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X. BAKERIAN LECTURE.—*On the Diffusion of Metals.*

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[PLATES 7, 8.]

PART I.—DIFFUSION OF MOLTEN METALS.

GOLD, PLATINUM, AND RHODIUM, DIFFUSING IN MOLTEN LEAD AND IN MOLTEN BISMUTH.

THE diffusion of molten and solid metals has long demanded investigation, their molecular mobility being of great interest in relation to the constitution of matter, and its results of much industrial importance.

The analogy of alloys to ordinary saline solutions has often been pointed out, and many experiments have recently been devoted to comparing the action of osmotic pressure in saline solutions and in alloys, as measured by the lowering of the freezing point which is caused by the addition to the solvent of a small quantity of another body.* The general effect is the same whether the solvent is a liquid like water or a molten metal. Very little attention has, however, been given to the consideration of the molecular movements which enable two or more molten metals to mix spontaneously and form a truly homogeneous fluid mass, although it is by such an investigation that the analogy of an alloy to a saline solution may reasonably be expected to be more clearly revealed than by any other method of research. A single example of the spontaneous mixing of two metals may be useful. In preparing the alloy of gold and copper used for coinage, some 33 kilos. of gold and 3 kilos. of copper are melted together in a single crucible, and the results of assays on the first and the last portions of metal poured from the crucible, seldom differ by more than one ten-thousandth part. Such a fluid mass of standard gold owes this remarkable uniformity in composition not only to the mechanical stirring by which the blending of

* HEYCOCK and NEVILLE, 'Trans. Chem. Soc.,' vol. 55, 1889, p. 666; vol. 57, 1890, pp. 376 and 656; vol. 59, 1891, p. 936; vol. 61, 1892, pp. 914 and 888; vol. 65, 1894, pp. 31 and 65; vol. 67, 1895, p. 1024; and ROBERTS-AUSTEN, 'Proc. Roy. Soc.,' vol. 49, 1891, p. 347.

the gold and copper was roughly effected. The molecular mobility of the metals has influenced the result, and the metals dissolved in each other, become, by a spontaneous process, spread or diffused uniformly; in this case the uniformity is not materially disturbed when the solidification of the mass is effected.

In view of the great interest connected with such action, the absence of direct experiments is remarkable, but this may perhaps be explained by the difficulty of conducting them. The sources of these difficulties are many. Such metals as are suitable for study require a more or less elevated temperature to melt them, and, where diffusion is concerned, small variations in temperature may be of much importance, for, as GRAHAM showed, the rate of diffusion of salts in water is greatly increased by a small rise in temperature, the diffusibility of chloride of sodium, for instance, being more than doubled by a rise of 33° . It is now well-known that the osmotic pressure of a salt in solution is measured by the diffusion which takes place. A rise of temperature, therefore, which augments the osmotic pressure, must also increase the rate of diffusion. GRAHAM further pointed out that the inequality of diffusion which various saline substances exhibit at a low temperature, becomes less at a high temperature, and he therefore concluded that "it would appear to be the effect of a high temperature to assimilate diffusibilities" of different salts.*

In the case of molten metals, the necessity for working at high temperatures, which until quite recently could not be readily measured even with approximate accuracy, and the fear that the value of the results would be impaired by the action of convection currents, must have deterred physicists from undertaking experiments on the diffusion of molten metals. OSTWALD'S statement† with reference to the diffusion of salts, that "to make accurate experiments on diffusion is one of the most difficult problems in practical physics," may well have given rise to doubts whether any method which seemed to be available for conducting such investigations with molten metals would afford trustworthy results. The difficulties are obvious, but my long connection with GRAHAM'S researches made it almost a duty to attempt to extend his work on liquid diffusion to metals, and, therefore, fourteen years ago the present investigation was undertaken, but it was abandoned because I was unable to measure with sufficient accuracy the temperature at which diffusion took place, and it has only been resumed during the past two years.

As regards the history of the subject, I believe that a brief communication of my own on the mobility of gold and silver in molten lead, to the Chemical Section of the British Association at the meeting at Southport in September, 1883, embodied the results of the first experiments which were ever made with the direct object of investigating the diffusion of molten metals and alloys, other than those of mercury which are fluid at the ordinary temperature. I stated that "while molten copper and antimony interpenetrate but slowly, the mobility of gold and silver in molten lead is

* GRAHAM, 'Collected Papers,' p. 570, or 'Phil. Trans. Roy. Soc.,' 1861, p. 183-224.

† OSTWALD, 'Solutions,' English Edition, 1891, p. 122.

comparatively rapid.”* As regards mercury and its fluid amalgams, the history is more extended, for in 1713 HOMBERG † may be said to have at least foreshadowed the diffusion of metals, both solid and liquid, in his paper “On Substances which Penetrate and which pass through Metals without their being Melted.” He incidentally showed, by experiment, the extreme rapidity with which mercury will penetrate a bar of tin.

In November, 1883, GUTHRIE ‡ published a remarkable paper “On Certain Molecular Constants,” in which the diffusion of zinc, lead, tin, sodium, and potassium in mercury was studied, and he stated that these metals, which, of course, are much lighter than mercury, “appear after a month’s interval in appreciable quantity at a depth of a foot beneath the surface, when the temperature is about 16° or 17°.” He concludes his paper by offering “a general curve of amalgamation,” which he thought would represent the rate at which the metals examined by him alloy with mercury, and this curve may also, he says, “represent the relative rates of elementary atomic and molecular diffusion generally.”

GUTHRIE held that as the mercury he employed was a good conductor of heat, there was not much fear of the disturbing influence of convection currents. The existence of such currents, nevertheless, gave me much anxiety in the earlier experiments with molten metals which were begun in the year 1881, and will now be described.

From the outset of this research both molten lead and bismuth were chosen as suitable fluids in which the diffusion of other metals could be studied. Advantage was also taken of the fact that at temperatures well above the melting point, neither of these metals unite with iron. The precious metals, also, when alloyed with lead or bismuth, do not show any tendency to unite with iron unless it is very clean and bright. Tubes of wrought iron, therefore, proved to be most useful in conducting the inquiry. In the first instance single tubes filled with lead were arranged vertically in a bath of lead which was kept well above its melting point. Weighed quantities of heated, but still solid, gold or platinum were then rapidly lowered through the lead in little covered receptacles of iron to the bottom of the tube, and when by the aid of a rigid steel wire the removal of the covers was gently effected, the gold was exposed to the lead; it became rapidly dissolved, and diffusion began. The tubes filled with molten lead, in which diffusion took place, were about 200 millims. long, and many such tubes were arranged in a single bath, which was carefully kept hotter at the top than at the bottom so as to avoid as much as possible the carrying of the precious metal upwards by any streams of lead which might rise as convection currents from the bottom of the tube. The main result of

* ROBERTS-AUSTEN, ‘British Association Report,’ 1883, p. 402.

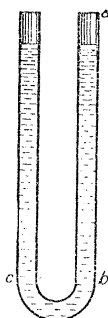
† HOMBERG, ‘Mém. de l’Acad. Royale des Sciences,’ 1713 (vol. published 1739), p. 306.

‡ GUTHRIE, ‘Phil. Mag.,’ vol. 16, 1883, p. 321. W. S. HUMPHREYS has recently made experiments on the diffusion of zinc, lead, tin, bismuth, silver and copper in mercury. ‘Trans. Chem. Soc.,’ vol. 69, 1896, p. 243.

these earlier experiments was to show that samples of lead (which were removed by sucking them from the upper part of the tubes into stems of tobacco pipes) always revealed the presence of weighable quantities of gold after a lapse of the first three hours, while a sample withdrawn at the end of a second period of three hours did not indicate the presence of a commensurate amount of the precious metal. This fact either pointed to defects in the method, to the transmission of gold by convection currents, or to the very rapid diffusion of gold when minute quantities of this metal are present in lead. I believe that the latter will ultimately prove to afford the true explanation of the facts observed.

The vertical tubes were then replaced by U-tubes of wrought iron, each limb of which was 230 millims. long and 10 millims. internal diameter. The tubes were filled with lead, and heated externally in a bath of molten lead, in an appliance which will be described immediately, and the precious metal, in the form of a rich alloy with lead, was inserted into one limb of the tube. Experiments proved that the gold falling by gravity became rapidly and uniformly distributed through the column of lead in that side of the tube, *a, b*, Fig. 1, into which it was introduced, and

Fig. 1.



in the rounded part of the tube, *b, c*, at the base of the U. After a given number of days the tubes were cautiously withdrawn from the bath and cooled from the bottom so as to solidify the alloy. The tube was then carefully divided by transverse saw cuts into measured sections, which were numbered consecutively, and the alloy could then be readily melted from each section and weighed, after which the amount of precious metal it contained was determined by analysis.

It was found, however, that the use of U-tubes greatly increases the difficulties of calculation, as there is great uncertainty in any assumption as to the distribution of the diffusing metal during the experiment at points near the bend. It was found that in all these experiments, the gold or platinum was very evenly distributed by gravity through the limb into which the metal was first introduced.

The calculations were finally made on the assumption that the concentration at the bend was, throughout the experiment, equal to the mean of its initial and final concentration. I, nevertheless, determined to sacrifice a long series of results, as they are less trustworthy than those obtained later by the use of single tubes.

The continuance of these experiments is mainly due to the interest which Lord KELVIN has always taken in them, and in a letter dated 4th of November, 1883, he reminded me of the necessity for maintaining a graduated temperature from the top to the bottom of the diffusion tubes, and he has from time to time given me, on points of detail, suggestions, which I need hardly say have been adopted.

Description of the Apparatus employed in the later Experiments.

