in the present state of our knowledge to formulate any definite law on the relation between the atomic volume and the physical properties produced by alloying one element with another, and much research work remains to be done before it will be wise to generalise in this direction.

Effect of Temperature on Strength of Alloys.—With reference to the strength of alloys at different temperatures, Prof. Unwin[1] observes that, in the case of commonly used alloys, such as gun-metal and brass, the question is one of practical importance. Some experiments made by him in 1877 for the Admiralty proved that Muntz-metal and phosphor-bronze showed a fairly regular decrease in tenacity, as the temperature was raised to 260°, and in the case of gun-metal the tenacity diminished *regularly* up to a temperature of 150° to 175°, while beyond that temperature there was a *sudden* decrease of tenacity, generally of more than 50 per cent., and in several cases at a temperature of 260° the tenacity had very greatly decreased. This is important, because at the high pressures and correspondingly high temperatures at which

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[1] *Proc. Roy. Soc.*, vol. xliii. (1888), p. 425; and *Phil. Trans.*, vol. clxxix. (1888), A., p. 339.

[1] *Report Brit. Assoc.*, 1889, p. 746.

steam engines are often worked, gun-metal may be exposed to temperatures of 175° to 230°; and in order to ascertain whether at such temperatures the strength of such alloys is seriously impaired, Prof. Unwin has made a further series of experiments.

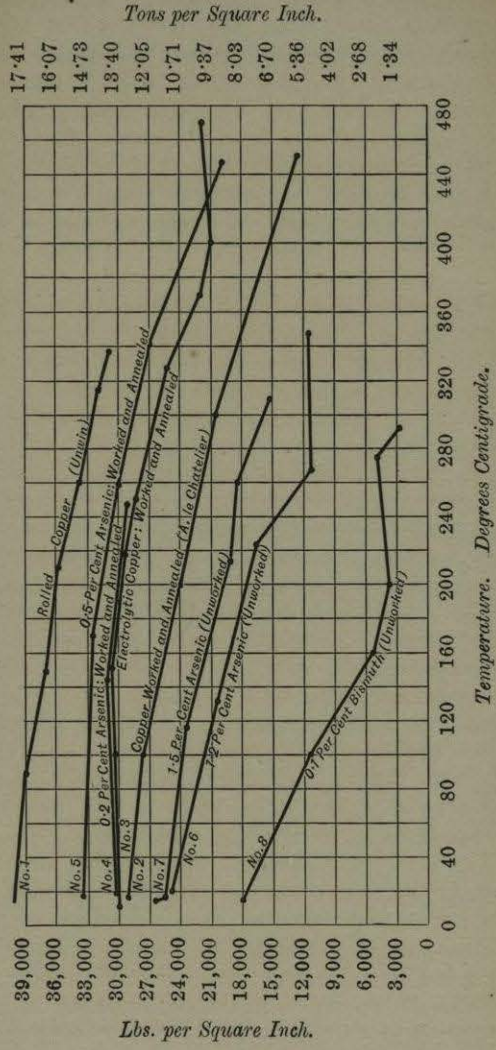

FIG. 41.—Tensile Strength of Copper Rods.

The results showed that with yellow-brass, Muntz-metal, and Delta-metal the decrease of tenacity follows a regular law without any sudden loss of strength. Even at temperatures of 315° to 345° all the bars had a not inconsiderable tenacity. The ultimate elongation of the bars was measured, and a peculiarity in the influence of temperature was observed. In most cases the ultimate elongation diminishes with increase of temperature. With Muntz-metal the decrease is regular, and there is still a considerable elongation before fracture at temperatures above 340°. With yellow-brass the decrease is more rapid, and there is very little elongation before fracture at temperatures above 260°. The elongations of the gun-metal bars were very irregular, and at temperatures of over 260° the elongations were but small. On the other hand, in the case of Delta-metal bars, the elongation increased regularly with the increase of temperature.

The preceding series of curves (fig. 41) shows the results obtained with copper of varying degrees of purity at temperatures ranging between 15° C. and 470°. It will be observed that the effect of bismuth is very noteworthy.[1]

A number of determinations have been made of the strength of aluminium-copper alloys at high temperatures, and some of these will be found in the Eighth Report to the Alloys Research Committee,[2] where the method of heating electrically during the testing is also described. The following results are the mean figures obtained for two alloys at the temperatures given:—

Temperature.	Ultimate Stress. Tons per Sq. In.	
	Cu 90·06 per cent.; Al 9·9 per cent.	Cu 93·23 per cent.; Al 6·73 per cent.
Ordinary	38·1	28·8
200° C.	36·4	
300° C.	33·4	20·7
400° C.	24·0	17·9
500° C.	12·1	10·9
550° C.	9·1	

It will thus be seen that with rise of temperature there is a gradual decrease of tenacity, the alloy containing 9·9 per cent. Al becoming rapidly weaker at 450°; the loss of tenacity in this case was accompanied by a rise in ductility up to 500°, whereas in the alloy containing 6·73 per cent. Al the decrease of tenacity was also accompanied by a gradual decrease of ductility.

The Effect of Low Temperatures on the Properties of Alloys.—The effect of low temperatures on the properties of metals was given on p. 25, and it will now be shown that the effect on alloys is very similar, the tenacity of all the common alloys being increased at low temperatures. Solder and fusible metal, for

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[1] *Proc. Inst. Mech. Eng.*, 1893, p. 102.

[2] *Ibid.*, 1907, p. 290.

instance, stretch less, and the cross section of the break is much less at - 182° than at ordinary temperatures.

