that the rate of saline diffusion is greatly augmented by a comparatively small increase of temperature, a fact which suggests that the thermal measurements in diffusion experiments must be accurately made.

The want of a ready method for the measurement of comparatively high temperatures, which led to the abandonment of the author's earlier work, is overcome by the recording pyrometer, and the use of thermo-junctions in connection with this instrument rendered it possible to measure and record the temperature at which diffusion occurred.

The tubes containing the lead in which the diffusion was to take place were arranged in a little furnace of special construction. In the earlier experiments the tubes were placed in a bath of molten lead, but this was abandoned in favour of an air bath with double walls, which could be heated above the melting-point of lead and readily maintained at definite temperatures. The drawing (fig. 19) shows the general arrangement. The diffusion tubes are closed at the base, and two of such tubes are shown at T T′, placed in a cylinder of iron, I, 3 inches in diameter and 7 inches high. The sectional plan shows six of the diffusion tubes arranged symmetrically in this iron cylinder, which is enclosed in a second cylinder of thick copper, C, 4¼ inches in diameter and 8¼ inches high. The lower half of this copper vessel is surrounded with a layer of asbestos cloth, A. There is a lid composed of two discs of copper, D D′, with asbestos between them. If, for any special reason, U tubes should be employed, one open end of each tube might communicate with a hole in the double lid, and the metals the diffusion of which is to be studied could be introduced through this hole. They fall by gravity to the base of the U tube, and then rise by diffusion up to its opposite limb.

The heating is effected by a series of clay gas-burners, B B′, mounted on a ring, R R′, the burners surrounding the upper portion of the copper cylinder. Investing cases of fireclay, G G′ G″ G‴, and a lid of clay, H, complete the construction of the furnace.

It is, of course, a matter of great importance to obtain a gas supply of constant volume, and this has been effected by means of a regulator; a delicate gauge is also provided, and by its aid any variation in the pressure of the gas is indicated.

The absence of a trustworthy method for the measurement of the temperature would have rendered it impossible to conduct these experiments, but by the aid of thermo-junctions such measurement can readily be effected. These thermo-junctions, J J′ J″, are shown in fig. 19, and it was only necessary to connect them in turn with the recording pyrometer in order to obtain a continuous record of the temperature at three positions in the air bath, but as regards each of the three positions this record is

SIX DIFFUSION TUBES.
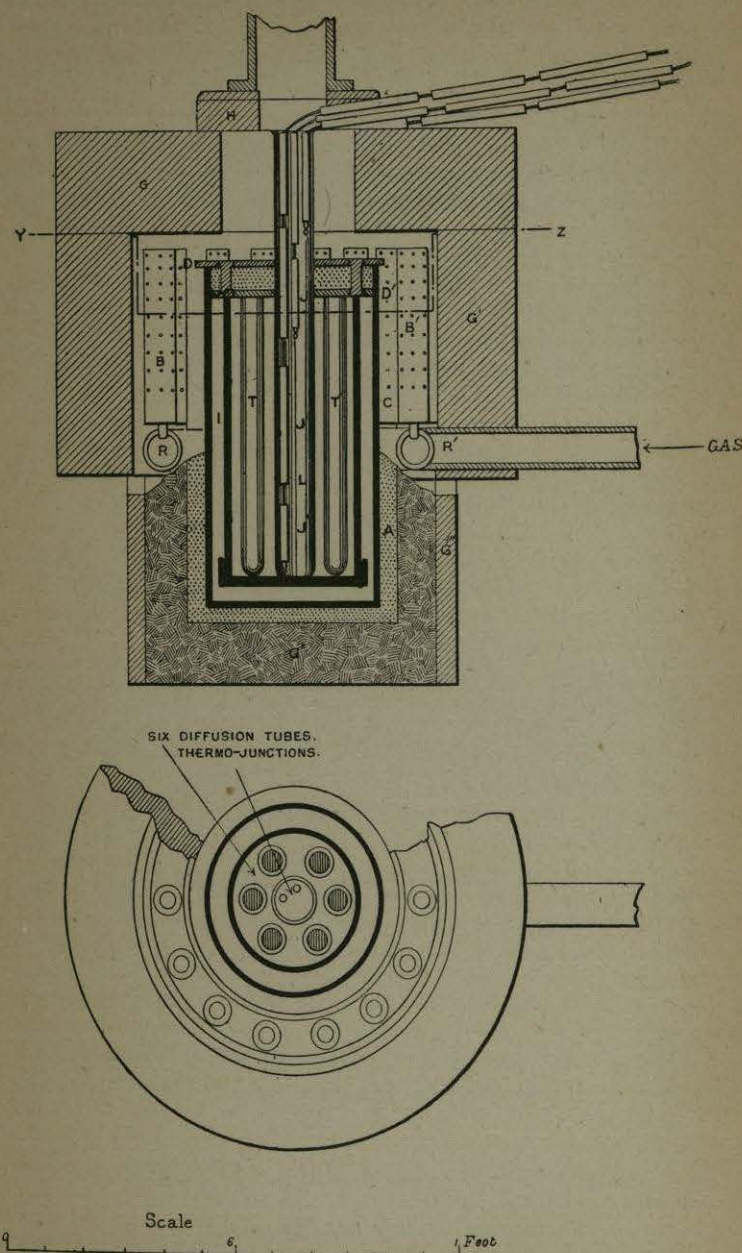THERMO-JUNCTIONS.