The tubes that contain the lead in which the diffusion takes place are arranged in a little furnace of special construction. In the earlier experiments they were, as has been already stated, placed in a bath of molten lead, but this was abandoned in favour of an air bath with double walls which can be heated above the melting point of lead and readily maintained at definite temperatures. The drawing, fig. 2, Plate 7, shows the general arrangement. The diffusion tubes are closed at the base, and two of such tubes are shown at TT', fig. 2, Plate 7, placed in a cylinder of iron, I, 3 inches in diameter and 7 inches high. The sectional plan (fig. 2, Plate 7) shows six of the diffusion tubes arranged symmetrically in this iron cylinder, which is enclosed in a second cylinder of thick copper, C, $4\frac{1}{4}$ inches* in diameter and $8\frac{1}{4}$ 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, DD', 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, are introduced through this hole. They fall by gravity to the base of the U-tube, and then rise by diffusion up its opposite limb.

The heating is effected by a series of clay gas-burners BB', mounted on a ring RR'; the burners surrounding the upper portion of the copper cylinder. Investing cases of fireclay GG'G''G''', and a lid of clay H, completes 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, shown in fig. 3, Plate 7, and a delicate gauge not shown in the plate 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 JJ'J'', are shown in fig. 2, Plate 7, and the method of using them will now be indicated. I have, however, already fully described the method elsewhere,† and the general

* It is convenient to give these dimensions in inches, but a metric scale is also provided with the drawing.

† 'Roy. Soc. Proc.,' vol. 49, 1891, p. 347. 'Inst. Civil Engineers Proc.,' vol. 110, 1891-2, Part iv.

distribution of the apparatus which may be used for such measurement of temperature up to the melting-point of platinum, and a brief enumeration of the several parts of the appliance is, therefore, all that need be given here. As shown in Plate 7, fig. 1, it consists of a camera about five feet long, in which the galvanometer is placed. This camera has three doors, and is made separate from the portion of the apparatus which contains the moving photographic plate. The two parts are connected at J, by flexible leather, the object being to enable the plane of the sensitized plate to be adjusted at right angles to the ray of light from the stationary galvanometer mirror F. Inside the camera is a focussing tube T, containing a lens L, which receives external light from the mirror H, and transmits it to the galvanometer mirrors F and M. Of these mirrors, M is movable, and is carried by the coil of the galvanometer, while F is stationary on an adjustable arm fixed to the supports of that instrument, its function being to send a ray of light from the mirror H to the slit B, and thus to trace a datum line as the photographic plate travels upwards. The temperature is recorded by the variations in the position of the spot of light derived from the movable mirror M. There is a screen S to cut off light reflected from the brasswork of the galvanometer. The end of the tube T is provided with an adjustable brass slit, by means of which the width of the photographic lines traced on the plate can be varied. The mirror H is mounted on a block, which can be adjusted so that external light may be brought from either side. The focussing of the lens L may be effected from outside the camera. Plug connections are provided at the back of the instrument, and the wires *a*, *b*, connect the galvanometer with the thermo-junctions at the source of heat; cold junctions being interposed, as shown in fig. 4, Plate 7. The photographic plate is secured to its carrying slide C by means of little cams, and the carrier C is enclosed in a case K provided with a light-tight door, N. The case K is held in position by a pin, P. The connection of the photographic plate with the driving clock is shown at D. The sensitized plate moves in front of the slit B, and is lifted by a weight actuating a fine clock, constructed by the well-known horologist, Mr. DAVID GLASGOW. It may be mentioned that the galvanometer stands on three plates, which ensure steadiness by providing the well-known combination of the "hole," "slot," and "plane."

It will be seen on reference to Plate 7, fig. 2, that in the centre of the inner cylinder of iron which contains the diffusion tubes there is a central tube of metal L. Into this tube several thermo-junctions, JJ'J'', usually three in number, are inserted to various depths. Each thermo-junction is, as fig. 2 shows, suitably protected and insulated by clay tubes. These clay tubes nearly block up the inner space and prevent the free circulation of air, and the four cold junctions with which they communicate are shown in fig. 4, Plate 7. These junctions are, by the aid of a switch S, fig. 4, actuated by clockwork, placed in turn in communication with the galvanometer, and by the deflection of its mirror M (fig. 1) the temperature of any given junction at any moment can either be observed on a transparent scale, or recorded

on a photographic plate. By this means a continuous record of the temperature at three positions in the air bath may be readily obtained, but as regards each of the three positions this record is 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 experiments which are now in progress a thermostat is 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.

Now that the possibility of making accurate measurements on the diffusion of molten metals has been demonstrated, and as it has been shown that convection currents are not established, even when the temperatures at the top and the bottom of the diffusion tubes only differ by 35° C., it will be well to attempt to do without this graduated temperature altogether, trusting to the difference in densities of the solvent and the diffusing metal. It will also be necessary to set up apparatus which will automatically maintain for lengthy periods any given temperature between the ordinary temperature and 600° C.

At the end of a given period varying from six hours to seven days, the diffusion tubes were removed, cooled from below, carefully measured, and then cut into transverse numbered sections; the metallic contents of each of which were weighed and analysed. When gold is the diffusing metal, determination of its amount in the various sections of lead can be effected with remarkable precision by the ordinary method of cupellation assay, provided that check assays on samples synthetically prepared are made simultaneously, and the rigorous accuracy of such assays is so well known to the chemists who have had actual experience in the matter, that it is unnecessary to submit evidence on this point. The estimation of platinum or of rhodium in lead is a matter of greater difficulty, but details of the analysis need not be given.

If the bath is unprotected below, and heated from the top, the top will be very much hotter than the bottom, and thus the rate of diffusion would be considerably greater near the top than near the bottom of each tube. The value of the results would also be much impaired if the bath were inadequately protected on the top, for

if the upper surface of the bath is cooled, convection currents will be established. The lead, moreover, at the surface oxidises, and forms a detachable slag, and so relatively increases the percentage of gold or platinum in the upper layer of lead. It was frequently noticed that the top layer in the tubes was slightly richer than the one next below it.

In the experiments, the results of which are plotted in figs. 3 and 4 (p. 399), to which reference will subsequently be made, the temperature, as indicated by the top thermo-junction, was gradually raised to 550° , at which point it was maintained practically without variation during the greater part of the experiment, which lasted nearly seven days. The temperature, however, slowly fell during the last two days to 500° , owing to the choking up of the burners. The middle thermo-junction showed temperature 25° , and the lowest one 35° , below this; the mean temperature shown by the middle junction being given as the temperature of the experiment. It should be pointed out that these temperatures are based on measurements which assume the melting point of gold to be 1045° , and lead 325° . Recent work seems to show that 1045° may be some 15° too low.*

It may be well to offer here a few general considerations respecting the phenomena to be observed.

It is now held that liquid diffusion is the result of osmotic pressure.† A movement of the particles (molecules or atoms) of the dissolved substance takes place, and a molecular force drives them from the place where they are more closely packed and, therefore, exert greater pressure, and impels them to positions in which they are more widely distributed. This movement continues until the concentration, and, therefore, the pressure of the diffusing metal, is constant throughout the liquid. GRAHAM'S method of studying liquid diffusion consisted in filling wide-mouth phials of glass with the solutions of salts, which were allowed to diffuse outwards into water contained in capacious cylinders. This method could not well be imitated in the present experiments, as the manipulation, and the calculation of the results obtained by such a method present great difficulty. Hence the adoption in the present research of vertical tubes, as has already been described. In the earliest experiments made by me, in 1883, the little spheres of precious metal obtained from each measured section of lead were arranged on a card scale at measured distances;‡ each of the little spheres, therefore, represented the amount of gold in the section of the tube from which it had been derived, and their general appearance, when arranged as has just been described, suggested that a trustworthy method had been secured. It appeared probable that the law of diffusion of salts, framed by FICK, would also apply

* See HEYCOCK and NEVILLE, 'Trans. Chem. Soc.,' vol. 67, 1895, p. 160. ROBERTS-AUSTEN, 'Nature,' May 9, 1895, p. 40. LE CHATELIER, 'Comptes Rendus,' vol. 121, 1895, p. 323.

† NERNST, 'Zeitsch. für Physikal. Chemie,' vol. 2, 1888, p. 613.

‡ Specimens of these records were exhibited to Section B. of the British Association, at the Montreal Meeting, 1884.

to the diffusion of one metal in another. FICK'S law states that "the quantity of salt, which diffuses through a given area, is proportional to the difference between the concentrations of two areas infinitely near each other."

FOURIER'S theory of thermal conduction was applied by FICK to the phenomena of material diffusion generally. The law of diffusion is thus stated by Lord KELVIN :* The rate of augmentation of the "*quality*," per unit of time, is equal to the diffusivity multiplied into the rate of augmentation per unit of space of the rate of augmentation per unit of space of the "*quality*." In the case of diffusion of salts or metals, the "*quality*" is concentration of the matter diffused, or deviation of concentration from some mean or standard considered.

The movement in linear diffusion may therefore be expressed by the differential equation

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

In this equation, x represents the distance in the direction in which the diffusion takes place; v is the degree of concentration of the diffusing metal, and t 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. centim.) in unit time (one day) when unit difference of concentration (in grammes, per cubic centim.) is maintained between the two sides of a layer one centim. thick. The unit of diffusivity has the dimensions $[L^2T^{-1}]$; so that diffusion constants may be expressed in square centimetres per day. The constant has a definite value for each pair of metals (that is for the diffusing metal and its solvent) at a particular temperature, and the object of the experiments on diffusion is to determine this value.

In the equation, dv/dt denotes the increase in the degree of concentration which takes place at any point during unit time, dv/dx represents the difference between the degrees of concentration at the two sides of a layer of unit thickness, and d^2v/dx^2 in the equation represents the change which takes place in dv/dx as the position of the point under consideration is moved unit distance along the tube.