Sir James Dewar illustrated the profound changes which take place in the elastic constants of a metallic body by comparing the deflection produced on a rod of fusible metal by means of a weight at different temperatures; the Young's modulus was found to be between four and five times as great at the temperature of liquid air as at the ordinary temperature. He also showed by experiments on a spiral spring made of fusible metal that the rigidity of metals was greatly changed. At ordinary temperatures an ounce weight was sufficient to draw the spring into a straight wire, whereas the same spring supported a two-pound weight and vibrated like a steel spring at - 182°.

Hadfield[1] showed that with nickel steels low in carbon the effect of the liquid air is to double the tenacity, but the ductility is not reduced to the same extent as with most steels. This is an important fact, and proves that the brittleness of iron at low temperatures can be modified by another element, such as nickel. In a steel, however, containing 12 per cent. of nickel and 0·97 per cent. of carbon, there was no change in tenacity or ductility at low temperature.

In manganese steels the results are similar, there being either an increase in tenacity and a decrease in ductility, or else no change at all, depending on the amount of manganese and carbon present. An important point brought out by the experiments on manganese steels is, that at no range of increase or decrease of temperature does any change in magnetic properties occur unless the carbon present is given time to dissociate by many days' continued heating.

In steels containing nickel, manganese, and carbon the effect of liquid air varies considerably, according to the percentage of the various elements present. A specimen containing C 0·60, Mn 5·04, Ni 14·55 per cent. showed remarkable results; for whereas the nickel and manganese added separately to iron in these proportions would cause intense brittleness, the double combination confers extraordinary toughness. This specimen also remained practically non-magnetic at temperatures high and low, and it is useful to remember here that nickel steels containing about 20 per cent. Ni, which are non-magnetic at ordinary temperatures, become magnetic at - 180° C., and again lose this property on heating. Another interesting alloy contained C 1·18, Mn 6·05, Ni 24·3 per cent.; it was the first specimen met with which showed an increase of tenacity from 51 to 84 tons, and also an increase of ductility from 60 to 67 per cent.

The alloys containing 6 per cent. of manganese and 14 to 24 per cent. of nickel show remarkable toughness and ductility, are almost non-magnetic, and possess a very high electrical resistance.

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[1] *Journ. Iron and Steel Inst.*, 1905, i. p. 147.

The Rarer Metals and their Alloys.—With the exception of platinum, the rarer metals are little used except when alloyed, and it may be well, therefore, to show how the rarer metals may be isolated, and to indicate the nature of the influence they exert. With the exception of the action of carbon upon iron, probably nothing is more remarkable than the action of the rare metals on steels; but their peculiar influence often involves the presence of carbon in the alloy.

The metals which, for the purposes of this book, may be included among the rarer metals, are (1) those of the platinum group, which occur in nature in the metallic state; and (2) certain metals which in nature are usually found as oxides or in an oxidised form of some kind, such as chromium, manganese, vanadium, tungsten, titanium, tantalum, zirconium, uranium, and molybdenum (which occurs as sulphide). Incidental reference will be made to nickel and cobalt.

As regards the rarer metals which are associated with oxygen, the problem is to remove the oxygen, and this is usually effected either by affording the oxygen an opportunity for uniting with another metal, or by reducing the oxide of the rare metal by carbon, aided by the dissociating effect of an electric current. When an intimate mixture, in atomic proportions of oxide of chromium and finely divided metallic aluminium, is heated locally to a temperature of 1010°, energetic action takes place; the temperature suddenly rises above the melting-point of platinum, and when cold, if the crucible be broken open, it will be seen that a mass of metallic chromium has been liberated.

The use of alkaline metals in separating oxygen from other metals is well known. Its history is associated with the honoured names of Berzelius, Wöhler, and Winkler.[1] The industrial importance of this method of reduction as the result of experimental work was dealt with in a lecture by the author.[2]

Mr Vautin has shown that granulated aluminium may readily be prepared, and that it renders great service when employed as a reducing agent; and his assistant, Mr Picard, who was formerly a student at the Royal School of Mines, isolated certain specimens of rare metals in the laboratory at the Mint.

The relation of aluminium to other metals is very singular. When, for instance, a small quantity of aluminium is present in cast iron, it protects the silicon, manganese, and carbon from oxidation.[3] The presence of silicon in aluminium greatly adds to the brilliancy with which aluminium itself oxidises and burns. It is also known that aluminium, even in small quantity, exerts

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[1] An interesting paper by H. F. Keller, on the reduction of oxides of metals by other metals, will be found in the *Journal of the American Chemical Society*, December 1894, p. 833.

[2] *Nature*, Aug. 8, 1901.

[3] *Bull. Soc. Chim. Paris*, vol. xi., 1894, p. 377.

a powerful protective action against the oxidation of the silver zinc alloy, arising from the desilverisation of lead by zinc.

Moreover, if a mass of aluminium be heated to redness in air, the film of oxide which is formed will protect the mass from further oxidation.[1] On the other hand, if finely divided aluminium finds itself in the presence of an oxide of a rare metal at an elevated temperature, it at once acts with energy and promptitude, and releases the rare metal from the bondage of oxidation. Aluminium, moreover, retains the oxygen it has acquired with great fidelity, and will only part with it again by electrolytic action, or at very high temperatures under the influence of the electric arc in the presence of carbon.

If a suitable mixture of red-lead and aluminium be placed in a small crucible heated in a wind furnace, in two minutes an explosion will announce the termination of the experiment. The crucible will be shattered to fragments.

