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*February 20, 1896.*

Sir JOSEPH LISTER, Bart., President, in the Chair.

A List of the Presents received was laid on the table, and thanks ordered for them.

The Bakerian Lecture was delivered as follows:—

BAKERIAN LECTURE.—“On the Diffusion of Metals.” By W. C. ROBERTS-AUSTEN, C.B., F.R.S., Professor of Metallurgy, Royal College of Science. Received February 20, 1896.

(Abstract.)

PART I.—*Diffusion of Molten Metals.*

In the first part of the paper the author alludes to some earlier experiments he made in 1883 on the diffusion of gold, silver, and platinum in molten lead. He points out that although the action of osmotic pressure in lowering the freezing point of metals has been carefully examined, very little attention has been devoted to the measurement, or even to the consideration, of the molecular movements which enable two or more metals to form a truly homogeneous fluid mass. The absence of direct experiments on the diffusion of molten metals is probably explained by the want of a sufficiently accurate method. Ostwald had stated, moreover, with reference to the diffusion of salts, that “to make accurate experiments in diffusion is one of the most difficult problems in practical physics,” and

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the difficulties are obviously increased when molten metals diffusing into each other take the place of salts diffusing into water.

The continuation of the research was mainly due to the interest Lord Kelvin had always taken in these experiments. The want of a ready method for the measurement of comparatively high temperatures, which led to the abandonment of the earlier work, was overcome when the author arranged his 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. Thermo-junctions were placed in three or more positions in either a bath of fluid metal or an oven carefully kept hotter at the top than at the bottom. In the bath or oven, tubes filled with lead were placed, and in this lead, gold, or a rich alloy of gold, or of the metal under examination, was allowed to diffuse upwards against gravity. 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 grams diffusing through unit area (1 sq. cm.) in unit time (one day) when unit difference of concentration (in grams per c.c.) is maintained between the two sides of a layer 1 cm. thick. The author's 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, and the values of the diffusivity of various metals in lead are then given.

The values for  $k$ , the diffusivity, given in sq. cm. per day, are as follows :—

	<i>k.</i>
Gold in lead .....	3·19 at 500°.
„ bismuth ....	4·52 „
„ tin .....	4·65 „
Silver in tin .....	4·14 „
Lead in tin .....	3·18 „
Rhodium in lead ....	3·04 „
Platinum in lead ....	1·69 at 490°.
Gold in lead .....	3·03 „
Gold in mercury ....	0·72 at 11°.

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.

The author at present refrains from drawing any conclusion as to the evidence which the results afford respecting the molecular constitution of metals. It is, however, evident that they will be of value in this connection, because, with the exception of the gases, they present the simplest possible case of diffusion which can occur—the diffusion of one element into another.

Thus the relatively slow rate of diffusion of platinum as compared with gold, points to its having a more complex molecule than the latter.

#### PART II.—*Diffusion of Solid Metals.*

The second part of the paper is devoted to the consideration of the diffusion of solid metals. Much of the evidence is historical, for there has long been a prevalent belief that diffusion can take place in solids, and the practice in conducting important industrial operations supports this view. In this connection the author cites two truly venerable “cementation” processes. The object in the first of these is the removal of silver from a solid gold-silver alloy, while the second is employed in steel-making by the carburisation of solid iron. In both of these processes, however, a gas may intervene, though the carburisation of iron by the diamond, which had been effected *in vacuo* by the author, suggests that if a gas does intervene in the latter case, its quantity must be very minute. In connexion with the mobility of various elements in iron the work of Colson, of Osmond, and of Moissan is specially referred to.

The author points out that in 1820 Faraday and Stodart showed that platinum will alloy with steel at a temperature at which even the steel is not melted, and they express their interest in the formation of alloys by cementation, that is by the union of solid metals.