In Plate 8, and in the figures in the text, x is represented by abscissæ, v by ordinates, dv/dx is the tangent of the inclination of the curve to the horizontal, and d^2v/dx^2 is the change in this value occurring for unit change in x ; that is, the curvature of the diffusion curve.

It was not, however, until the experiments and calculations of the results were far advanced that evidence was obtained as to the applicability to the present method of investigation of the tables calculated by STEFAN† for the diffusion of salts. By the help of these tables the diffusion constant can be determined, in the case of the single-tube experiments, if the distribution of the dissolved diffusing metal is known.

* 'Mathematical and Physical Papers,' vol. 3, 1890, p. 428.

† STEFAN, 'Wien. Akad. Ber.,' vol. 79, 1879, p. 161.

Experimental Results.

The following tables, A, B, C, D, embody the results of four diffusion experiments, made simultaneously, two with gold and two with platinum, in straight vertical tubes. They serve to indicate the method of calculating the diffusivity of the respective metals from the data afforded by the experiments. In the case given in Table A, for example, the alloy of gold and lead was allowed to diffuse upwards into pure lead in the way already described. This comparatively rich alloy of gold and lead containing 30 per cent. of gold, occupied 2·108 centims. of the length of the tube. The tube (the whole length of which was about 16 centims.) was subsequently cut into sections, each of which was 1·054 centims. long, or half the length occupied by the rich alloy of gold. The reason for the adoption of this length was as follows:— In GRAHAM'S experiments on the diffusion of salts, which form the basis of STEFAN'S tables, the concentrated solution from which diffusion started, occupied two of the sections into which the contents of the diffusion cylinders were divided for analysis. The length of one of these sections, or half of the length of the portion of the tube occupied by the alloy from which diffusion takes place, is denoted in the calculation by the letter *h*. In Table A there are fourteen such sections, and these are numbered consecutively in column 1, while column 2 gives the weight in grammes of the lead-gold alloy obtained from each of the respective sections and of the pure gold extracted from it. Column 3 gives the percentage of gold present in each section calculated from the numbers given in column 2. In column 4 these percentages of gold have been corrected so as to give the amounts of gold in equal volumes of the "solution." It must be remembered that the density of the gold-lead alloys increases with the percentage of gold, so that the concentration of the gold, that is, the weight present in equal volumes of the alloy, is not truly represented by the percentage given in column 3. A correction of sufficient accuracy may, however, be introduced by assuming that the fluid densities of the alloys are proportional to their calculated densities, and the numbers so corrected are given in column 4.

EXTRACT of four pages from the note book, showing method of calculating the results of two gold and two platinum diffusions in lead. The experiments were begun on October 9, 1894, and occupied 6·96 days. The mean temperature was 492° C.

TABLE A.—Tube 1. Gold in Lead.

1 Number of section of diffu- sion tube.	2 Weight in grammes of metal from each section—		3 Per- centage of gold in each section.	4 Corrected for density to equal volumes.	5 Divided by 0·005719.	6 Theoretical numbers for—		7 $\frac{h}{2\sqrt{kt}}$ (by inter- polation).
	lead-gold alloy.	gold.				$\frac{h}{2\sqrt{kt}}=0\cdot11.$	$\frac{h}{2\sqrt{kt}}=0\cdot12.$	
1	2·63	0·1876	7·13	7·38	1291	1217	1322	0·117
2	3·20	0·2247	7·02	7·26	1270	1188	1286	0·118
3	3·15	0·2096	6·65	6·87	1201	1135	1217	0·118
4	3·02	0·1846	6·11	6·29	1100	1058	1120	0·117
5	3·57	0·1950	5·46	5·60	979	965	1004	0·113
6	2·52	0·1212	4·81	4·92	860	860	874	0·110
7	3·16	0·1317	4·17	4·25	743	749	742	0·119
8	2·93	0·1030	3·52	3·58	626	640	613	0·115
9	3·19	0·0903	2·83	2·87	502	538	496	0·119
10	2·67	0·0593	2·22	2·24	392	447	393	0·120
11	2·74	0·0477	1·74	1·75	306	370	308	0·120
12	2·61	0·0354	1·35	1·36	238	310	244	0·121
13	3·16	0·0308	0·97	0·97	170	269	201	0·125
14	4·37	0·0374	0·85	0·85	149	249	180	0·125
			Sum.	57·19			Mean .	0·1184

$h = 1\cdot054$ centims. when cold = $1\cdot082$ centims. at 492° C., therefore $kt = 20\cdot88$.

$t = 6\cdot96$ days, therefore $h = 3\cdot00$ sq. centims. per diem.

The tables given by STEFAN for calculating absolute diffusivities from the results of GRAHAM'S experiments with salts, give for special values of the factor $\frac{h}{2\sqrt{kt}}$ the concentrations in each section of a diffusion cylinder, on the assumption that the original *two* volumes of diffusing solution of a salt, taken by GRAHAM, contained 10,000 units of salt.

It follows from this that the sum of the numbers representing the concentration of the total number of sections will always equal 10,000. The numbers given in column 4 must therefore be divided by such a number as will make the sum of their quotients 10,000. This common divisor is found by adding up the numbers in column 4 and dividing the result by 10,000, and column 5 gives the quotients of the numbers in column 4 divided by the common divisor 0·005719.

Column 6 gives the theoretical concentration in each section in cases where the factor $\frac{h}{2\sqrt{kt}}$ has the values 0·11 and 0·12, because the actual results of this experiment (on the diffusion of gold in lead) were seen by inspection to lie between these values.

STEFAN* applied the formal analogy between diffusion-movements and wave-motions, to the calculation of GRAHAM'S results ; both motions are expressed by the differential equation already quoted, $\frac{dv}{dt} = k \frac{d^2v}{dx^2}$. STEFAN calculated his results for the case of a cylinder of infinite length. In order to apply his results to a cylinder of limited length, which is the case in these lead-gold experiments, use is made of the principle of reflection and superposition, in accordance with which the quantity of a substance that would have passed beyond the end of this limited cylinder is considered to be totally reflected, distributed by diffusion, and retained in the several sections of the tube.

The figures in column 6 have been adjusted in this manner to suit the diffusion tube, which was divided (as column 1 of Table A shows) into fourteen sections.

The final column, 7, gives for each section the value of $\frac{h}{2\sqrt{kt}}$ equivalent to the concentration actually observed, calculating by interpolation the figures which lie between those actually given in the double column 6. If the diffusion were in accordance with FICK'S law and the experiments free from error, all the numbers in column 7 should be identical. It will be seen that they do agree closely, and that the differences which occur may be attributed to experimental errors. It will be evident that the value to be attached to an experiment may be gathered from the degree of uniformity exhibited by the numbers in column 7.

* STEFAN, *loc. cit.*, and OSTWALD, 'Solutions,' p. 130.

TABLE B.—Tube 2. Gold in Lead.

1 Number of section of diffu- sion tube.	2 Weight in grammes of metal from each section—		3 Per- centage of gold in each section.	4 Corrected for density to equal volumes.	5 Divided by 0·0054785.	6 Theoretical numbers for—		7 $\frac{h}{2\sqrt{kt}}$ (by inter- polation).
	lead-gold alloy.	gold.				$\frac{h}{2\sqrt{kt}}=0\cdot13.$	$\frac{h}{2\sqrt{kt}}=0\cdot14.$	
1	2·44	0·1855	7·603	7·887	1440	1427	1530	0·1313
2	3·72	0·2768	7·442	7·717	1408	1381	1474	0·1329
3	3·64	0·2529	6·948	7·186	1312	1295	1369	0·1321
4	3·35	0·2111	6·302	6·500	1187	1176	1225	0·1322
5	3·50	0·1931	5·518	5·666	1034	1035	1056	
6	3·54	0·1688	4·769	4·879	891	882	878	
7	3·20	0·1242	3·882	3·954	722	728	706	0·1327
8	3·36	0·1050	3·125	3·170	579	585	544	0·1315
9	3·85	0·0928	2·411	2·439	445	475	407	0·1324
10	3·79	0·0691	1·823	1·839	336	352	298	0·1330
11	3·29	0·0451	1·371	1·379	252	272	217	0·1338
12	3·17	0·0349	1·101	1·107	202	218	163	0·1330
13	2·99	0·0313	1·047	1·062	194	191	136	
			Sum.	54·785			Mean .	0·1325

$h = 1\cdot194$ centims. cold = $1\cdot225$ centims. at 492° C., therefore $kt = 21\cdot37$.

$t = 6\cdot96$ days, therefore $k = 3\cdot07$ sq. centims. per diem.

TABLE C.—Tube 3. Platinum in Lead.

1 Number of section of diffu- sion tube.	2 Weight in grammes of metal from each section—		3 Per- centage of platinum in each section.	4 Corrected for density to equal volumes.	5 Divided by 0·0048654.	6 Theoretical numbers for—		7 $\frac{h}{2\sqrt{kt}}$ (by inter- polation).
	lead platinum alloy.	platinum.				$\frac{h}{2\sqrt{kt}}=0\cdot18.$	$\frac{h}{2\sqrt{kt}}=0\cdot19.$	
1	3·11	0·2805	9·020	9·744	2003	1927	2023	0·188
2	3·37	0·2845	8·442	9·076	1865	1817	1895	0·186
3	3·40	0·2527	7·434	7·925	1629	1614	1664	0·183
4	3·68	0·2265	6·155	6·492	1334	1352	1368	
5	3·67	0·1850	5·041	5·268	1083	1067	1054	
6	3·94	0·1383	3·510	3·619	744	793	760	0·194
7	3·84	0·0933	2·430	2·482	510	556	513	0·190
8	3·32	0·0530	1·596	1·618	332	368	324	0·188
9	3·98	0·0404	1·015	1·024	210	230	193	0·185
10	3·65	0·0216	0·592	0·595	122	137	108	0·185
11	3·16	0·0132	0·418	0·420	86	83	60	0·179
12	4·33	0·0169	0·390	0·391	80	57	39	
			Sum . .	48·654			Mean . .	0·186

$h = 1\cdot245$ centims. cold = $1\cdot277$ centims. at 492° , therefore $kt = 11\cdot79$.