It is admitted that a metal will abstract oxygen from another metal if the reaction is more exothermic than that by which the oxide to be decomposed was originally formed. The heat of formation of alumina is 391 calories, that of oxide of lead is 51 calories; so that it might be expected that metallic aluminium, at an elevated temperature, would readily reduce oxide of lead to the metallic state.

The experiment just referred to proved that the reduction of oxide of lead by aluminium is effected with explosive violence, the temperature engendered by the reduction being sufficiently high to volatilise the lead. Other experiments show that the explosion takes place with much disruptive power when aluminium reacts on oxide of lead *in vacuo*, and that if coarsely-ground fused litharge be substituted for red-lead, the action is only accompanied by a rushing sound. The result is, therefore, much influenced by the rapidity with which the reaction can be transmitted throughout the mass. It is this kind of experiment which makes us turn with such vivid interest to the teaching of the school of St Claire Deville, the members of which have rendered such splendid services to physics and metallurgy. They do not advocate the employment of the mechanism of molecules and atoms in dealing with mechanical problems, but would simply accumulate evidence as to the physical circumstances under which chemical combination and dissociation take place, viewing these as belonging to the same class of phenomena as solidification, fusion, condensation, and evaporation. They do not even insist upon the view that matter is minutely granular, but in all cases of change of state make calculations on the basis of work done, viewing changed "internal energy" as a quantity which should reappear when the system returns to the initial state.

A verse, of some historical interest, may appeal to them. It occurs in a thirteenth-century poem of the period, that is, the *Roman de la Rose*, and it expresses Nature's protest against those who attempt to imitate her works by the use of mechanical methods. The "argument" runs thus:

> "Comme Nature se complaint,
> Et dit sa douleur et son plaint
> A ung sot souffleur sophistique
> Qui n'use que d'art méchanique."

If the "use of mechanical art" includes the study of chemistry on the basis of the mechanics of the atoms, the modern school may be offered the following rendering of Nature's plaint:

> "How Nature sighs without restraint,
> And grieving makes her sad complaint
> Against the subtle sophistry
> Which trust atomic theory."

An explosion such as is produced when aluminium and oxide of lead are heated in presence of each other, which suggested the reference to the old French verse, does not often occur, as in most cases the reduction of the rarer metals by aluminium is effected quietly.

Vanadium and uranium may readily be reduced from their oxides by means of aluminium, as well as manganese, tungsten, and titanium. Allusion will be made subsequently to the uses of these metals. Some properties of titanium are of special interest. It burns with brilliant sparks in air, and it appears to be, from the experiments of M. Moissan, the most difficultly fusible metal known; but it has the singular property of burning in nitrogen—it presents, in fact, the only known instance of vivid combustion in nitrogen. Lord Rayleigh has recently stated that titanium does not combine with argon; and M. Guntz points out that lithium in combining with nitrogen produces incandescence. M. Moissan has also shown that uranium does not absorb argon.

Electrolytic Fusion.—The other method by which the rarer metals may be isolated is that which involves the use of the electric furnace. In this connection the name of Sir W. Siemens should not be forgotten. He described the use of the electric arc furnace in which the carbons were arranged vertically, the lower carbon being replaced by a carbon crucible; and in 1882 he melted in such a furnace no less than ten pounds of platinum. It may fairly be claimed that the large furnaces with a vertical carbon, in which the bath is maintained fluid by means of the electric current, the aluminium and other metals being reduced by electrolytic action, are the direct outcome of the work of Siemens.

In the development of the use of the electric arc for the isolation of the rare, difficultly fusible metals, Moissan stands in the

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[1] *Zeitschr. Electrochem.*, xiv. p. 766, Nov. 30, 1908.

front rank. He points out[1] that Despretz[2] used in 1849 the heat produced by the arc of a powerful pile; but Moissan was the first to employ the arc in such a way as to separate its heating effect from the electrolytic action it exerts. This he did by placing the poles in a horizontal position, and by reflecting their heat into a receptacle below them. He has shown, in a series of classical researches, that employing 800 amperes and 110 volts a temperature of at least 3500° may be attained, and that many metallic oxides which until recently were supposed to be irreducible may be readily made to yield the metal they contain.[3]

A support or base for the metal to be reduced is needed, and this is afforded by magnesia, which appears to be absolutely stable at the utmost temperatures of the arc. An atmosphere of hydrogen may be employed to avoid oxidation of the reduced metal, which, if it is not a volatile one, remains at the bottom of the crucible, almost always associated with carbon—forming, in fact, a carbide of the metal. As an illustration of the way in which the furnace is used the following experiment may be described.

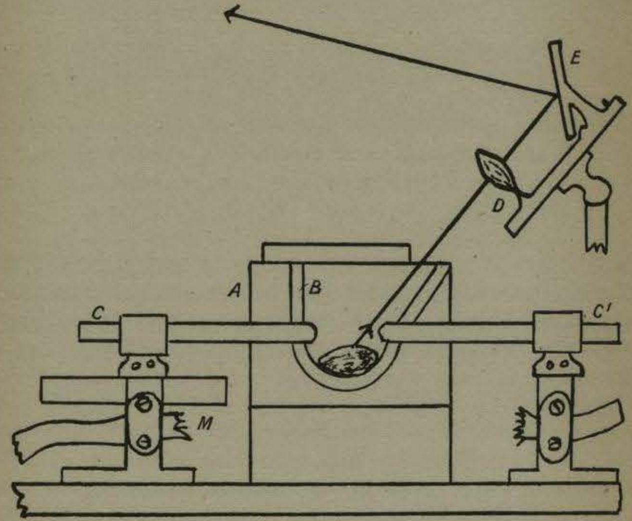

FIG. 42.

