CCCXCVIII.—*The Diffusion of Zinc in the α-Series of Solid Solution in Copper.*

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THE phenomenon of diffusion in solid substances presents many points of considerable interest, but the experimental difficulties encountered, *e.g.*, by Roberts Austen (Bakerian Lecture, 1896; *Proc. Roy. Soc.*, 1900, 67, 101), van Ostrand and Dewey (U.S. Geol. Survey, 1915, Paper 95G), and von Hevesy (*Ann. Physik*, 1921, 65, 218), have deterred investigators from making a thorough quantitative study of the process.

Several points connected with the phenomenon of diffusion require further elucidation. Von Hevesy (*Nature*, 1925, 115, 674) and Geiss and van Liempt (*Z. Metallk.*, 1924, 16, 316) claim to have shown that diffusion into single crystals does not occur. On the other hand, microscopic evidence indicates that diffusion takes place throughout the whole mass and not merely along the crystal boundaries. Von Hevesy suggested that the phenomena of diffusion and of electrolytic conductivity in crystals are due to the presence of loosened patches in the crystal lattice through which the atoms and ions may move with comparative ease. The author investigated this idea theoretically (*Proc. Roy. Soc.*, 1926, 111, 203) and found that an expression of the type

$$D = Ae^{-Q/RT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

should describe the variation of the diffusion coefficient (and by a natural extension that of the conductivity) with temperature. (Here, D is the diffusion coefficient or conductivity, R and T have their usual significance, and A and Q are constants.) It has been shown that this equation describes with considerable accuracy the diffusion of oxygen through films of metallic oxide, and the data of Horton (*Phil. Mag.*, 1906, 11, 505), Streintz (" Das Leitvermogen von Gepressten Pulvern "), Rasch and Hinrichsen (*Z. Elektrochem.*,

1908, **14**, 41), Konigsberger (*Physikal. Z.*, 1907, **8**, 883), and Phipps, Lansing, and Cooke (*J. Amer. Chem. Soc.*, 1926, **48**, 112) show a similar agreement for conductivity phenomena.

Although Dushman and Langmuir have claimed the validity of this equation for diffusion in solid metals, the published data upon this point might well be amplified, for the figures of Roberts Austen, on the one hand, and of van Ostrand and Dewey on the other, show considerable variation.

The objects of the present investigation were : (1) To work out a simpler technique for the investigation of diffusion phenomena; (2) to measure the diffusion coefficient in circumstances which admit of little doubt concerning the fact of diffusion within the crystal; and (3) to test the validity of equation (1) and, incidentally, of von Hevesy's theory of lattice loosening.

It has long been known that when brass is heated in an inert gas or in a vacuum it loses zinc in the form of vapour. Turner (*J. Inst. Metals*, 1912, **7**, 105) showed that the whole of the zinc might be removed from molten brass and, together with Thorneycroft (*ibid.*, 1914, **12**, 214), made a study of a series of the brasses when heated in a vacuum. It was not realised, however, that this phenomenon afforded a remarkably simple method for the study of the diffusion of zinc in solid brass.

If zinc is allowed to evaporate in a vacuum from a brass surface the process becomes analogous to a well-known physical process—the cooling of a semi-infinite solid under the conditions of initially uniform temperature and boundary conditions $T = 0$ for $t > 0$, t representing time. The problem is indeed identical with that investigated by Rayleigh in his estimation of the age of the earth from the temperature gradient at the surface. A somewhat similar method has been used by Langmuir to determine the diffusion coefficients of thorium in tungsten (*Physical Rev.*, October, 1923), but his mathematical treatment is more involved since his experimental conditions did not permit of the use of the semi-infinite solid as an approximation.

The solution of the diffusion equation under these conditions is

$$C = \frac{2C_0}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-u^2} du.$$