Scale

Fig. 19.

intermittent, and the indications afforded by each individual thermo-junction form a dotted, not a continuous line. The intermittence is, however, very rapid, and the result is three clear and distinct time-temperature records, which enable any variation in temperature to be readily detected and measured. The records, which are very numerous, show that while there was no rapid variation of temperature, there was, however, a gradual fall in temperature from the beginning to the end of the experiment, and this is due to the fact that the burners became slightly obstructed by the products of the combustion of the gas, and in later experiments a thermostat was employed. The occasional slight adjustment of the gas-taps by hand, in accordance with the indications of the thermo-junctions, rendered it possible to maintain a very constant temperature. Much care was taken to prove that the method of inserting the thermo-junctions down a central tube really indicated the mean differences of temperature between the upper, middle, and lower portions of the bath, and it was shown that there was no object in continuing the use of a lead bath, which was first adopted, as it greatly complicated the manipulation.

The amount of metal diffusing in a given time was ascertained by allowing the lead in the tubes to solidify ; the solid metal was then cut into sections, and the amount of metal in the respective sections determined by analysis.

The movement in linear diffusion is expressed, in accordance with Fick's law, by the differential equation

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

In this equation x represents distance in the direction in which diffusion takes place, v is the degree of concentration of the diffusing metal, and t is the time ; k is the diffusion constant, that is, the number which expresses the quantity of the metal in grammes diffusing through unit area (1 sq. cm.) in unit time (one day) when unit difference of concentration (in grammes per c.c.) is maintained between the two sides of a layer 1 cm. thick. The experiments have shown that metals diffuse in one another just as salts do in water, and the results were ultimately calculated by the aid of tables prepared by Stefan for the calculation of Graham's experiments on the diffusion of salts.

The necessary precautions to be observed and the corrections to be made are described at length in the author's paper, to which reference has been made.

The results of the diffusion during twenty-four hours of platinum and gold in fluid lead, contained in tubes placed side by side, and heated to a temperature of 500°, are represented in the accompanying diagram (fig. 20). The columns A B represent the columns

of fluid lead $2\frac{3}{4}$ in. long and $\frac{3}{16}$ in. wide. The spheres represent the relative sizes of the buttons of gold and of platinum extracted from the several sections, shown by horizontal lines, into which the columns of lead were divided after the metal had been allowed to solidify. With regard to the curves which are marked respectively gold and platinum, the vertical ordinate represents the *distance* in which diffusion takes place, and the horizontal ordinate, concentration. Each of the metals, gold and platinum, which diffused into the fluid column of lead, occupied, in the form of an alloy with lead, the length $a\,d$ of the tube, and in both cases the initial concentration of the
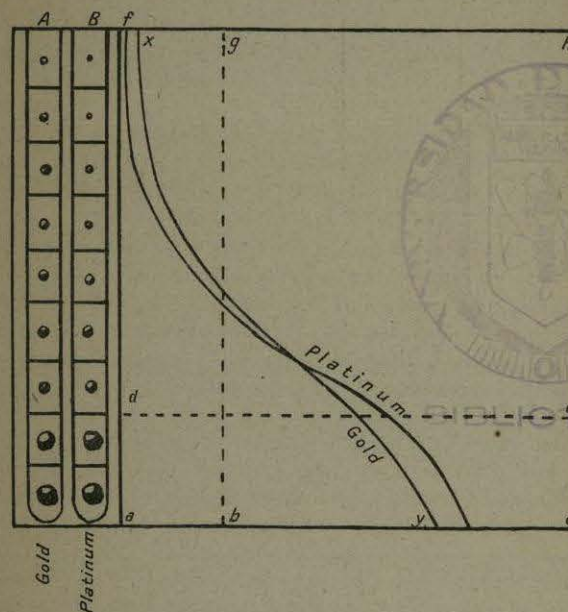

FIG. 20.

alloy denoted by $a\,c$, from which diffusion proceeded, was the same, so that the area $a\,c\,e\,d$ represents the total amount of gold or platinum employed in the experiments, the whole quantity of either metal being initially below the line $d\,e$. The final state of complete diffusion would be represented by the area $a\,b\,g\,f$, which is the same as $a\,c\,e\,d$, since the quantity of gold or platinum remains unaltered. In the same manner, the area $a\,y\,x\,f$ would represent the distribution of the gold at the end of the experiment, and consequently, in experiments which have lasted for equal times, the nearer the curve approximates to the line $b\,g$, the more rapid is the diffusion of the metal it represents.

The results for a few metals are given in the following table.

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

In order to afford a term of comparison, it may be stated that the diffusivity of chloride of sodium in water at 18° is 1·04.

In these experiments on the diffusion in liquid metals, the prevailing conditions in the ordinary diffusion of liquids were maintained, that is, there was always present a large excess of the solvent metal which is supposed to exert but little chemical action on the diffusing substance. It must also be remembered that Van't Hoff[1] has made it highly probable that the osmotic pressure of substances existing in a *solid* solution is analogous to that in liquid solutions and obeys the same laws, and it is also probable that the behaviour of a solid mixture, like that of a liquid mixture, would be greatly simplified if the solid solution were very dilute.

Nernst expresses the hope that it may be possible to measure by indirect methods the osmotic pressure of substances existing in solid solutions. The following experiments may sustain this hope by affording measurements of the results of osmotic pressure in masses of *solid metals* at the ordinary atmospheric pressure, and at a temperature at which it has hitherto been scarcely possible to detect diffusion in them.

The experiments constitute, so far as the author is aware, the first attempt to actually measure the diffusivity of one solid metal in another. It must be borne in mind that the union of two clean surfaces of metal, and even the interpenetration of two metals to a slight depth below the surfaces, does not necessarily depend on diffusion alone, as the metals become united in a great measure by viscous flow. The nature of welding demands

[1] *Zeitschr. Phys. Chem.*, vol. v., 1890, p. 322.

investigation, but the union of metals by welding is effected most energetically when the metals are in the colloidal condition, in which true diffusion is least marked. It may be observed that discs of gold and lead, pressed together at the ordinary temperature for three months, were found to have welded together more perfectly than two similar discs kept in contact at 100° for six weeks, although at least ten times more metal had interdiffused in the latter case than in the former.