The furnace (fig. 42) consists of a clay receptacle A, lined with magnesia B. A current of 60 amperes at 100 volts is introduced by the carbon poles C C′; an electro-magnet M is provided to deflect the arc on to the metal to be melted. By means of a lens and mirror D E the image of the arc and of the molten metal may be projected on to a screen. For this purpose it is found convenient to make the furnace much deeper than would ordinarily be the case.

The result is very beautiful, and when arranged for the melting of metallic chromium, directly the current is passed the picture reflected by the mirror E (fig. 42) shows the interior of the furnace as a dark crater, the dull red poles revealing the metallic lustre and grey shadows of the metal beneath them. A little later these poles become tipped with dazzling white, and in the course of a few minutes the temperature rises to about 2500° C. Such a temperature will keep chromium well melted, though a thousand degrees more may readily be attained in a furnace of this kind. Each pole is soon surrounded with a lambent halo of the green-blue hue of the sunset, the central band of the arc changing rapidly from peach-blossom to lavender and purple. The arc can then be lengthened, and as the poles are drawn further and further asunder the irregular masses of chromium fuse in silver droplets below an intense blue field of light, passing into green of lustrous emerald; then the last fragments of chromium melt into a shining lake, which reflects the glowing poles in a glory of green and gold, shot with orange hues. Still a few minutes later, as the chromium burns, a shower of brilliant sparks of metal are projected from the furnace amid the clouds of russet or brown vapours which wreath the little crater; whilst, if the current is broken and the light dies out, you wish that Turner had painted the limpid tints, and that Ruskin might describe their lovelinesss.

The effect when either tungsten or silver replaces chromium is much the same, but in the latter case the glowing lake is more brilliant in its turbulent boiling, and blue vapours rise to be condensed in the iridescent beads of distilled silver which stud the crater walls.

It must not be forgotten that the use of the electric arc between carbon poles renders it practically impossible to prepare the rare metals without associating them with carbon, often forming true carbides; and it is impossible in many cases to separate the carbon by subsequent treatment. Moissan has, however, opened up a vast field of industrial work by placing at our disposal practically all the rarer infusible metals which may be reduced from oxides, and it is necessary for us now to consider how we may best enter upon our inheritance. Those members of the group which we have known long enough to appreciate are chromium, manganese, tungsten, vanadium, and molybdenum, and these we have only known free from carbon for a few years.

The question naturally arises—Why do small quantities of these rarer metals either increase or diminish the strength of masses of metals to which they are added? The answer would appear to

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[1] *Ann. de Chim. et de Phys.*, vol. iv., 1895, p. 365.

[2] *Comptes Rendus*, vol. xxviii. p. 755, and vol. xxix., 1849, pp. 48, 545, 712.

[3] See *Le Four Électrique*, Paris, 1897; English translation, 1904.

be as follows: Most alloys have more than one solidifying point. Sometimes, if the added element forms a possible alloy with the metal which constitutes the mass in which it is hidden, the second or even the third solidifying point will be low in the scale of temperature. If the subordinate point is low, the metal will be weak; if it is high in relation to the main setting point, then the metal will be strong. The rarer metals which demand for their isolation from their oxides either the use of aluminium or the electric arc, appear not to produce low freezing-points when they are added in small quantities to those metals which are used for constructive purposes. How these rarer metals act, why the small quantities of the added rare metals strengthen the metallic mass, we do not know; we are only gradually accumulating evidence which is afforded by very delicate methods of investigation.

The Industrial Use of the Rarer Metals.—It may be well to point to a few instances in which the industrial use of such of the rarer metals as have been available in sufficient quantity is made evident. Modern developments in armour-plate and projectiles will occur to many of us at once, and the effect of projectiles of approximately the same weight, when fired with the same velocity against 6-inch plates, enables comparative results to be studied, and illustrates the fact that the rivalry between artillerists who design guns, and metallurgists who attempt to produce both impenetrable armour-plates and irresistible projectiles, forms one of the most interesting pages in our national history. When metallic armour was first applied to the sides of war vessels, it was of wrought iron, and proved to be of very great service by absolutely preventing the passage of ordinary cast-iron shot into the interior of the vessel, as was demonstrated through the American Civil War in 1866. It was found to be necessary, in order to pierce the plates, to employ harder and larger projectiles than those then in use, and the chilled cast-iron shot with which Colonel Palliser's name is identified proved to be formidable and effective. The point of such a projectile was sufficiently hard to retain its form under impact with the plate, and it was only necessary to impart a moderate velocity to a shot to enable it to pass through the wrought-iron armour.

It soon became evident that in order to resist the attack of such projectiles with a plate of any reasonable thickness, it would be necessary to make the plate harder, so that the point of the projectile should be damaged at the moment of first contact, and the reaction to the blow distributed over a considerable area of the plate. This object could be obtained by either using a steel plate, in a more or less hardened condition, or by employing a plate with a very hard face of steel, and a less hard but tougher back. The authorities in this country during the decade 1880–90 had a very high opinion of plates that resisted attack without the

development of through-cracks, and this led to the production of the compound plate. The backs of these plates are of wrought iron, the fronts are of a more or less hard variety of steel, either cast on, or welded on by a layer of steel of an intermediate quality cast between the two plates. Armour-plates of this kind differ in detail, but the principle of their construction is now generally accepted as correct.