The remarkable view expressed by Graham, in 1863, that the “three conditions of matter (liquid, solid, and gaseous) probably always exist in every liquid or solid substance, but that one predomi-

nates over the other," is shown to have afforded ground for the anticipation that metals would diffuse into each other at temperatures far below their melting points. Reference is then made to the important work by Spring in 1886 on the lead-tin alloys, which retained a certain amount of molecular activity after they had become solid, and special importance is attached to the proof afforded by Spring, that alloys may be formed either by the strong compression of the finely divided constituent metals at the ordinary temperature (1882) or (1894) by the union of solid masses of metal compressed together at temperatures which varied from  $180^{\circ}$  in the case of lead and tin, to  $400^{\circ}$  in the case of copper and zinc; tin melting at  $227^{\circ}$  and zinc at  $415^{\circ}$ .

The evidence as to the volatilisation of solid metals is then traced, and allusion is made to the expression of Robert Boyle's belief, that even such solid bodies as glass and gold might respectively "have their little atmospheres, and might in time lose their weight."

Merget's experiment on the evaporation of frozen mercury is quoted in relation to Gay-Lussac's well-known discovery that the vapours emitted by ice and water both at  $0^{\circ}$  C, are of exactly equal tension.

Demarçay's experiments on the volatilisation of metals *in vacuo* at comparatively low temperatures is connected with the evidence afforded by Spring (1894), that the interpenetration of two metals at a temperature below the melting point of the more fusible of the two is preceded by volatilisation.

The author then points out that, interesting as the results of the earlier experiments are, as affording evidence of molecular interpenetration, they do not, for the purpose of measuring diffusivity, come within the prevailing conditions in the ordinary diffusion of liquids, in which the diffusing substance is usually in the presence of a large excess of the solvent, a condition which has been fully maintained in the experiments on the diffusion of liquid metals described in the first part of the paper. 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 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.

The author proceeds to describe his own experiments on the diffusion of solid metals. They are of the same nature as in the case of fluid metals, except that the gold, which is the metal chosen for examination, was placed at the bottom of a solid cylinder of lead instead of a fluid one.

In the first series of experiments, cylinders of lead, 70 mm. long, with either gold, or a rich alloy of gold and lead at their base, were

maintained at a temperature of  $251^{\circ}$  (which is  $75^{\circ}$  below the melting point of lead) for thirty-one days. At the end of this period the solid lead was cut into sections, and the amount of gold which had diffused into each of them was determined in the usual way. Other experiments follow, in which the lead was maintained at  $200^{\circ}$ , and at various lower temperatures down to that of the laboratory. The following are the results :—

			<i>k.</i>
Diffusivity of gold in fluid lead at $550^{\circ}$ ....			3.19
„	solid	„ $251^{\circ}$ ....	0.03
„	„	„ $200^{\circ}$ ....	0.007
„	„	„ $165^{\circ}$ ....	0.004
„	„	„ $100^{\circ}$ ....	0.00002

The experiments at the ordinary temperature are still in progress, but there is evidence that slow diffusion of gold in lead occurs at the ordinary temperature. The author points out that if clean surfaces of lead and gold are held together *in vacuo* at a temperature of only  $40^{\circ}$  for four days, they will unite firmly, and can only be separated by the application of a load equal to one-third of the breaking strain of lead itself.

The author thinks it will be considered remarkable that gold placed at the bottom of a cylinder of lead, 70 mm. long (which is to all appearance solid), will have diffused to the top in notable quantities at the end of three days. He points out that at  $100^{\circ}$  the diffusivity of gold in solid lead can readily be measured, though its diffusivity is only 1/100,000 of that in fluid lead at a temperature of  $500^{\circ}$ . He also states that experiments which are still in progress show that the diffusivity of solid gold in solid silver, or copper, at  $800^{\circ}$  is of the same order as that of gold in solid lead at  $100^{\circ}$ .

He concludes by warmly thanking Mr. A. Stansfield, B.Sc., who assisted him in all but the earlier portion of the work, and by expressing the hope that the experiments described in the paper will show that the diffusion can readily be measured in solid metals, and that they will carry one step further the work of Graham.

*Presents, February 20, 1896.*

#### Transactions.

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