This expression may be integrated with the aid of tables, and we then know the concentration of zinc, C, at a distance x from the surface for an arbitrarily chosen value of D. Plotting concentration against distance, the total amount of zinc lost in a constant time, t, can be calculated by a graphic integration. It can be seen by inspection that the amount of zinc diffusing to the
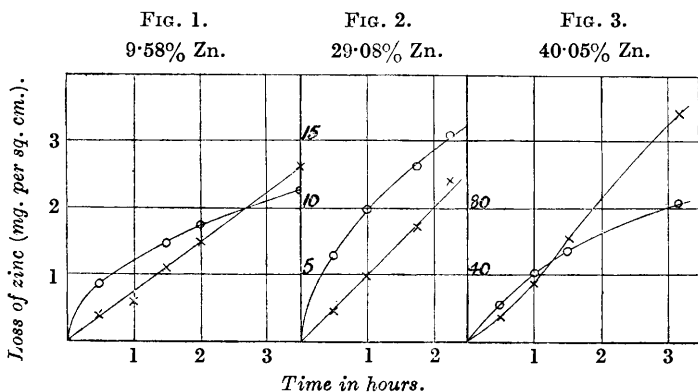
surface and across is proportional to $\sqrt{Dt}$. If, therefore, an arbitrary value be assigned to D, the amount of zinc lost in a time t can be calculated, and the value of D which obtains for the specimen under examination is then found by simple proportion.

A numerical example will make this clear. For a value of $D = 1/360^2 = 0.0_577$ by graphic integration we find that $9.39 \times 2/\sqrt{\pi}\% = 10.7\%$ of the total zinc is lost from 2 c.c. of brass across a surface of 1 sq. cm. in an hour. For a brass of d 8.86 containing 9.58% of zinc this corresponds with a loss of $(8.86 \times 2 \times 10.7/100) \times (9.58/100) = 0.1816$ g. $= 181.6$ mg. At 842° the actual loss is 1.201 mg./sq. cm. Hence if D is the required diffusion coefficient,

$$\sqrt{0.0000077} : \sqrt{D} = 181.6 : 1.201,$$

i.e., $$D = 3.36 \times 10^{-12} \text{ cm.}^2 \text{ per second.}$$

FIG. 1.	FIG. 2.	FIG. 3.
9.58% Zn.	29.08% Zn.	40.05% Zn.

Time in hours.

(*Points denoted thus* × *represent squares of corresponding* ○ *values.*)

The experimental work entailed in such a determination occupies little more than an hour and the only observations necessary are two weighings.

The apparatus was comparatively simple. The specimen in the form of a helical coil of wire was placed in a silica tube sealed at one end and connected to a Töpler pump at the other. After exhaustion the closed end of the silica tube was placed in an electric furnace, the specimen resting on the other end which projected some inches from the furnace and remained cool. When thermal equilibrium had been established, the specimen was allowed to slide down to the hot end of the tube, the Töpler pump being kept in constant operation. At the end of the experiment the tube was withdrawn from the furnace and allowed to cool rapidly; the loss of zinc was then estimated by weighing.

The theory demands that the amount of zinc lost shall vary as

the square-root of the time, *i.e.*, $W = k\sqrt{t}$. This relationship is obeyed accurately for alloys containing up to 30% of zinc, but for an alloy containing 40% of zinc a departure is observed, too much zinc being lost over long time intervals.

The results obtained for the loss of zinc with time are shown in Table I, and are plotted in Figs. 1, 2, and 3. The circles represent zinc lost and the crosses the squares of this quantity. The conformity of the two specimens to the equation $W = k\sqrt{t}$ is shown by the fact that the crosses lie on a straight line passing through the origin.

TABLE I.

Rate of Loss of Zinc from a Brass Surface.

Comp. of brass : 90·42% Cu, 9·58% Zn. Temp. 842°.		Comp. of brass : 70·86% Cu, 29·08% Zn. Temp. 842°.		Comp. of brass : 59·90% Cu, 40·05% Zn. Temp. 775°.	
Time (hrs.).	Loss (mg.).	Time (hrs.).	Loss (mg.).	Time (hrs.).	Loss (mg.).
0·5	0·835	0·5	6·46	0·5	22·4
1·0	0·98	1·0	9·90	1·0	41·55
1·5	1·47	1·75	13·25	1·5	55·1
2·0	1·73	2·25	15·49	3·16	83·4
3·5	2·25				

The zinc loss per sq. cm. rose rather rapidly with increasing zinc content, obeying approximately the equation $L = ae^{C}$, where zinc lost in unit time $= L$; percentage of zinc $= C$; and a is a constant. The diffusion coefficient varies in a somewhat similar manner. The experimental data are set out in Table II and plotted in Fig. 4, where the circles denote the actual amounts of zinc lost and the crosses the logarithms of these numbers.

TABLE II.

The Influence of Composition upon the Rate of Loss of Zinc from a Brass Surface.