Such plates resisted the attack of large Palliser shells admirably, as when such shells struck the plate they were damaged at their points, and the remainder of the shell was unable to perforate the armour against which it was directed. An increase in the size of the projectiles led, however, to a decrease in the resisting power of the plates, portions of the hard face of which would at times be detached in flakes from the junction of the steel and the iron. An increase in the toughness of the projectiles by a substitution of forged chrome-steel for chilled iron secured a victory for the shot, which was then enabled to impart its energy to the plate faster than the surface of the plate itself could transmit the energy to the back. The result was that the plate was overcome, as it were, piecemeal; the steel surface was not sufficient to resist the blow itself, and was shattered, leaving the projectile an easy victory over the soft back. It must not be forgotten, in this connection, that the armour of a ship is but little likely to be struck by heavy projectiles in the same place, although it might be by smaller ones.

Plates made entirely of steel, on the other hand, were found, prior to 1888, to have a considerable tendency to break up completely when struck by the shot. It was not possible, on that account, to make their faces as hard as compound plates; but while they did not resist the Palliser shot nearly as well as the rival compound plate, they offered more effective resistance to steel. It appears that Berthier recognised, in 1820, the great value of chromium when alloyed with iron; but its use for projectiles, although now general, is of comparatively recent date, and these projectiles now commonly contain from 1·2 to 1·5 per cent. of chromium, and will hold together even when they strike steel plates at a velocity of 2000 feet per second;[1] and unless the armour-plate is of considerable thickness, such projectiles will even carry bursting charges of explosives through it.

It now remained to be seen what could be done in the way of toughening and hardening the plates so as to resist the chrome-steel shot. About the year 1888 very great improvements were made in the production of steel plates. Devices for hardening and tempering plates were ultimately obtained, so that the latter were hard enough throughout their substance to give them the necessary resisting power without such serious cracking as had occurred in previous ones. In 1889 Mr Riley exhibited, at

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[1] *Journal U.S. Artillery*, 1893, vol. ii. p. 497.

the meeting of the Iron and Steel Institute, a thin plate that owed its remarkable toughness to the presence of nickel in the steel. The immediate result of this was that plates could be made to contain more carbon, and hence be harder, without at the same time having increased brittleness; such plates, indeed, could be water-hardened and yet not crack.

For hardening, Éverard had developed the use of the lead bath in France, while Captain Tressider[1] had perfected the use of the water-jet in England for the purpose of rapidly cooling the heated plates. The principle adopted in the design of the compound plates has been again utilised by Harvey, who places the soft steel or nickel steel plate in a furnace of suitable construction, and covers it with carbonaceous material such as charcoal, and strongly heats it for a period, which may be as long as 120 hours. This is the old Sheffield process of cementation. The result is to increase the carbon from 0·35 per cent. in the body of the plate to 0·6 per cent. or more at the front surface, such increase only extending to a depth of 2 or 3 inches in the thickest armour.

The carburised face is then "water-hardened," the result being that the best chrome-steel shot are shattered at the moment of impact, unless they are of very large size as compared with the thickness of the plate. The intense hardness of the chilled plates gave rise at first to some little difficulty when it was desired to drill them for the purpose of attaching fittings when in position upon the ship; this has, however, been surmounted by adopting the device of heating the required portion of the plate locally by the aid of electric arcs, and thus to anneal it sufficiently to allow of the subsequent use of ordinary metal working tools.

D. Carnegie[2] has recently stated that modern projectiles are composed of steel containing carbon, associated with one or more of the metals nickel, chromium, manganese, and molybdenum. In hardening, three mediums are used, water, oil, and air. These mediums differ in intensity of action, and the choice of the method to be used is determined by the composition of the material to be hardened. Each medium might also be varied in temperature in the case of water and oil, and in pressure in the case of air. Carbon steels are, as a rule, hardened in water, or partly in water and partly in oil; nickel steels in water, in oil, or in air under pressure; chrome-nickel steels in oil, or in air under pressure; and steels having self-hardening properties, by simply heating and allowing to cool in air.

The penetrating power of projectiles has been increased in recent years by capping,[3] and by improvements in the explosives used.

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[1] Weaver, "Notes on Armour," *Journal U.S. Artillery*, vol. iii., 1894, p. 417.

[2] *Min. of Proc. Inst. Civil Eng.*, vol. cliii. pp. 1–57.

[3] *Engineer*, vol. xcvii. pp. 21–22.

Another alloy of interest is iron alloyed with 25 per cent. of nickel. Hopkinson has shown that its density is permanently reduced 2 per cent. by an exposure to a temperature of − 30°, that is, the metal expands at that temperature. Supposing, therefore, as has been previously stated in this volume, that a ship-of-war was built in our climate of ordinary steel, and clad with some 3000 tons of such nickel-steel armour, we are confronted with the extraordinary fact that if such a ship visited the Arctic regions, it would actually become some 2 feet longer, and the shearing which would result from the expansion of the armour by exposure to cold would destroy the ship.

The immense strides made in recent years in motor-car construction has been largely due to the use of special steels, and Guillet has given an account of these steels used by the French manufacturers.[1]

He divides the steels into the following classes:—

(1) Steels with low percentages of carbon and nickel (Ni 1 to 6 per cent., C 0·1 to 0·25 per cent.), which are used for parts that require case-hardening and quenching—*i.e.* shafts, gears which engage directly, etc.

(2) Steels with medium percentages of carbon and low percentages of nickel (Ni 1 to 6 per cent., C 0·25 to 0·4 per cent.), which are used, after quenching and reheating, for shafts, forgings, axles, bearings, etc.

(3) Steels low in carbon and with high percentages of nickel (Ni 32 to 36 per cent., C 0·12 to 0·2 per cent.), which are used in the making of valves.