$t = 6\cdot96$ days, therefore $k = 1\cdot69$ sq. centims. per diem.

TABLE D.—Tube 4. Platinum in Lead.

1 Number of section of diffu- sion tube.	2 Weight in grammes of metal from each section—		3 Per- centage of platinum in each section.	4 Corrected for density to equal volumes.	5 Divided by 0·0048556.	6 Theoretical numbers for—		7 $\frac{h}{2\sqrt{kt}}$ (by inter- polation).
	lead- platinum alloy.	platinum.				$\frac{h}{2\sqrt{kt}}=0\cdot18.$	$\frac{h}{2\sqrt{kt}}=0\cdot19.$	
1	3·17	0·2795	8·817	9·509	1958	1927	2023	0·183
2	3·85	0·3435	8·922	9·613	1980	1817	1895	0·201
3	3·49	0·2690	7·707	8·235	1696	1614	1664	0·196
4	4·47	0·2761	6·177	6·517	1344	1352	1368	0·175
5	2·62	0·1280	4·885	5·093	1049	1067	1054	0·194
6	4·12	0·1471	3·571	3·682	758	793	760	0·191
7	3·62	0·0891	2·462	2·514	517	556	513	0·189
8	3·40	0·0491	1·444	1·462	301	368	324	0·195
9	3·73	0·0342	·917	0·925	190	230	193	0·191
10	3·57	0·0169	·473	0·475	102	137	108	0·191
11	3·26	0·0099	·304	0·305	62	83	60	0·189
12	3·28	0·0074	·226	0·226	46	57	39	0·186
			Sum	48·556			Mean	0·190

$h = 1\cdot27$ centims. cold = $1\cdot303$ centims. at 492° , therefore $kt = 11\cdot76$.

$t = 6\cdot96$ days, therefore $k = 1\cdot69$ sq. centims. per diem.

In figs. 3, 4, the diffusions which are given in Tables B and C are plotted in thick lines, with distance and concentration as coordinates. The curves in dotted lines give theoretical distributions for two values of $\frac{h}{2\sqrt{kt}}$, which nearly agree with the experimental results, and between which the true value of $\frac{h}{2\sqrt{kt}}$ appears to lie.

In these curves the horizontal length of the figure, which represents the height of the diffusion-tube, is divided by the sectional lines into as many equal parts as there are sections of the tube. The concentration in each section was marked by a horizontal pencil line, and the continuous curve shown in fig. 2, and in figs. 3, 4, was drawn through these lines in such a way that the area included in each section still represented the average concentration in it. This method was adopted to avoid the slight error which would have been introduced if the average concentration had been plotted at the mid-point of each section. This mode of plotting, fig. 2, in which the area $a = a'$, $b = b'$, and $c = c'$, renders it impossible to specify the *points* through which the curve has been drawn, but it may be remembered that the average position of the curved line in each section represents the result of one analysis.

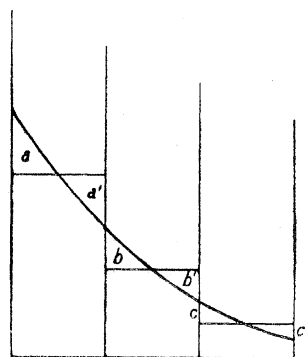
The dotted lines are plotted from figures calculated from STEFAN'S tables for two

values of the factor $\frac{h}{2\sqrt{kt}}$, between which the experimental values are found to fall in most of the sections. They are plotted in the same manner as the thick continuous lines, and the value of k corresponding to each value of $\frac{h}{2\sqrt{kt}}$ is calculated and placed opposite the dotted line to which it belongs.

In fig. 4 it was necessary to plot these dotted lines for more widely divergent values of k than was the case in fig. 3.

Fig. 3, representing the diffusion of gold in lead, is seen to agree very well with theory, while fig. 4, representing the diffusion of platinum in lead, shows considerable irregularities, which are probably due to errors in the platinum assay. The mean of the figures in column 7 is taken as the correct value for $\frac{h}{2\sqrt{kt}}$, and from this, knowing the values of h and t , that of k may be obtained.

Fig. 2.



It will be remembered that the length of each section (Table A) was 1.054 centims., which is equal to half the length of the part of the tube occupied by the rich gold alloy. As, however, this measurement was made on cold solidified metal, it must be corrected to the temperature at which the experiment was actually conducted. This correction is based on experimental determinations of the linear expansion by heat of the molten metals contained in the iron tubes. The corrected value of h , 1.082 centims., and the value of t , 6.96 days, are substituted in the equation $\frac{h}{2\sqrt{kt}} = 0.1184$, giving 3.00 as the value of k , the units being the *centimetre* and *day*. The experiments, the results of which are embodied in Tables B, C, and D, were conducted simultaneously with those in Table A, which have just been described. All the experiments in this series were, therefore, subjected to exactly the same conditions as regards time and temperature.

Experiments A and B were diffusions of gold, and C and D of platinum, in lead. The results of these gave k for gold in lead as 3.00 and 3.07, and for platinum in lead as 1.69 and 1.69 respectively, the temperature in each case being 492° C. It may

Fig. 3 (plotted from Table B).

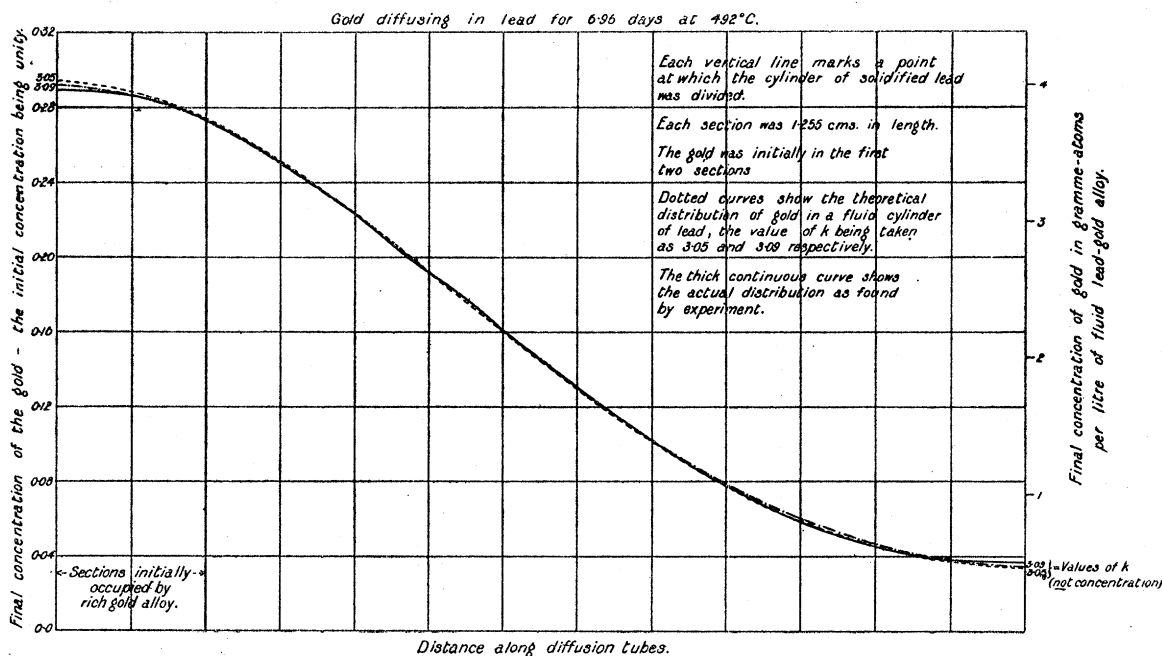
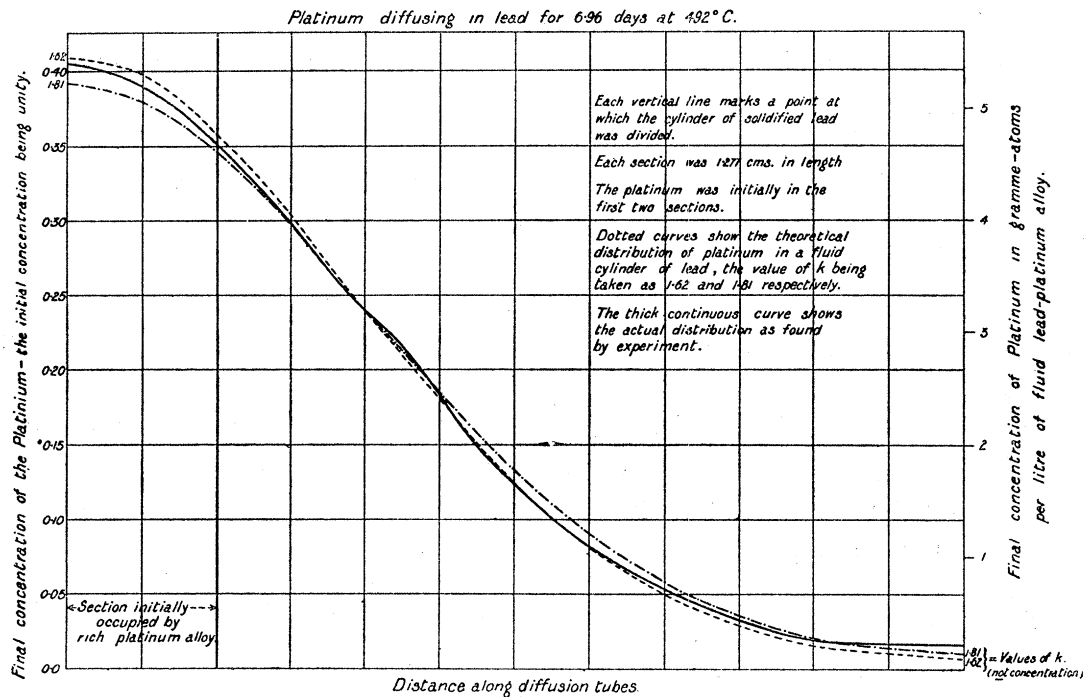


Fig. 4 (plotted from Table C).



be thought that this is an unnecessarily high temperature, but as some experiments are in progress in which lead alloys rich in gold are used, it was considered advisable to work at a temperature at which the entire series of alloys would melt.