For a complete description of the experiments and results, reference should be made to the original paper.[1] It may be sufficient to point out that a curve indicating the diffusion of gold in solid lead would have the same general form as the curve shown above recording the diffusion of gold in fluid lead (fig. 20), but the time required for gold to penetrate to different points of the cylinder would be far greater in the case of solid lead than in the fluid metal. This will be evident by referring to the following figures, which give the value of k — that is, the diffusivity of gold in solid lead—at various temperatures, from 251° to 100° C., and these figures show that the diffusivity of gold in solid lead at 100° is only $\frac{1}{100000}$th of that in fluid lead at a temperature of 550°.

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

These experiments naturally suggested the inquiry whether gold will permeate lead at the ordinary temperature, or must a certain amount of viscosity be given to it by the application of a moderate heat? In order to test this matter, pure lead cylinders, each with a smooth surface at its base, were clamped into close contact with the clean surface of a disc of gold, and so maintained undisturbed at a temperature of about 18° C. for four years. Successive slices were then cut at right angles to the axis of the cylinders and assayed for gold. These assays showed that the portion in contact with the gold had absorbed a quantity equivalent to 1 oz. 6 dwts. of gold per ton of lead, while the slice 6 mm. above the gold[2] had absorbed a quantity equivalent to 1½ dwts. per ton.

"**Kernel Roasting.**"—There has long been a prevalent belief that diffusion can take place in solids, and the practice in conducting certain important industrial processes supports this view. One of these processes, which is of comparatively ancient date, has certainly been employed since 1692 at Agordo, and its results are as follows:—When lumps of cupriferous iron pyrites are

[1] *Bakerian Lecture*, 1896.
[2] *Proc. Roy. Soc.*, lxvii., 1900, p. 101.

subjected to very gradual roasting with access of air, the copper becomes concentrated as a "kernel" of nearly pure sulphide of copper in the centre of a mass of ferric oxide, while, at the same time, the silver originally present in the ore travels outwards and forms a glistening shell on the exterior. These complicated changes must be effected in the solid by a movement allied to diffusion. The kernel often consists of nearly pure Cu_2S which melts at 1135° C., and kernels are formed in ore roasted at lower temperatures in the roasting heaps or kilns.

Cementation Processes.—Of all the processes which depend on the diffusion of solids, probably the most interesting is the truly venerable one by which silver may be recovered from either plates or globules of solid gold by "cementation," the name being derived from the "cement" or compound in which the plates were heated. Its nature was indicated by Pliny, and the manipulation it involved was minutely described by Geber in the eighth century, as well as by many of the early metallurgists; Savot,[1] for instance, pointed out in the early part of the seventeenth century that "cementation" will deprive gold of the silver it contains, "however small" the amount of the latter metal may be, so that it will be evident that the elimination of the silver from the centre of a mass of solid gold must also be effected by an intermolecular movement allied to diffusion. The evidence, however, is not conclusive, because gaseous chlorine intervenes, and may even play an important part in the penetration of the solid metal.

In another ancient "cementation" process, the conversion of strongly heated but still solid iron into steel is effected by the passage of solid carbon into the interior of the mass of iron, and the explanations which have from time to time been given of the process form a voluminous literature. Le Play considered cementation, which is really a slow creeping action of one solid into another, to be "an unexplained and mysterious operation," and he attributed the transmission of the carbon to the centre of the iron solely to the action of gaseous carbonic oxide. Gay-Lussac[2] confessed that a study of the process shook his faith "in the belief generally attributed to the ancient chemists that *corpora non agunt nisi soluta*," for it is certain, he adds, "that all bodies, solid, liquid, or aeriform, act upon each other, but, of the three states of bodies, the solid state is the least favourable to the exercise of chemical affinity."

In 1881 M. A. Colson[3] communicated a paper to the Académie des Sciences, in which he showed that when iron is heated in carbon there is a mutual interpenetration of carbon and iron at so low a temperature as 250°. The interpenetration of solids, as distinguished from the diffusion of two metals in each other,

[1] *Discours sur les Médailles antiques*, 1627, p. 76.
[2] *Ann. de Chim. et de Phys.*, vol. xvii., 1846, p. 221.
[3] *Comptes Rendus*, vol. xciii., 1881, p. 1074; vol. xciv., 1882, p. 26.

has received attention from many experimenters, of whose work brief mention will only be given, as the subject of this part of the book is the diffusion of solid metals. Colson pointed out that pure silver diffuses as chloride in dry chloride of sodium, and he states that calcium passes into platinum when the latter is heated in lime, and that silica diffuses through carbon and yields its silicon to platinum. The permeation of strongly heated porcelain by carbon has been demonstrated by Marsden, Violle, and other experimenters. Spring,[1] in 1885, showed that solid barium sulphate and sodium carbonate react on each other until an equilibrium is established.

Any lingering doubt as to whether gas need necessarily intervene in the cementation of iron was removed by an experiment of the author's,[2] in 1889, which showed that pure iron may be carburised by diamond *in vacuo*, at a temperature far below the melting-point of iron, and under conditions which absolutely preclude the presence or influence of occluded gas.