(4) Chrome steels with high carbon and low chromium percentages (C 1·0 to 1·2 per cent., Cr 1·0 to 2·5 per cent.), used for bearings.

(5) Silicon steels containing C 0·3 to 0·7 per cent., and Si 0·8 to 2·5 per cent., used for springs.

(6) Chrome-nickel steels (C 0·25 to 0·45 per cent., Ni 2·5 to 2·7 per cent., Cr 0·275 to 0·6 per cent.), employed for numerous parts requiring resistance to shock and a certain degree of hardness.

There is little doubt but that many valuable results will be obtained as a result of the large amount of research work now being carried out in reference to the effect of rare metals on the properties of other metals, and on the correct heat treatment necessary to ensure certain results.

Colour of Alloys.—It will now be well to examine some effects of uniting metals by fusing them together, and also to consider the direct influence of a minute quantity of one metal in changing the mass of another in which it is hidden, causing it to behave in a different way in relation to light, and consequently to possess a colour different from that which is natural to it. The

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[1] *Journ. Iron and Steel Inst.*, 1905, ii. 166.

added metal may so change the chemical nature of the metallic mass that varied effects of colour may be produced by the action of certain "pickling" solutions. This portion of the subject is so large that reference can only be made to certain prominent facts.[1]

First, with reference to the colour produced by the union of metals. Take, for example, a mass of red copper and one of grey antimony; the union of the two by fusion produces a beautiful violet alloy when the proportions are so arranged that there is 51 per cent. of copper and 49 per cent. of antimony in the mixture. This alloy was well known to the early chemists, but, unfortunately, it is brittle and difficult to work, so that its beautiful colour can hardly be utilised in art. The addition of a small quantity of tin to copper hardens it, and converts it, from a physical and mechanical point of view, into a different metal. The addition of zinc and a certain amount of lead to tin and copper confers upon the metal copper the property of receiving, when exposed to the atmosphere, varying shades of deep velvety brown, characteristic of the bronze which has from remote antiquity been used for artistic purposes. But by far the most interesting copper-alloys, from the point of view of colour, are those produced by its union with zinc, namely, brass. Their preparation demands much care in the selection of the materials.

The most remarkable case known of a coloured alloy is that published by the author,[2] who found that gold alloyed with 10 per cent. of aluminium is brilliantly white, but from this point, as aluminium is added, the tint deepens until flecks of pink appear, and when 78 parts of gold are added to 22 parts of aluminium, an intensely ruby-coloured alloy, $AuAl_2$, is obtained.

The colouring power of metals in alloys is very variable. Ledebur[3] arranges the principal metals in the following order:—Tin, nickel, aluminium, manganese, iron, copper, zinc, lead, platinum, silver, gold.

Each metal in this series has a greater decolorising action than the metals following it. Thus, the colours of the last members are concealed by comparatively small amounts of the first members. A good example is afforded by the alloy used for the Continental nickel coinage. This consists of three parts of red copper with only one part of white nickel. The comparatively small quantity of nickel is, however, sufficient to completely hide the red colour of the copper.

Of the very varied series of alloys the Japanese employ for art

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[1] A list of books and papers dealing with the colours of metals and alloys, and with the production of coloured patina, is given by Prof. Ledebur in his work *Die Metallverarbeitung*, 1882, p. 285.

[2] *Proc. Roy. Soc.*, vol. xlix., 1891, p. 347.

[3] *Loc. cit.*, p. 51.

metal-work, the following may be considered the most important and typical. The first is called *shaku-do*; it contains, as will be seen from Analyses Nos. I. and II.,[1] in addition to about 95

	I.	II.
Copper	94·50	95·77
Silver	1·55	0·08
Gold	3·73	4·16
Lead	0·11	
Iron and Arsenic . . .	traces	
Totals .	99·89	100·01

per cent. of copper, as much as 4 per cent. of gold. The quantity of gold is, however, very variable, some specimens which have been analysed containing only 1·5 per cent. of the precious metal.

Another important alloy is called *shibu-ichi*. Analyses of this alloy gave:—

	III.	IV.
Copper	67·31	51·10
Silver	32·07	48·93
Gold	traces	0·12
Iron	0·52	
	99·90	100·15

There are numerous varieties of it, but in both these alloys, *shaku-do* and *shibu-ichi*, the point of interest is that the precious metals are, as it were, sacrificed in order to produce definite results, gold and silver, when used pure, being employed very sparingly to heighten the general effect. In the case of the *shaku-do*, we shall see presently that the gold appears to enable the metal to receive a beautiful, rich purple coat or patina, as it is called, when treated with certain pickling solutions; while *shibu-ichi* possesses a peculiar silver-grey tint of its own, which, under ordinary atmospheric influences, becomes very beautiful, and to which the Japanese artists are very partial. These are the principal alloys, but there are several varieties of them, as well as combinations of *shaku-do* and *shibu-ichi* in various proportions, as, for instance, in the case of *kiu-shibu-ichi*, the composition of which would correspond to one part of *shaku-do*, rich in gold, and two parts of *shibu-ichi*, rich in silver.

Now, as to the action of pickling solutions.

The Japanese art metal-workers are far ahead of their European brothers in the use of such solutions.