Table E contains the results of the more recent experiments which have been made; k is given in sq. centims. per diem, and also in sq. centims. per second. The result for the diffusion of lead in tin is, however, less trustworthy than the other data.

TABLE E.

Diffusing metal.	Solvent.	Temperature.	k in square centims.	
			Per diem.	Per second.
Gold	Lead	492	3.00	3.47×10^{-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	3.185	3.69 "
Rhodium	"	550	3.035	3.51 "

These results are presented graphically in Plate 8, which represents the theoretical distribution of the several metals after diffusion has proceeded for seven days, the temperature being close to 500° C.

The horizontal ordinate represents distance in the direction in which diffusion takes place, the actual length of the plate being the same as that of the tube. The vertical ordinate represents concentration. It will be evident that if the plate be turned so as to make the horizontal line vertical, the actual distance the metals diffused upwards will at once be apparent. Each of the diffusing metals occupied at the beginning of the experiment the length a , b of the tube, and they all had the same initial concentration.

If the time had been infinitely extended, the final condition of each experiment would be represented by the horizontal line d , e , and the relative diffusivity of each pair of metals is shown by the degree of approximation which the distribution in that experiment has made to the final condition of things.

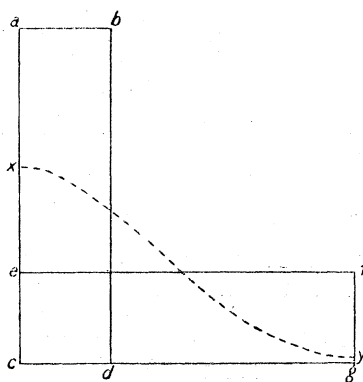
What this final condition would be may be made clear by the aid of fig. 5. The length c , d represents that part of the tube which is occupied by the gold alloy from which diffusion takes place, the alloy having an original concentration denoted by $c a$, so that the area $a b d c$, represents the whole quantity of gold in the experiment; all the gold being initially to the left of the line d , b . The final state of complete diffusion is represented by the area $c e f g$, which is the same as $a b d c$, since the quantity of gold remains unaltered.

In the same manner the area $c x y g$, would represent the distribution of gold at one particular stage of the diffusion.

The greater the diffusive power of the metal represented by the area $c x y g$, the sooner will it become identified with the area $c e f g$, and consequently in experiments which have lasted for equal times, the flatter the line x, y , the greater is the diffusivity of the metal it represents.

The diffusion of chloride of sodium in water at 18° C. has been plotted in Plate 8 (as a dotted line) for comparison. It will be seen that (at 18° C.) common salt is much less diffusive in water than the metals as yet examined are at 500° in the solvents lead or bismuth.

Fig. 5.



The conditions under which the experiments on the diffusion of metals were conducted differed so much, that it would have been meaningless to have plotted the actual distributions in a single plate. The time and temperature were different in each set of experiments, and the value of h was also variable. Plate 8 accordingly represents the theoretical distribution calculated from the experimental value of k corrected to 500° , and for the assumed time, 7 days, and the value of h , shown in this figure, 1.27 centims.; the tube being divided into 14 sections. The small extent to which these theoretical distributions differ from those actually measured, may be seen in figs. 3 and 4, and in tables A, B, C, and D. The curves were drawn, for convenience, by plotting the mean concentration of each section at its mid point. The error so introduced is almost invisible on the curves and does not affect their *relative* position. No scale of the initial concentration is attached because the distribution of the diffusing metal is but slightly affected by small differences in concentration.

The concentration of the diffusing metal, and as affecting this the duration of the experiment are, nevertheless, of much importance. The more rapid diffusivity in the alloys, poor in precious metal, is extremely marked. As this was especially the case in experiments which only lasted for a short period, where many of the segments contained very dilute solutions, it may be in part an effect requiring careful study, since it points to a possible simplification of the gold molecule when the osmotic

pressure is small. This effect appears to be connected with the dilution of the gold below a concentration of about 0.005 gramme-atom per litre of lead, corresponding, at 450°, to an osmotic pressure of about one-third of an atmosphere.

The results given in Table E show that the diffusion of metals is not increased nearly so rapidly by a rise in temperature of 50° as the ordinary aqueous diffusion of salts is. This is probably due to the fact that the resistance presented by metals to diffusing metallic molecules is not much reduced by heat, and it may be that the molecules of the diffusing substance are not so liable to disruption by a rise in temperature.

It may be well to wait until more results have been obtained before attempting to deduce evidence as to the molecular condition of the metals composing these alloys, though, in this respect, metallic diffusion presents several advantages over the diffusion of salt solutions, the latter being very limited as regards the choice of a solvent and range of temperature at which experiments could be made, and, moreover, if a salt is dissociated into its ions its diffusion rates will be modified. The fact that when water is used, both the salt and the solvent are chemical compounds, renders their diffusivities less directly significant than those of metals, because, with the exception of gaseous elements, molten metals present the simplest possible case which can occur, as they represent the diffusion of one element into another.

A few general deductions may, however, be drawn.

It will be seen that gold diffuses more rapidly in bismuth and in tin than it does in the heavier metal lead. It has also been observed (though Table E does not embody the results) that platinum diffuses faster in bismuth than in lead. The diffusion of platinum and of gold is increased in about equal ratio by the substitution of bismuth for lead as a solvent. On the other hand, platinum diffuses much more slowly in lead than gold does, although their atomic weights and their densities do not greatly differ. Rhodium, another metal of the platinum group, diffuses in lead nearly as fast as gold does, but if allowance be made for the smaller atomic weight, it will be found to agree fairly well with platinum. This would point to the conclusion that the platinum metals are molecularly more complex than either gold or silver, as a complex molecule exerts less osmotic pressure and diffuses more slowly than a comparatively simple one.

The early workers on diffusion of salts used water as a solvent; KAWALKI,* however, has recently given tables of diffusions of salts in both water and alcohol. He found that there is a fairly constant ratio between the diffusivities of salts in the two solvents. Experiments seem to show that this is also true of two metallic solvents such as lead and bismuth.

Calculations of the Older Results.—The results obtained from the earlier experiments (which were conducted in U-tubes) have, as already stated, been omitted, because the great difference of temperature between the top and bottom of the tubes made

* 'Wied. Ann,' vol. 52, 1894, p. 300.

the meaning of the final distribution rather uncertain. The results of these and some of the very early experiments have been dealt with by the aid of tables of theoretical distributions, similar to those of STEFAN, but calculated for the case of an infinite tube having constant concentration at one end, which nearly corresponded to the actual conditions under which my earlier experiments were conducted. The values given by these experiments agree very fairly with those obtained later, but the inequalities of temperature made the value of k vary from point to point of the tube, so that it was impossible to determine it with any degree of precision.

Diffusions of Amalgams in Mercury.—A number of experiments were made on the diffusion, at ordinary temperatures, of gold and other metals in mercury, which will be included in a subsequent communication. I may, however, mention, for the sake of comparison, that the diffusivity of gold in mercury at 11° C. is $0\cdot72$ sq. centim. per day, the diffusivity of gold in lead being $3\cdot0$ sq. centims. per day at 500° . As already stated, Dr. GUTHRIE* 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 paper, give the values of k , in square centimetres per day, as follows:—

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

* *Loc. cit.*

PART II.—DIFFUSION OF SOLID METALS.

GOLD, DIFFUSING INTO SOLID LEAD.

The experiments described in the first part of this paper naturally suggested the enquiry whether gold would still permeate lead if the temperature were maintained at a point far below the melting point of lead. Would diffusion take place through solid lead at the ordinary temperature, or must a certain amount of viscosity be given to it by the application of a moderate heat? These were questions which demanded attention.

Historical.

The history of the diffusion of solids is full of interest, and it may be convenient, as far as possible, to group the facts which are known, rather than to deal with them in strict chronological order.

“*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 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.

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 8th century, as well as by many of the early metallurgists; SAVOT,* for instance, pointed out in the early part of the 17th 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 inter-molecular 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

* ‘Discours sur les Médailles antiques,’ 1627, p. 76.

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* 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 æriform, 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† communicated a paper to the Académie des Sciences, in which he showed that when iron is heated in carbon there is a mutual interpenetration

Fig. 6.



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, has received attention from many experimenters, of whose work brief mention will only be given, as the subject of this part of the paper 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,‡ 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, I may point out, removed by an experiment of my own,§ in 1889, which showed that pure iron may be carburized 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. I am indebted to my friend, M. OSMOND, for a photograph (from which fig. 6 is prepared) of a section, magnified 100 diameters, through a piece of electro-iron, which had been heated to 1500° and carburized from the upper end by contact with the diamond form of carbon, and this section clearly shows the gradual penetration of the iron by carbon. The white grains at the base are unchanged iron. The beautiful work of OSMOND on the transforma-

* 'Ann. de Chim. et de Phys.,' vol. 17, 1846, p. 221.

† 'Comptes Rendus,' vol. 93, 1881, p. 1074; vol. 94, 1882, p. 26.

‡ 'Bull. de l'Acad. Roy. de Belgique,' vol. 10, 1885, p. 204.