The rate of diffusion of carbon in iron was studied by the author[3] in 1896, and since then much work has been published on this subject by Guillet, Charpy, Bauer, Arnold and M'William and others. Guillet,[4] in his work, investigated the influence of original carbon content, temperature, duration of experiment, and kind of carbonaceous matter or cements used. He found that the penetration of carbon into iron or steel was the same after eight hours' treatment at a temperature of 1000° in two cases, in which the original metal contained ·055 per cent. and ·5 per cent. of carbon respectively. He obtained the following depths of penetration of carbon on heating iron at 1000° in carbonaceous matter—

½ hour	. . . . .	·5 mm.
1 ,,	. . . . .	·8 ,,
2 hours	. . . . .	1·0 ,,
4 ,,	. . . . .	1·3 ,,
6 ,,	. . . . .	2·0 ,,
8 ,,	. . . . .	3·0 ,,

—and the following figures illustrate the influence of temperature, the specimens being heated for eight hours in each case:—

At 800°	. . . . .	·5 mm.
850	. . . . .	1·0 ,,
900	. . . . .	1·6 ,,
925	. . . . .	2·0 ,,
950	. . . . .	2·8 ,,
1000	. . . . .	4·2 ,,
1050	. . . . .	5·2 ,,

[1] *Bull. de l'Acad. Roy. de Belgique*, vol. x., 1885, p. 204.
[2] *Nature*, vol. xli., 1889, p. 14.
[3] *Journ. Iron and Steel Inst.*, 1896, i. p. 139.
[4] *Mémoires de la Société des Ingénieurs Civils de France*, 1904, No. 1, p. 177.

With regard to special steels, he divides them into two groups :—(1) Steels in which the cementation process is either reduced or actually prevented by increasing quantities of other constituents, such as nickel, titanium, silicon, aluminium. (2) Steels in which the other constituents assist the cementation process, such as manganese, chromium, tungsten, and molybdenum. Arnold and M'William[1] studied the diffusion of various elements in iron, by using cylinders of nearly pure iron, 3 inches long and 0·7 of an inch in diameter, bored through with a hole 0·35 inch in diameter ; bars of iron containing about 1·5 per cent. of the elements, the diffusive power of which was about to be determined, were turned dead true to the exact diameter of the hole in the jacket. The latter was heated to about 150° C. to expand the hole a little, and the core was driven home, so that, on cooling, the bright surfaces of the jacket and core were in close contact. A hole for the insertion of the thermo-couple was made in the core, and the compound bar was introduced into a porcelain tube and heated *in vacuo* in a tube furnace. After heating *in vacuo* for ten hours at a temperature ranging between 950° C. and 1050° C., portions were turned off the jacket and analysed to ascertain the amount of the element contained in the core that had passed into the jacket. The following table shows the diffusive power of elements in iron.

Element.	Original Percentage in Jacket.	Original Percentage in Core.	Percentage in the $\frac{1}{28}$th inch of Jacket adjacent to the Core after Experiment.	Percentage diffused in Ten Hours.
Carbon . .	0·05	1·78	0·55	0·50
Sulphur . .	0·02	0·97	0·12	0·10
Phosphorus .	0·015	1·36	0·11	0·095
Nickel . .	0·00	1·51	0·11	0·11
Manganese .	0·05	1·29	0·04	none
Silicon . .	0·027	1·94	0·028	,,
Chromium .	0·00	1·10	0·00	,,
Aluminium .	0·02	1·85	0·02	,,
Tungsten .	0·00	1·41	0·00	,,
Arsenic . .	0·02	1·57	0·012	,,
Copper . .	trace	1·81	trace	,,

This solid diffusion of metals is closely connected with the formation of alloys by cementation, a subject which will now be considered.

Formation of Alloys by Cementation.—The fact that alloys can be formed by the union of two metals at a temperature below

[1] *Journ. Iron and Steel Inst.*, 1899, i. p. 85.

the melting-point of the more fusible of the two has long been known to metallurgists, and perhaps the most striking fact in the more modern history of the subject was recorded in 1820 by Faraday and Stodart,[1] who, in the course of an investigation on the alloys of iron with other metals, noted their failure to produce certain alloys by "cementation," but consider it "remarkable," in the case of platinum, that it will unite with steel at a temperature at which the steel itself is not affected. They also show that solid steel and platinum, in the form of bundles of wires, may be welded together "with the same facility as could be done with iron or steel," and they observe that on etching the surface of the welded mass by an acid "the iron appeared to be alloyed with the platinum." Their interest in this singular fact led them to promise some direct experiments on "this apparent alloy by cementation," that is, by the interpenetration of solids. Since this time there have been many more or less isolated observations bearing on the subject, and brief reference may be made to the more important of them in chronological order. In 1877 Chernoff[2] showed that if two surfaces of iron of the same nature be placed in intimate contact and heated to about 650° they will unite. In 1882 Spring[3] made his remarkable experiments on the formation of alloys by strongly compressing their constituent metals at the ordinary temperature, while, in 1885, O. Lehmann[4] suggested, and in 1888 Hallock[5] demonstrated, that compression is not necessary, as alloys might be formed by placing carefully cleaned pieces of two constituent metals in juxtaposition and heating them to the melting-point of the alloy to be formed, which was, in some cases, 150° below the melting-point of the more fusible of the two metals. In 1889 Coffin showed—and the author has repeatedly verified the accuracy of his experiment—that if the freshly fractured surfaces of a steel rod 9·5 mm. square be placed together and heated to below redness, they will unite so firmly that it is difficult to pull them apart by hand. The steel was highly carburised, and the diffusion of a carbide of iron probably played an important part in effecting the union. There must have been molecular interpenetration in this case, though the steel was at least 1000° below its melting-point. In 1894 Spring[6] proved that if the carefully surfaced ends of cylinders of two metals were strongly pressed together and maintained for eight hours at temperatures which varied from 180° to 400°, interpenetration would

[1] *Quarterly Journal of Science*, vol. ix., 1820, p. 319.
[2] *Revue Universelle des Mines*, vol. i., 1877, p. 411.
[3] *Ber. der Deutsch. Chem. Gesell.*, xv., 1882, p. 595.
[4] *Wied. Ann.*, xxiv., 1885, p. 1.
[5] Communicated to Phil. Soc. of Washington, Feb. 18, 1888 ; *Zeitschr. Phys. Chem.*, ii., 1888, p. 6, or *Chem. News*, vol. lxiii., 1891, p. 17.
[6] *Bull. de l'Acad. Royale de Belgique*, vol. xxviii., 1894, p. 23.

take place, true alloys being formed at the junction of the two metals.