The South Kensington Museum contains a very valuable series

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[1] Analyses Nos. I. and III. were made by Prof. Gowland, late of the Imperial Japanese Mint at Osaka; Nos. II. and IV. by Prof. Kalischer, *Dingl. Polyt. Journ.*, vol. ccxv. p. 93.

of fifty-seven oblong plates, some plain and others richly ornamented, which were specially prepared as samples of the various metals and alloys used by the Japanese. The Geological Museum in Jermyn Street has a smaller but more instructive series of twenty-four plates, presented by an eminent metallurgist, the late Mr Hochstätter-Godfrey. From descriptions accompanying the latter, and from information gathered from certain Japanese artificers, it would appear that there are three solutions generally in use. They are made up respectively in the following proportions, 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 ,,	
Water . . .	1 gallon	...	1 gallon
Vinegar . . .	...	1 gallon	5 fluid drachms

The most widely employed is No. I. When boiled in No. III. solution, pure copper will turn a brownish-red, and *shaku-do*, which contains a little gold, becomes purple. Thus it is possible to appreciate the effect of small quantities of metallic impurity as affecting the colour resulting from the action of the pickle. Copper containing a small quantity of antimony gives a shade very different from that resulting from the pickling of pure copper. But the copper produced in Japan is often the result of smelting complex ores, and the methods of purification are not so perfectly understood as in the West. The result is that the so-called "antimony" of the Japanese art metal-workers, which is present in the variety of copper called *kuromi*, is really a complex mixture containing tin, cobalt, and many other metals, so that a metal-worker has an infinite series of materials at command with which to secure any particular shade; and these are used with much judgment, although the scientific reasons for the adoption of any particular sample may be hidden from him. It is strictly accurate to say that each particular shade of colour is the result of minute quantities of metallic impurity.

There is one other material to the production of which art workmen in this country will, it is to be hoped, soon direct their attention, as the possibilities of its applications are endless. It is called in Japanese *mokumé*, which signifies "wood grain." It is now very rare, even in Japan, but formerly the best specimens appear to have been made in Nagoya by retainers of the Daimio of Owari.

This diagram (fig. 43) shows the method of manufacture. Take thin sheets of gold, silver, *shibu-ichi*, *shaku-do*, and *kuromi* and solder[1] them together, layer upon layer, care being taken that the metals which will present diversity of colour come together. Then drill conical holes of varying depth (A) in the mass, or devices in trench-like cuts of V section (B), and then hammer the mass until the holes disappear; the holes will thus be replaced by banded circles and the trenches by banded lines. Similar effects may be produced by taking the soldered layers of the alloy, and, by the aid of blunted tools, making depressions on the back of the mass, so as to produce prominences on the front (C). These prominences are filed down until the sheet is again flat; the banded alloys will then appear on the surface in complicated sections, and a very remarkable effect is produced, especially when the colours of the alloys are developed by suitable "pickles." In this way any device may be produced. In principle the method is the same as that which produces the damascening of a sword-blade or gun-barrel, and depends on the fact that, under certain conditions, metals behave like viscous solids, and as truly "flow" as pitch or honey does. In the case of *mokumé* the art-workman has a wide range of tinted metals at command.

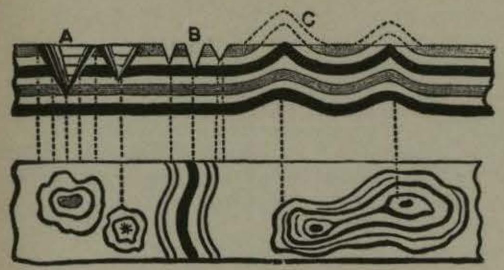

Fig. 43.

The Oriental art metal-workers often blend metals and alloys of different colours by pouring them together at a temperature near the solidifying point of the more infusible of the metals and alloys to be associated. In this way, by pouring the comparatively fusible grey silver-copper alloy on to fused copper which is just at the point of "setting," the metals unite, but do not thoroughly mix, and a mottled alloy is produced. The Japanese use such alloys in almost every good piece of metal-work.

Alloys of Industrial Importance.—The following tables indicate the composition of some of the more important alloys, which have been selected in order to give the student an idea of the way in which for industrial use metals are associated. The list is, however, necessarily a limited one, and reference should be made for fuller information to the standard treatises, of which

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[1] The following solder was found to answer well:—Silver, 55·5; zinc, 26·0; copper, 18·5.

a list is appended:—R. H. Thurston, Report on a Preliminary Investigation of the Properties of the Copper-Tin Alloys, Washington, 1879; A. Guettier, *Guide Pratique des Alliages Métalliques*, Paris, 1865; Roberts-Austen, The Alloys used for Coinage (Cantor Lectures, Society of Arts), 1884; A. Ledebur, *Metallverarbeitung*, Brunswick, 1882; Brannt, Krupp, and Wildberger, "The Metallic Alloys," Philadelphia, 1889; Reports of Alloys Research Committee, *Proc. Inst. Mech. Engineers*, 1891, 1893, 1895, 1897, 1899, 1904, 1905, and 1907; *Brasses, Bronzes, and other Alloys*, Thurston, New York, 1893; *Iron, Steel, and other Alloys*, H. M. Howe, 1903; *Étude Industrielle des Alliages Métalliques*, L. Guillet, Paris, 1906; *Alloys*, Law, 1908.

COPPER-ZINC ALLOYS.

	Cu.	Zn.		Cu.	Zn.
Tombac for buttons .	99·15	0·85	Bristol metal . .	75·00	25·00
Red Tombac, Vienna .	97·80	2·20	Sheet brass . .	74·58	25·42
Pinchbeck . .	93·60	6·40	Chrysorin . . .	72·00	28·00
Red Tombac, Paris .	92·00	8·00	Common brass . .	66·60	33·40
French gold . .	90·00	10·00	Forging brass . .	66·00	34·00
Brass for very delicate castings . . .	86·00	14·00	Good wire brass .	65·40	34·60
			Mosaic gold . .	65·30	34·70
Paris jewelry . .	85·00	15·00	Muntz metal . .	60·00	40·00
Gold leaf . . .	84·21	15·79	Very ductile brass .	54·00	46·00
Bronze powder . .	83·02	16·98	German brass . .	49·47	50·53
Bath metal . .	82·95	17·05	Strong solder for brass	33·34	66·66
Red-yellow jewelry .	82·50	17·50	Watchmakers' brass .	32·85	67·15
Dutch brass . .	79·56	20·44	White button metal .	19·65	80·35
Vienna gold leaf .	77·50	22·50			

COPPER-TIN ALLOYS.