§ 'Nature,' vol. 41, 1889, p. 14.

tions of iron, and of iron and carbon, affords, moreover, a striking proof of the molecular mobility of solid iron at a temperature which is at least 600° below its melting point.

The history of the formation of alloys by cementation will be traced subsequently.

The Penetration of Solid Metals by Gases.—This subject was, as is well known, investigated by GRAHAM, “the leading atomist of his generation,” but before his attention was specially directed to it, a mass of experimental evidence led him in 1863 to express views of singular interest in the beautiful paper* which embodied his “speculative ideas respecting the constitution of matter.” In this paper he pointed out that in solids, some of the molecules may still be in the liquid or even the gaseous condition, and his words are very definite. He says, “the three conditions [solid, liquid, and gaseous] probably always co-exist in every liquid or solid substance, but one predominates over the others. . . . Liquefaction or solidification may not, therefore, involve the suppression of either the atomic or the molecular movement, but only the restriction of its range.” He subsequently, in 1866,† gave singular point to these speculations by his discovery of the penetration of solid metals by gases.

After GRAHAM’S death, evidence as to the molecular mobility of metals came slowly. E. WIEDEMANN‡ showed, in 1878, that solid metals were not necessarily inert, as changes which involve atomic movement take place in bismuth-lead alloys, and the clear evidence thus afforded of allotropic change in the solid, recently formed the subject of some experiments of my own.§

Confirmation of the accuracy of GRAHAM’S views as to the co-existence of liquid and gaseous molecules in a solid, was afforded twenty years later by Professor W. SPRING.|| In 1886 his admirable investigation on the solidification of alloys of lead and tin, afforded him experimental evidence that in these alloys active molecular movement is continued after the alloys have become solid. He says, and it is well to quote his interesting words, “on serait porté à penser qu’entre deux molécules de deux corps solides il y a un va-et-vient perpétuel d’atomes,” and he adds, “if the two molecules are of the same kind, chemical equilibrium will not be disturbed, but if they are different this movement will be revealed by the formation of new substances.”

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

* ‘Phil. Mag.,’ February, 1864; ‘Collected Papers,’ p. 299.

† ‘Phil. Trans. Roy. Soc.,’ 1866, pp. 399–439.

‡ ‘WIED., Ann.,’ 3, 1878, p. 237.

§ Second Report Alloys Research Committee, ‘Proc. Inst. Mech. Engineers,’ 1893, p. 127.

|| ‘Bull. de l’Acad. Royale de Belgique,’ vol. 11, 1886, p. 355.

STODART,* 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† 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‡ made his remarkable experiments on the formation of alloys by strongly compressing their constituent metals at the ordinary temperature, while in 1885, O. LEHMANN§ suggested, and in 1888 HALLOCK|| 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 I have repeatedly verified the accuracy of his experiment, that if the freshly-fractured surfaces of a steel rod, 9·5 millims. 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 is highly carburized and the diffusion of a carbide of iron probably plays 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¶ 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 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

* 'Quarterly Journal of Science,' vol. 9, 1820, p. 319.

† 'Revue Universelle des Mines,' vol. 1, 1877, p. 411.

‡ 'Ber. der Deutsch. Chem. Gesell.,' 15, 1882, p. 595.

§ 'Wied. Anp.,' 24, 1885, p. 1.

|| Communicated to Phil. Soc. of Washington, Feb. 18, 1888; 'Zeitschr. Phys. Chem.,' 2, 1888, p. 6, or 'Chem. News,' vol. 63, 1891, p. 17.

¶ 'Bull. de l'Acad. Royale de Belgique,' vol. 28, 1894, p. 23.

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.

I observed in 1887 that an electro-deposit of iron on a clean copper plate will adhere so firmly to it that when they are severed by force a copper film is actually stripped from the copper plate and remains on the iron, thus affording clear evidence of the interpenetration of metals at the ordinary temperature. I found that this interpenetration of copper and iron will take place through films of electro-deposited nickel.* MYLIUS and FROMM have shown that metals interpenetrate and form alloys when they are precipitated by electrolysis from their aqueous solutions.†

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, and it will be well before describing the new experiments on diffusion in solid metals to briefly recall the facts which are already known. It is not necessary to go further back for definite views on the subject than to the time of BOYLE,‡ 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§ 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. DEMARÇAY|| has proved that *in vacuo* metals evaporate sensibly at lower temperatures than they do at the ordinary atmospheric pressure, and he suggests that even metals of the platinum group will be found to be volatile at comparatively low temperatures.

Thus he finds that cadmium volatilizes at 160°, zinc at 184°, and lead and tin at 360°, and subsequently SPRING¶ (1894) demonstrated that zinc is volatile at atmospheric pressure at about 300°, cadmium at about 400°, while even copper is slightly volatile at the latter temperature.

MOISSAN** has stated quite recently that the vapour tension of solid silicon enables it to unite with iron and chromium by true “cementation” at a temperature of 1200°, which is much below the fusing point of these metals.

It must be borne in mind that the interesting facts recorded by the various experimenters whose names I have cited hardly come within the prevailing conditions in

* ‘Journ. Iron and Steel Inst.,’ Part I., 1887, p. 73.

† ‘Ber. der D. Chem. Gesell.,’ vol. 27, 1894, p. 630.

‡ ‘Collected Works.’ Shaw’s edition, 1738, vol. 1, p. 400.

§ ‘Ann. de Chim. et de Phys.,’ vol. 25, 1872, p. 121.

|| ‘Comptes Rendus,’ vol. 95, 1882, p. 183.

¶ *Loc. cit.*, 1894, p. 42.

** ‘Comptes Rendus,’ vol. 121, 1895, p. 621.

the ordinary diffusion of liquids, in which the diffusing substance is usually in the presence of a large excess of the solvent which is supposed to exert but little chemical action on it. This condition has been fully maintained in the experiments on the diffusion of liquid metals which are described in the first part of the present paper. It must also be remembered that VAN'T HOFF* 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. I trust that the following experiments will 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 following experiments constitute, so far as I am 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 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.

Diffusion of Gold in Solid Lead.

The attempt was first made to ascertain whether diffusion of gold in solid lead could be measured at a temperature of 250°, that is 75° below the melting point of lead. With this object in view, thin plates of gold were fused on to the end of cylindrical rods of lead, 14 millims. in diameter and 7 centims. long. This could readily be effected by the point of a blow-pipe flame, and, when the cylinder of lead was kept cool by immersion in water to within a few millimetres of its end, the gold rapidly alloyed with the metal, but, as many analyses showed, did not penetrate the cylinder of lead more than a millimetre. Such cylinders were maintained for thirty-one days in a little iron chamber lined with asbestos, the temperature of which only varied by a degree or two from 250° C. The cylinders were then measured and

* 'Zeitschr. Phys. Chem.,' vol. 5, 1890, p. 322.

cut up into sections, and the amount of precious metal in the respective sections was determined by analysis. It should be observed that gold and lead are singularly well adapted for such an investigation, as the amount of precious metal diffusing can, by the aid of a delicate balance, be determined with wonderful precision. The balance used was a short-beam one, with a pointer at each end of the beam, moving over a graduated ivory scale, the divisions of which were read by means of fixed lenses. This balance was specially designed for the verification of the weights used in gold assaying at the Mint. Its maximum load is 0.5 gramme, and it will readily indicate the five hundred thousandth part of a gramme.

Gold in Lead at 251°.

The results of two experiments are shown in the following tables.

The total length of the cylinder was 6.5 centims., in the case of Experiment I, and 7.0 centims. in No. II; fragments of gold were fused on their lower ends. Time, thirty-one days.

Number of section (counting from base).	Weight of alloy in grammes.	Weight of gold in grammes.	Gold per cent.	Diffusivity in sq. centims. per diem.
I. 1	26.9	0.0824	0.3064	0.023
2	22.2	0.0053	0.0239	
3	19.6	0.0015	0.0076	
4	22.3	0.00013	0.0006	
5	24.6	0.00002	0.0001	
II. 1	2.83	0.1803	0.3700	0.03
2	2.55	0.0020	0.0784	
3	3.12	0.0013	0.0417	
4	2.84	0.0006	0.0211	
5	2.99	0.00026	0.0087	
6	5.92	0.00013	0.0022	
7	6.03	0.00001	0.0002	
8	4.40			

In calculating the diffusivity in this and in the following experiments, the initial concentration of the solid lead-gold alloy from which diffusion starts was deduced from the general trend of the concentration curve as plotted from the above figures. The first section in each case, which of course contained pieces of partially alloyed gold, was neglected.

Gold in Lead at 200°.

The next experiments were made at 200° and only lasted ten days. The results of two of these are given below. In No. I the cylinder of lead was 2.5 centims. long, and had a plate of gold fused on to its end. In No. II the cylinder was 1.0 centim. long, and the plate of gold was merely held against the carefully surfaced end by means of a binding screw.

Number of section (counting from base).	Weight of alloy in grammes.	Weight of gold in grammes.	Gold per cent.	Diffusivity in sq. centims. per diem.
I. 1	1.50	0.2147	14.3	
2	1.05	lost		
3	2.00	0.00055	0.0275	0.007
4	2.14	0.000185	0.0086	
5	2.18	0.000022	0.0010	
6	3.95	trace		
7	4.60	none		
II. 1	0.39	0.00082	0.210	0.008
2	0.49	0.000140	0.029	
3	0.82	0.000187	0.023	
4	2.12	0.000220	0.010	
5	2.50	0.000040	0.002	

There are many other results of similar experiments at 200°, which closely agree with those given. There is, however, one point that must not be lost sight of. The lead cylinder was solid, but the experiments just described were conducted at a higher temperature than the melting-point of the *eutectic* alloy of gold and lead, which melts at nearly 200°. It may be that directly gold diffuses into lead it forms an alloy which is fluid at the temperature of the experiment and, therefore, though the lead itself is solid, it may, nevertheless, contain the gold in the form of a fluid alloy which diffused as such. Great care was consequently taken to ascertain whether gold would still diffuse in solid lead at a temperature well below the melting-point of the eutectic alloy (200°), and for this purpose the temperature chosen was 165°.