In these experiments, which are of great interest, the temperatures at which the cylinders were maintained were below the melting-point of the more fusible of the two metals. Care appears to have been taken to avoid heating them up to the melting-point of the *eutectic* alloy, though it was in some cases close to it. The necessity for this precaution will be obvious, as the union of the two compressed cylinders might easily be effected by the fusion of an eutectic alloy with a relatively low melting-point.

Diffusion of Amalgams in Mercury.—A number of experiments have been made on the diffusion at ordinary temperatures of gold and other metals in mercury, from which it was found that the diffusivity of gold in mercury at 11° C. is 0·72 sq. centim. per day, the diffusivity of gold in lead being 3·0 sq. centims. per day, at 500°. As already stated, Dr Guthrie[1] published, in 1883, particulars of some experiments of this kind, the metals he selected being zinc, tin, lead, sodium, and potassium, diffusing in mercury. He did not make any calculations with a view to obtain either the absolute or the relative diffusivities of these metals in mercury; indeed, after giving the percentage of the diffusing metal in successive quantities of mercury, he observes: "It is scarcely worth while dividing these diffusion *percentages* by the so-called atomic weights of the metals." His experiments were complicated by the fact that in some cases he employed solid metals instead of fluid amalgams, as the source of the diffusing metal. Approximate results have, however, been obtained from his data, and from certain measurements of the original apparatus, now deposited in the South Kensington Museum. These show that his inference "that potassium and sodium have a far greater diffusive energy than the heavier metals examined" is not supported by the actual result of his experiments. His results, calculated by the method given in the present chapter, give the values of k in sq. centims. per day as follows:—

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

The diffusion of certain metals in mercury has also been studied by Humphreys,[2] whose results substantially confirm those of Guthrie, and more recently by Wogan,[3] who gives

[1] *Phil. Mag.*, vol. xvi., 1883, p. 321.
[2] *Trans. Chem. Soc.*, 1896, p. 243 and p. 1679.
[3] *Ann. de Physik*, 23, ii. p. 345, 1897.

the following figures for the value of k at the temperatures stated :—

	Temperature.	k.		Temperature.	k.
Lithium . .	8·2	·66	Zinc . .	11·5	2·19
Sodium . .	9·6	·64	,, . .	99·2	2·90
Potassium . .	10·5	·53	Cadmium .	8·7	1·45
Rubidium . .	7·3	·46	,, .	99·1	2·96
Cæsium . .	7·3	·45	Lead . .	9·4	1·50
Calcium . .	10·2	·54	,, .	99·2	1·92
Strontium . .	9·4	·47	Tin . .	10·7	1·53
Barium . .	7·8	·52	Thallium .	11·5	·87

With regard to the diffusivity at high temperatures, he found that all metallic amalgams, with the exception of zinc, cadmium, and lead, attacked the glass vessels.

Volatility of Metals.—The diffusion of metals in each other must be closely connected with the evaporation of solid metals or alloys at temperatures far below their melting-points. It is not necessary to go further back for definite views on the subject than to the time of Boyle,[1] who thought that "even such (bodies) as are solid may respectively have their little atmospheres, ... for," he adds, "no man, I think, has yet tried whether glass, and even gold, may not in length of time lose their weight."

Boyle's opinion was correct, for mercury which has been *frozen* by extreme cold does, as Merget[2] showed two centuries later, evaporate into the atmosphere surrounding it; a fact which is of much interest in connection with Gay-Lussac's well-known observation that the vapours emitted by ice and by water both at 0° C. are of equal tension. Demarcay[3] has proved that *in vacuo* metals evaporate sensibly at lower temperatures than they do at the ordinary atmospheric pressure, and he suggested that even metals of the platinum group will be found to be volatile at comparatively low temperatures, a fact which has been well established by recent work. Holborn and Henning[4] have shown that platinum, iridium, and rhodium lose weight appreciably at high temperatures. Thus, when maintained at a white heat for eight hours, weighed pieces of iridium lost 70 milligrams, platinum 7, rhodium 6, platinum-iridium alloy containing 10 per cent. of iridium 24, and a similar platinum-rhodium alloy lost 9 milligrams. With regard to the volatilisation of metals *in vacuo*, Krafft[5] has published interesting figures which confirm the work

[1] Collected works, Shaw's edition, 1738, i. p. 400.
[2] *Ann. de Chim. et de Phys.*, vol. xxv., 1872, p. 121.
[3] *Comptes Rendus*, vol. xcv., 1882, p. 183.
[4] *Preuss. Akad. Wiss. Berlin Sitz. Ber.*, xxxix. p. 936, 1902.
[5] *Ber. Deut. Chem. Gesell.*, xxxviii. p. 262, 1905.

of Demarcay and Spring,[1] the following table being taken from his work :—

	Temperature at which Evaporation begins *in vacuo*.	Boiling-point *in vacuo*.	Boiling-point at 760 mm.
Mercury . . .	− 40	155	357
Cadmium . .	156	450	749
Zinc . . .	184	550	920
Potassium . .	63	365	667
Sodium . . .	98	418	742
Bismuth . . .	270	993	1700
Silver . . .	680	1360	2040

Some very interesting work has recently been done on the volatilisation of solids at the ordinary temperature, and Zenghelio[2] claims to have proved that lead, copper, and many metallic compounds volatilise appreciably in the course of time. In these experiments, silver leaf was hung over the solid body under observation, in a desiccator, for lengths of time up to six months, and he found that he could then determine the volatilised metal in the silver.