	Cu.	Sn.
Mild bronze	92·00	8·00
Ordnance metal	91·70 to 88·39	8·30 to 11·61
Toothed wheels	91·30	8·70
Railway car bearings . . .	90·00	10·00
Carriage wheel boxes . . .	84·00	16·00
Chinese gong	80·43	19·57
Bell metal	77·50	22·50
,, (Big Ben) . . .	75·80	24·20
Swiss clock bells	75·00	25·00
Speculum metal	68·21	31·79
,, ,, ...	66·60	33·40
White bell metal	40·00	60·00

COPPER-NICKEL ALLOYS.

	Cu.	Ni.	Zn.
Nickel coin	75·0	25·0	
German silver	55·0	17·5	28·5
English "German silver" . .	62·4	15·05	22·15
Vienna ,, ,, . .	50·0	25·0	25·0
,, ,, ,, . .	60·0	20·0	20·0
Chinese ,, ,, . .	26·3	36·8	36·8
Paris white metal . . .	69·8	19·8	5·5
Packfong (Chinese alloy) . .	43·8	15·6	40·6
Berlin Argentan . . .	56·0	26·0	22·0

OTHER COPPER ALLOYS.

	Cu.	Zn.	Sn.	Other Constituents.
Metal for cocks . . .	88·0	2·0	10·0	
Bearing metal for loco axles .	82·0	8·0	10·0	
,, hard . .	82·0	2·0	16·0	
,, medium hard .	69·5	5·8	21·7	
,, for railroad car axles	75·0	2·0	20·0	
Metal for steam whistles .	80·0	2·0	18·0	
,, mechanical instruments	81·2	5·1	12·8	
Algier's metal . . .	5·0	...	94·5	Sb 0·5
Sterro ,, . . .	55·33	41·8	...	Fe 4·66
Aich's ,, . . .	60·0	38·12	...	Fe 1·5
Japanese art bronze . . .	82·7	1·8	4·7	Pb 9·9
,, ,, . . .	71·4	6·0	5·9	Pb 16·3
Chinese ,, . . .	74·0	10·0	1·0	Pb 15·0
Egyptian chisel . . .	94·0	...	5·9	Fe 0·1
Attic coin	88·46	...	10·04	Pb 1·5
Manganese bronze . . .	83·45	...	...	Mn 13·48; Fe 1·24
,, ,, . .	81·03	...	...	Mn 16·86; Fe 1·67

TIN ALLOYS.

	Sn.	Sb.	Cu.	Other Constituents.	Remarks.
Britannia metal	90·62	7·81	1·46	...	Birmingham sheet.
White metal .	82·00	12·00	6·00	...	For bearings. The composition of white metal is very variable.
,, .	53·00	10·60	2·40	Pb 33·0; Zn 1·0	
Ashberry metal .	77·8	19·4	...	Zn 2·8	
Pewter . .	80·0	...	...	Pb 20·0	
Solder, fine .	66·6	...	...	Pb 33·3	The melting-point increases with the proportion of lead.
,, tin .	50·0	...	...	Pb 50·0	
,, plumbers'	33·3	...	...	Pb 66·6	Authorised by the Plumbers' Company.

LEAD ALLOYS.

	Pb.	Sb.	Sn.	Other Constituents.	Remarks.
Type metal .	70·0	18·0	10·0	Cu 2·0	
,, .	82·0	14·8	3·2	...	For stereotyping.
Bearing metal .	84·0	16·0	...	...	For slowly revolving axles.
,, .	60·0	20·0	20·0		
Shot metal .	99·6	...	...	As 0·2 to 0·35	

ZINC ALLOYS.

	Zn.	Sn.	Cu.	Other Constituents.	Remarks.
Antifriction metal . .	85·0	...	5·0	Sb 10·0	For bearings.
Babbitt's metal	69·0	19·0	4·0	Sb 3·0; Pb 5·0	(Ledebur).

BISMUTH ALLOYS (FUSIBLE METAL).

	Bi.	Pb.	Sn.	Cd.	Melting-point. °C.
Newton's alloy . .	50·0	31·25	18·75	...	95
Rose's ,, . .	50·0	28·10	24·64	...	100
Darcet's ,, . .	50·0	25·00	25·00	...	93
Wood's ,, . .	50·0	24·00	14·00	12·00	66–71
Lipowitz's ,, . .	50·0	27·00	13·00	10·00	60

ALLOYS FOR COINAGE.

	Au.	Cu.	Ag.	Other Constituents.	Remarks.
Gold coin . .	91·66	8·33	...	...	British standard.
,, . .	90·0	10·0	...	...	"Latin Union" and American.
,, . .	1·33	82·73	15·93	...	Roman, Septimus Severus, 265 A.D.
Silver coin .	0·1	7·1	92·5	Pb 0·2	Roman, B.C. 31, almost same as British silver coin.
Gold coin .	40·35	19·63	40·02	...	Early British, B.C. 50.
Silver coin .	...	7·5	92·5	...	British standard.