Gold in Lead at 165°.

The length of the cylinder in Experiment 1 was 0.64 centim., and it was maintained at this temperature for thirty days. The length of the cylinder in Experiment 2 was 0.60 centim., and it was heated for twenty-nine days. In each case diffusion started from a 5 per cent. alloy of gold and lead, pressed against the end of the lead cylinder,* and there was no need, therefore, to reject the first section of the cylinder.

* This precaution was necessary, as the diffusion must be very slow, and it was important to avoid

Number of section (counting from base).	Weight of alloy in grammes.	Weight of gold in grammes.	Gold per cent.	Diffusivity in sq. centims. per diem.
I. 1	0.64	0.00025	0.039	0.005
2	2.33	0.00069	0.030	
3	2.02	0.00030	0.015	
II. 1	0.80	0.00031	0.039	0.004
2	2.06	0.00060	0.029	
3	1.40	0.00027	0.019	

Gold in Lead at 100°.

In the following, and concluding experiment of the series, the lead cylinders, 0.45 centim., were maintained in a water oven at a temperature of 100° for forty-one days. Each cylinder had a plate of very pure gold pressed against its surfaced end.

Number of section (counting from base).	Weight of alloy in grammes.	Weight of gold in grammes.	Gold per cent.	Diffusivity in sq. centims. per diem.
I. 1	0.22	0.00013	0.059	0.00002
2	1.19	0.00006	0.005*	
3	1.98			
II. 1	0.22	0.00034	0.155	0.00002
2	1.52	0.00010	0.007	
3	1.43			

It is remarkable that gold placed at the bottom of a cylinder of *solid* lead, 7 centims. long, should, at 250°, appear in notable quantity at the top of it in less than a month. The diffusivity of gold in *solid* lead is, however, slow when compared with diffusion in the *fluid* metal. The diffusivity of gold in lead at 500° was shown in the first part of this paper to be 3.0. In *solid* lead, on the other hand, the diffusivity at 250° is 0.03, or $\frac{1}{100}$ th of the diffusivity at 500°. It is also clear that gold will diffuse into solid lead at the very moderate temperature of 100°, which is 225° below its melting point, a fact which must be considered to be remarkable, and one the existence of which has hitherto been unsuspected. The diffusivity is, however, only $\frac{1}{100,000}$ th of that which occurs in fluid lead.

any complication which might arise if the cylinder were heated by fusing gold on to the lead. At the conclusion of the experiment the gold alloy was simply detached by breaking it off the lead cylinder.

* It may be thought that 0.005 per cent. of gold is rather a small quantity to measure with accuracy, but it represents no less than $1\frac{1}{2}$ oz. of gold per ton of lead, an amount of precious metal far in excess of that which assayers are accustomed to deal with in the valuation of auriferous commercial lead.

Welding of Gold and Lead, and Diffusion of Gold in Lead at the Ordinary Temperature.

The fact that two clean surfaces of lead will weld together at the ordinary temperature is well known. It may be well, however, to state in connection with the experiments of DEMARÇAY (see p. 408) on the volatilization of metals *in vacuo* at comparatively low temperatures that if the ends of small bars of gold or silver be surfaced, pressed against lead, and maintained for four days *in vacuo* at a temperature of only 40°, the interpenetration of the two metals will be so complete that their separation can only be effected by the application of a load of 70 lbs. per square inch of the sectional area of the bars, or no less than $\frac{1}{3}$ of the breaking strain of lead.

It remains to be seen whether diffusion can be measured in solid lead at the ordinary temperature, and, with this object in view, cylinders have been prepared and set aside for future examination.

In searching for evidence of diffusion in solid metals at the ordinary temperature, it will be well to examine certain alloys used in art metal-work by the Japanese, who often employ an alloy of copper containing a small proportion of gold (called *Shakudo*), which is soldered or welded in alternate layers with pure copper. The gold in the copper enables it to assume a beautiful purple patina when it is treated with suitable pickling solutions, which leave the pure copper of a red colour. In this way very singular banded effects are produced. Many of the specimens are centuries old, and I have attempted, by grinding away the existing patina and re-pickling the surface, to ascertain whether the widening of the coloured bands would show that, in the course of time, gold had diffused from the *Shakudo* layers and had passed into the copper. I believe that there is evidence that it does do so, but the enquiry is full of difficulty, and needs training in micrography, of which my friend, M. OSMOND, is a master. We propose to study this part of the subject together, and I only allude to it here because, if diffusion occurs in copper, silver, and gold at the ordinary temperature, its results should be revealed in the products of this ancient oriental art.

Diffusion of Gold in Solid Silver.

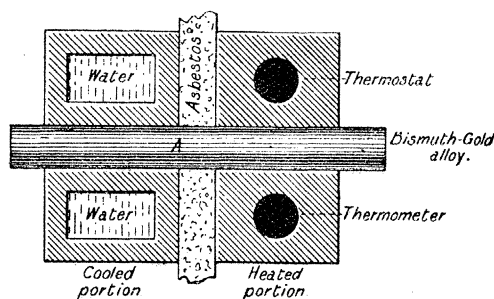
A short cylinder of silver, containing 20 per cent. of gold, was pressed against the carefully-surfaced end of a cylinder of pure silver, 1 centim. in diameter and 2.5 centims. long. These cylinders were kept in an annealing furnace for ten days, at a temperature which never exceeded 800°, and was, therefore, 160° below the melting point of silver (960°). The lowest melting point of the gold-silver series of alloys is 850°. The cylinder was then cut into sections in the usual way, and the amount of diffused gold determined by analysis. As the temperature was intermittent the true diffusivity cannot be taken, but I am satisfied that the diffusivity of solid gold in solid silver at 800° is of the same order as that of gold in lead at 200°. It would

appear, therefore, that the melting points of the metals have a dominating influence on the resistance offered to diffusion.

Diffusion from a Hot to a Cold Portion of Solid Metal.

It is well known that, in the liquid diffusion of salt solutions, osmotic pressure will drive molecules from the hot to the cold portions. Professor THORPE suggested that an experiment of this nature should be tried with solid alloys. The principle of "reflection," which would, of course, be involved in such an experiment, has already been alluded to under the liquid diffusion of metals (see Part I., p. 394). The difficulty is to obtain a solid alloy of uniform composition, but, after many experiments, a rod of bismuth was obtained, in which it was believed that 3·75 per cent. of gold was uniformly distributed. This was arranged, as shown in fig. 7, which represents, in sectional plan, a double block of brass, enabling half the rod to be heated

Fig. 7.



to 170°, which is below the melting point of the bismuth-gold *eutectic* alloy, while the other half can be cooled by a stream of water. The heating was maintained for six days. The result proved that there was a distinct concentration of 0·1 per cent. gold at the point A, where the bar entered the cooled chamber. Similar results have been obtained with gold-lead alloys, and, if the bar be maintained at 240°, which is above the melting point of the *eutectic* alloy, the effect is very marked. I offer these statements with some reserve, as they require confirmation.

The data now published form but a small portion of the investigation which has been long in progress. The manipulation it involved was singularly difficult and tedious, and it would probably have been far less advanced than it is, if I had not had the advantage of the aid of one of my former students at the Royal School of Mines, Mr. ALFRED STANSFIELD, B.Sc. He made the calculations which were necessary to extend STEFAN'S tables to the range covered by the present experiments, and has shown untiring interest in conducting that part of the series which has been undertaken during the past two years.

The founder of this lectureship directed in 1768 that the subject be selected from "Such part of Natural History or Experimental Philosophy as the Council of the Royal Society shall be pleased to appoint," and in the century which followed the date of Mr. BAKER'S bequest, these branches of knowledge seemed to diverge widely. The investigation and measurement of molecular movement has, however, gradually joined them in the closer union which GRAHAM did so much to effect. His work in experimental physics, more than that of any other investigator, taught the physiologist that tracing the relations of the phenomena of life as revealed in diffusion, transpiration, and osmosis will afford Natural History its most precious records.

The evidence gathered by the metallurgist of active atomic movement in fluid and solid metals may sustain the hope of the physiologist that he will ultimately be able to measure the atomic movements upon which vitality and thought depend.