Magnetic Properties of Metals.—The fact that metals differ widely in their behaviour when placed in a magnetic field is well known. When considering magnetic properties, it has been customary to speak of metals as being either paramagnetic or diamagnetic. Paramagnetic bodies are such that, if a bar be presented to a north-seeking pole of a magnet, a south-seeking pole is induced on the nearer end, attraction results, and the magnetised bar tends to move into the stronger part of the field. On the other hand, diamagnetic bodies are such that, if presented to a north-seeking pole of an intense magnetic force, a north-seeking pole is induced on the nearer end, repulsion follows, and the bar tends to move into the weaker parts of the field. Again, paramagnetic bodies are such that if a strip be freely suspended from its centre and placed in a magnetic field, the induced magnetism causes it to set itself parallel to the direction of the magnetising force. On the other hand, diamagnetic bodies under similar conditions tend to take up a position at right angles to the direction of the magnetic force.

Thus, iron, nickel, and cobalt are typically paramagnetic, while copper and bismuth are diamagnetic. This is otherwise stated by saying that the magnetic permeability of iron, nickel, and cobalt is greater than that of air, while that of copper and bismuth is less.

[1] *Comptes Rendus*, 1894, p. 42.
[2] *Zeitschr. Phys. Chem.*, I. p. 219.

The magnetic permeability of any substance is the ratio of the induction to the magnetising force, and is generally indicated by
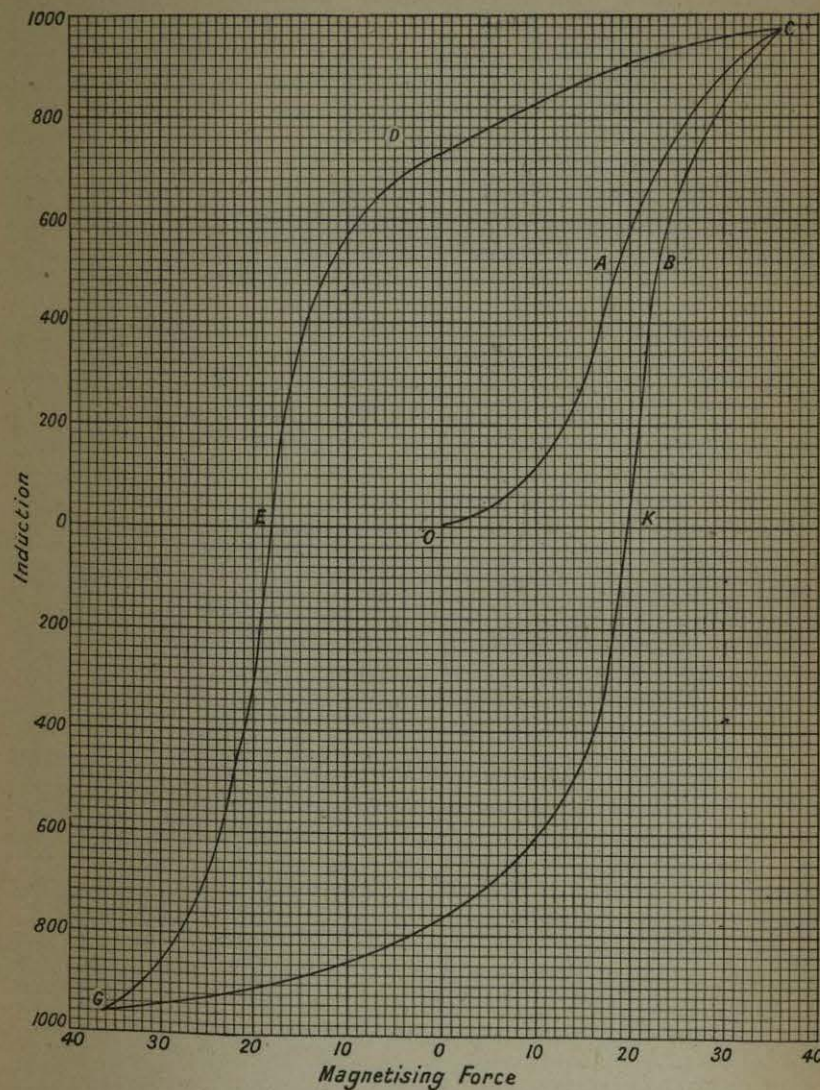

FIG. 21.

the letter μ. The induction is measured by applying various magnetising forces to the specimen under examination, either in the form of wires or as closed rings, the intensity of the magnetisation being measured by a magnetometer when wires

are used, or by means of a ballistic galvanometer in the case of closed rings. Retentivity is the property magnetic bodies possess of retaining a large proportion of the total magnetisation after the magnetising force has been removed.

Hysteresis is the term applied to the well-known phenomenon of the magnetisation of a body lagging behind the magnetising force. This may be well illustrated by the examination of fig. 21, which is a hysteresis curve of a steel wire.

If, starting with an unmagnetised bar of iron or steel, we gradually increase the magnetising force and determine the corresponding values of the induction, we shall obtain a curve similar to O A C in the figure. When the point C is reached, assuming the magnetising force is gradually decreased and the value of the induction is again measured as the magnetising force decreases, it will be found that the curve obtained does not coincide with the curve obtained as the magnetising force increases, but has the form C D; thus, when the magnetising force is zero, the induction, instead of being zero, has the value O D.

On reversing the direction of the magnetising force, the curve D E G will be obtained; and on decreasing the magnetising force to zero, and then starting with it in its original direction, the branch G K B C of the curve will be obtained. The magnetising force represented by O E or O K denotes the force required to deprive the bar of its residual magnetisation.

When a bar of iron or steel is heated to redness, it loses its power of becoming magnetised, or if permanently magnetised, all this permanent magnetism will be lost. Similar changes take place in the case of nickel and cobalt. The temperature at which metals lose their magnetic properties is called the critical temperature, and in the case of iron and carbon steels corresponds with Ar_2 point, being about 770° C. (see Chapter IV.).

For nickel the critical point is at about 300°, and when nickel is alloyed with iron some very peculiar magnetic effects may be produced; thus a special steel containing 25 per cent. of nickel is unmagnetisable at ordinary temperatures; if, however, it be cooled down to a temperature a few degrees below zero it becomes magnetisable, and this magnetisation is retained up to a temperature of 580°, when it again becomes non-magnetic, and remains in this state until it has again been cooled below zero.

The question of soft iron for the armature cores of dynamos is one of great importance to the electrical engineer, the aim being to attain high permeability but low retentivity.

Not only has the chemical composition to be considered, but also the thermal and mechanical treatment. The exact conditions of annealing [1] which will give the best effect, that is, the minimum

[1] Hans Kemp, *Stahl und Eisen*, Dec. 1 and 15, 1899, trans. by Dr R. Moltenke. *Iron Trade Review*, Feb. 15, 1900.—Madame Curie, "Magnetic Properties of Hardened Steels," *Bull. Soc. d'Encouragement pour l'Ind. Nat.*

hysteresis loss, seem to depend on the rate of cooling, but to be independent of the rate of heating.

Electrical Resistance of Metals.—The resistance of a conductor is the ratio of the electromotive force applied at its ends to the current passing, and it follows from this that a conductor has unit resistance when unit difference of potential produces unit current in it. The unit of resistance is the ohm, and is such that the E.M.F. between the terminals of a conductor of which the resistance is one ohm, when a current of one ampere is passing through it, is one volt. The ohm is equal to 10^9 c.g.s. units.

In metallic conductors, the resistance varies with the nature of the material, the dimensions of the conductor, and the temperature. For a wire of a given material, under constant temperature, the resistance is found to be directly proportional to the length, and inversely proportional to the cross section. The specific resistance of a metal is the resistance of a length of one centimetre with a cross section of one square centimetre. The reciprocal of the resistance of a conductor is known as its conductivity.

In the following table the specific resistance of some pure metals is given, but it must be remembered that a minute trace of impurity may very largely influence this property. The specific resistance also depends to a considerable extent on the state of the material as to hardness produced by work on it, or the conditions of annealing if this hardness has been removed by annealing.

SPECIFIC RESISTANCE OF METALS.

Metal.	Resistance in Ohms of a Rod 1 cm. long and 1 sq. cm. Cross-section at 0° C. $\times 10^6$.
Silver	1·50
Copper	1·57
Gold	2·24
Aluminium . . .	2·62
Magnesium . . .	4·31
Iron	10·68
Platinum . . .	11·19
Nickel	12·00
Lead	19·80

Commission des Alliages, Jan. 1898; also in *Metallographist*, 1898, p. 107, and *Electrical Review*, Jan. 1899.—Osmond, "Steel for Magnets," *Comptes Rendus*, June 19, 1899; also *Metallographist*, 1900, p. 35.—Harbord and Twynam, "Hardening of Steel," *Journ. West of Scotland Iron and Steel Inst.*, 1898.—Osmond, "Magnetic Changes at Ar_2 and Ar_0, *Metallographist*, 1898, p. 158.—Barrett, Brown, and Hadfield, "On the Electrical Conductivity and Magnetic Properties of Alloys," *Trans. Roy. Dublin Soc.*, vol. vii., series ii., p. 67, 1900; *Proc. Inst. Elec. Eng.*, vol. xxxi. p. 674, 1900; *Trans. Roy. Dublin Soc.*, vol. viii., series ii., p. 1, 1902.

In the case of pure metals, the specific resistance always increases with increase of temperature. In the same manner the resistance decreases as the temperature is lowered, in such a way as to suggest that at absolute zero the resistance would be zero.[1] Thi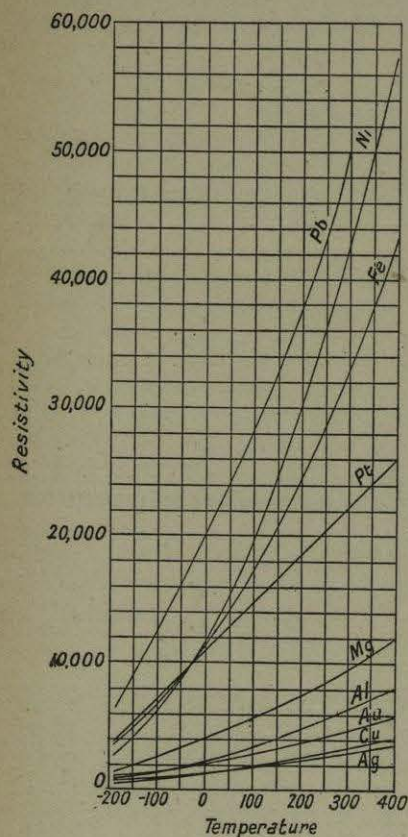s, however, has proved to be incorrect, as Onnes and Clay have shown that at very low temperatures points of inflection occur, and it is probable that points of minimum value are reached at low temperatures, after which an increase in resistance is obtained.

Niccolai[2] has recently determined the resistance of metals between the temperatures 400° and −189°, and from his results the curves in fig. 22 are deduced.

Specific Heat of Metals. — The quantity of heat necessary to raise the temperature of 1 gramme of a substance through 1° C. at any given temperature is called the specific heat of the substance at that temperature.

Recent experiments by Tilden, Behn, and others show that the influence of temperature on the specific heats of metals is much greater than was formerly supposed.

FIG. 22.

There appears to be no one condition or set of conditions under which the law of Dulong and Petit is true for all the elements, this law, as originally enunciated, stating that the atoms of all the elements have the same thermal capacity, or in other words, "the product of the specific heat and the atomic weight is constant."