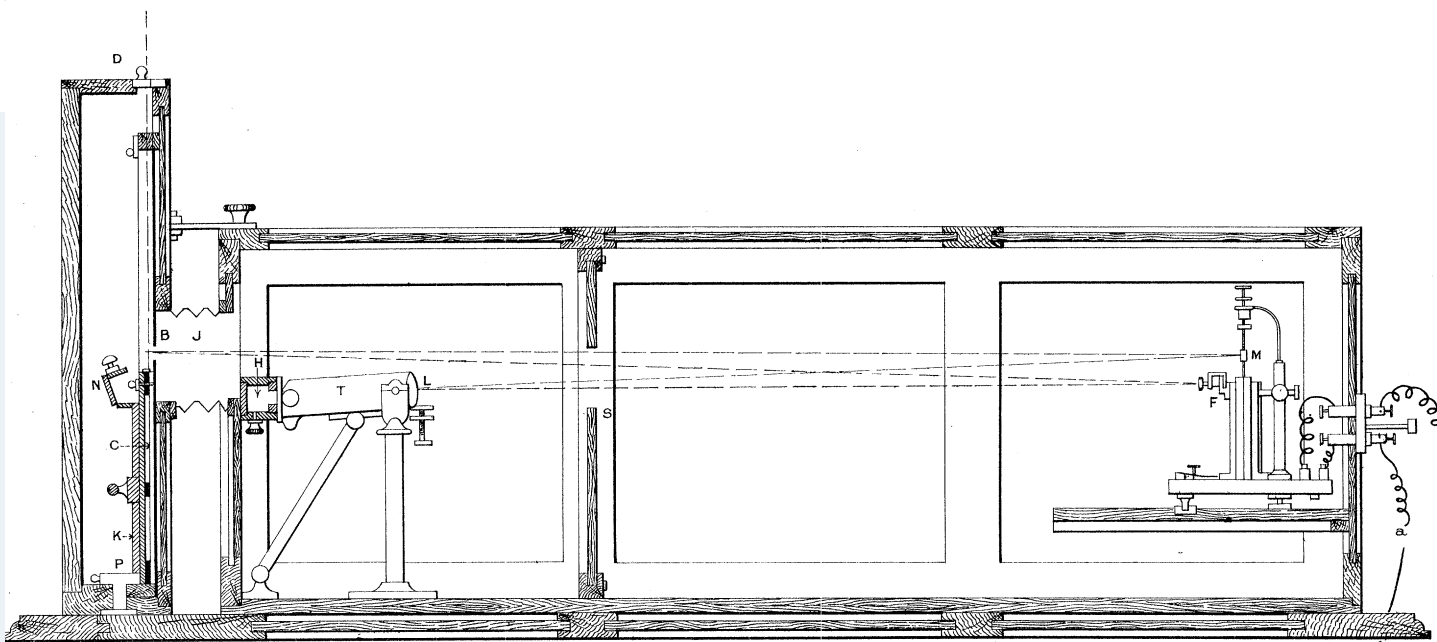
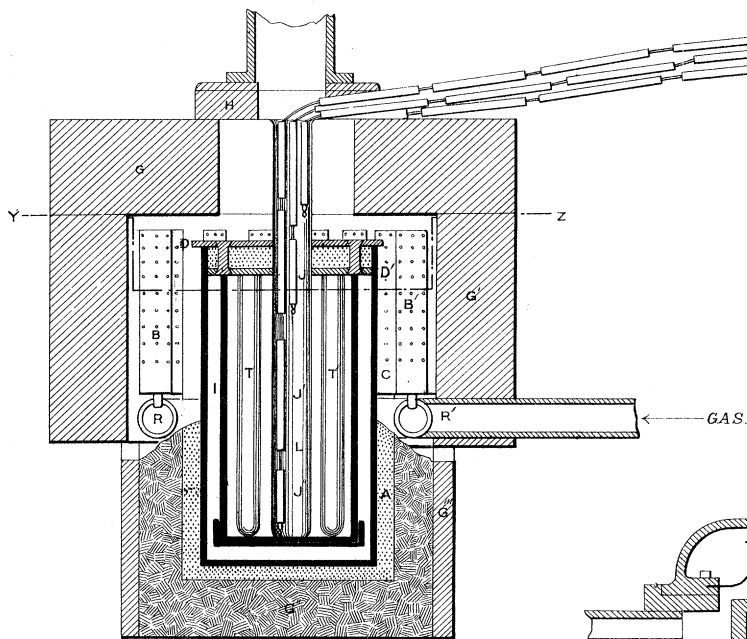
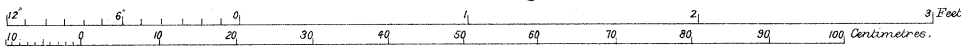
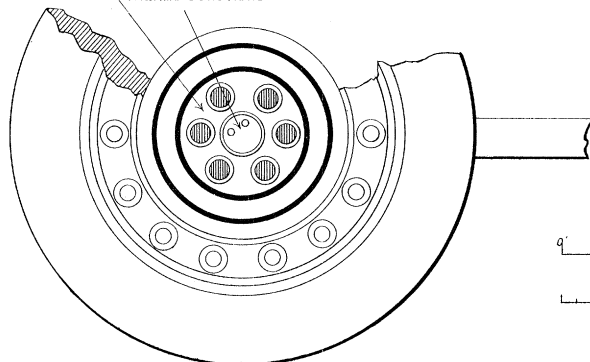


Fig. 1.

Scale for Fig. 1.



SIX DIFFUSION TUBES.
THERMO-JUNCTIONS.



SECTION ON LINE Y. Z.

Fig. 2.

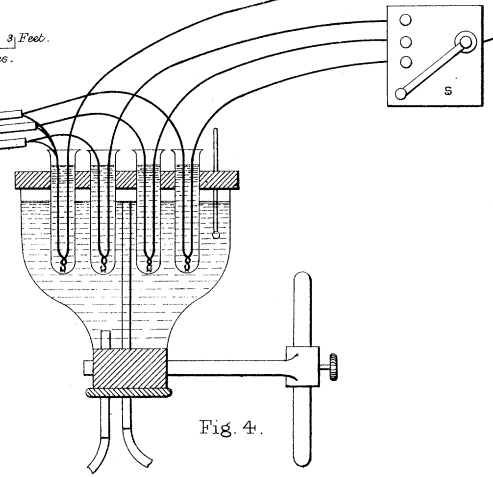


Fig. 4.

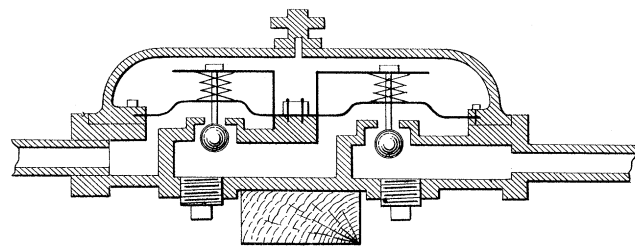
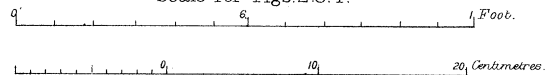


Fig. 3.

Scale for Figs. 2.3.4.



The results of Diffusion for seven days of fluid metals at 500°,
and of Chloride of Sodium in Water at 18°.

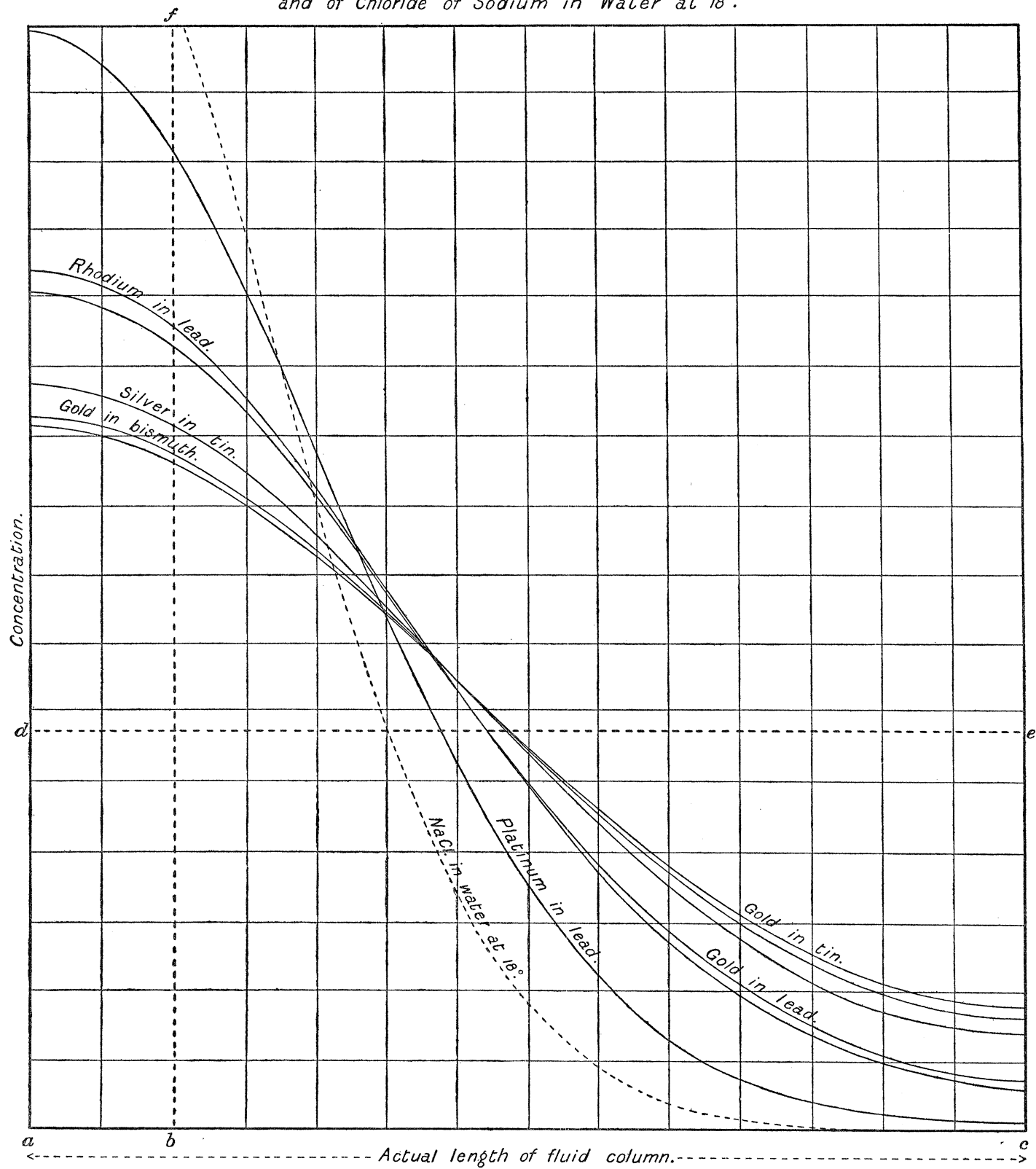


Fig. 6.