The specific heat of metals increases in value as the temperature

[1] Dewar and Fleming, *Phil. Mag.*, vol. xxxiv., 1892, p. 326 ; vol. xxxvi. (1893), p. 271.
[2] *Accad. Lincei Atti*, xvi. p. 757, and also p. 906.

is raised and decreases in value as the temperature is lowered below 0° C. Harker[1] has determined the mean specific heat of iron between 0° and various high temperatures : between 0° and 200° he found it to be ·1175, between 0° and 850° it had increased to ·1647, but in the case of iron this increase is not continued at higher temperatures, for between 0° and 1100° a mean value of ·1534 only was obtained.

PHYSICAL CONSTANTS OF METALS.

Metal.	Symbol.	Atomic Weight. 0=16	Atomic Volume.	Specific Gravity.	Specific Heat.	Melting-point. ° C.	Coefficient of Linear Expansion.	Therm. Cond. C.G.S. Units.	Elect. Cond. C.G.S. Units.
ALUMINIUM .	Al	27·1	10·6	2·56	0·218	657	0·0000231	·502	390,000
ANTIMONY .	Sb	120·2	17·9	6·71	0·051	632	0·0000105	·042	31,471
ARSENIC .	As	74·96	13·2	5·67	0·081	450 under pressure	0·0000055	..	32,425
Barium . .	Ba	137·37	36·3	3·78	0·047	850			
BISMUTH .	Bi	208·0	21·2	9·80	0·031	266	0·0000162	·019	9,091
CADMIUM .	Cd	112·4	13·2	8·60	0·056	322	0·0000306	·219	99,800
Cæsium . .	Cs	132·81	71·0	1·87	0·048	26	0·0001316		25,400
Calcium . .	Ca	40·09	25·5	1·57	0·170	780			150,818
Cerium . .	Ce	140·25	21·0	6·68	0·045	623	..	..	
CHROMIUM .	Cr	52·0	7·6	6·80	0·120	1482			
COBALT . .	Co	58·97	6·9	8·50	0·103	1464	0·0000123	..	106,140
Columbium .	Cb	93·5	13·0	7·2	0·071	1950			
COPPER . .	Cu	63·57	7·1	8·93	0·098	1084	0·0000167	·924	640,615
Gallium . .	Ga	69·9	11·8	5·90	0·079	30			
Glucinum .	Gl	9·1	4·7	1·93	0·621	Below 960			
GOLD . . .	Au	197·2	10·2	19·32	0·031	1064	0·0000144	·700	455,166
Indium . .	In	114·8	15·5	7·42	0·057	155	0·0000417	·219	112,400
IRIDIUM . .	Ir	193·1	8·6	22·42	0·033	1950	0·0000070		
IRON . . .	Fe	55·85	7·2	7·86	0·110	1505	0·0000121	·147	110,314
Lanthanum .	La	139·0	22·7	6·10	0·045	810			
LEAD . . .	Pb	207·1	18·2	11·37	0·031	327	0·0000292	·084	49,067
Lithium . .	Li	7·0	13·0	0·54	0·941	186			
MAGNESIUM .	Mg	24·32	13·9	1·74	0·250	633	0·0000269	·343	119,428
MANGANESE .	Mn	54·93	7·3	7·50	0·120	1207			229,616
MERCURY . .	Hg	200·0	14·7	13·59	0·032	−39	0·0000610	·015	10,630
MOLYBDENUM	Mo	96·0	11·2	8·60	0·072	2500			
NICKEL . .	Ni	58·68	6·7	8·80	0·108	1427	0·0000127	·141	144,196
Osmium . .	Os	190·9	8·5	22·48	0·031	2500	0·0000065	..	105,300
Palladium .	Pd	106·7	9·3	11·50	0·059	1535	0·0000117	·168	97,857
PLATINUM .	Pt	195·0	9·1	21·50	0·032	1745	0·0000089	·166	91,600
POTASSIUM .	K	39·1	45·5	0·86	0·170	62	0·0000841	..	141,990
RHODIUM .	Rh	102·9	8·5	12·10	0·058	1660	0·0000085		
Rubidium .	Rb	85·45	55·8	1·53	0·077	38			
Ruthenium .	Ru	101·7	8·3	12·26	0·061	1800	0·0000096		
Scandium .	Sc	44·1	17·6	2·5	0·153	1200		·	
SILVER . .	Ag	107·88	10·2	10·53	0·056	962	0·0000192	·993	681,198
SODIUM . .	Na	23·0	23·8	0·97	0·290	95	0·0000710	·365	253,973
Strontium .	Sr	87·62	34·5	2·54	..	800			45,708
Tantalum .	Ta	181·0	14·1	12·8	0·033	2910	0·0000079	..	60,600
Tellurium .	Te	127·5	20·4	6·25	0·049	440	0·0000167	..	46,600
Thallium .	Tl	204·0	17·2	11·85	0·033	303	0·0000302	..	56,712
Thorium .	Th	232·42	20·9	11·10	0·028	1450			
TIN . . .	Sn	119·0	16·3	7·29	0·055	232	0·0000232	·155	76,640
Titanium .	Ti	48·1	13·5	3·54	0·13	2000 ?			
TUNGSTEN .	W	184·0	9·6	19·10	0·034	3100			11,600
URANIUM .	U	238·5	12·8	18·7	0·028				
VANADIUM .	V	51·2	9·3	5·50	0·125	1680			
Yttrium . .	Yt	89·0	23·4	3·80		1000 ?			
ZINC . . .	Zn	65·37	9·1	7·15	0·094	419	0·0000291	·269	171,381
Zirconium .	Zr	90·6	21·8	4·15	0·066	1500			

[1] *Phys. Soc. Proc.*, xix. p. 703, 1905.

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

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