	Loss of zinc (in mg. per sq. cm.) in 30 mins.	
Zinc in alloy (%).	At 775°.	At 842°.
9·58	0·441	0·850
13·34	0·840	1·41
17·30	—	2·09
23·13	2·60, 2·85	4·60
29·08	2·76, 2·83	6·47
40·05	18·8	58·0

Both the rate of zinc loss and the diffusion coefficient vary exponentially with temperature, a result foreshadowed by the author's work upon diffusion of gases through solid oxide films and that of Langmuir and Dushman on metallic diffusion.

The experimental values are in Table III. On plotting the logarithm of the diffusion coefficient against the reciprocal of the

absolute temperature (Fig. 5), a fairly straight line is obtained for the 29%-zinc alloy and an excellent one for the 9·5% alloy, thus establishing equation (1).

TABLE III.

Temp.	Loss of zinc (mg. per sq. cm.) in 30 mins.	$10^{12} \times D.$ (cm.²/per sec.).	Loss of zinc (mg. per sq. cm.) in 30 mins.	$10^{12} \times D.$ (cm.²/per sec.).
	Alloy containing 9·58% Zn.		Alloy containing 29·08% Zn.	
641°	0·104	0·0507	0·649, 0·667	0·226
725	0·296	0·409	1·73	1·62
775	0·441	0·910	2·76, 2·83	4·10, 4·32
842	0·850	3·36	6·47	22·6
884	1·165	6·33	7·87	33·6

FIG. 4.   FIG. 5.

Loss of zinc in 30 min. (mg. per sq. cm. of surface) at 842°.

Percentage of Zn in alloy. $10^3 \times 1/T.$

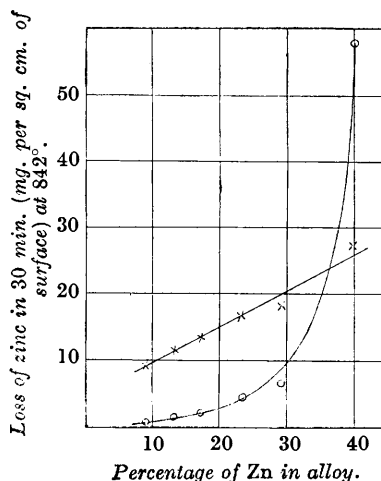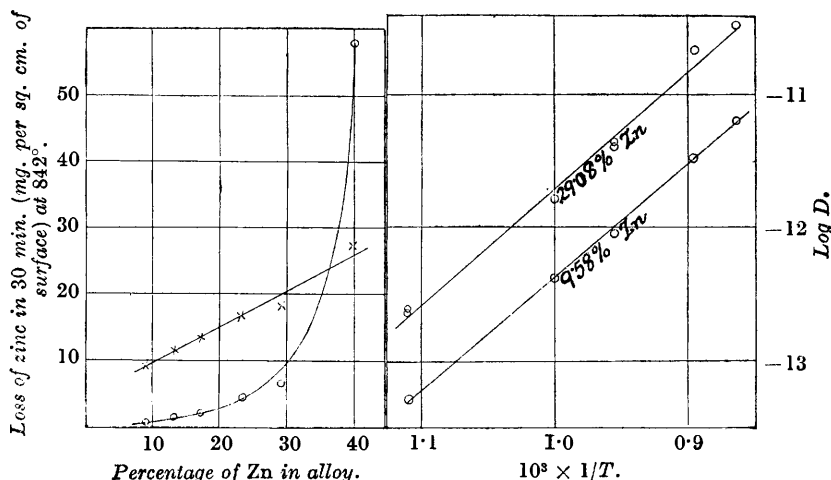Log D.

Discussion.

The form of the zinc loss–time curves calls for little discussion in the case of alloys containing up to 30% zinc. They are quadratic parabolas as demanded by theory and justify the use of this method for the study of diffusion in solid solutions.

The case of the alloy containing 40% of zinc is anomalous and may be complicated by the fact that during the course of diffusion the interior of the brass consists of the β-constituent, whilst the surface layers are composed of the α-brass only. A more detailed study of a 40%-zinc alloy is projected.

The possible diffusion of copper into brass has been ignored in the foregoing considerations. This is probably of minor importance for small losses of zinc, but when these reach the magnitude observed

in the 40%-zinc alloys it is no longer safe to neglect it, and the departure of these alloys from the parabolic law may be due in some measure to this factor of which the intervention would cause a departure from the ideal law in the same sense as that actually observed.

The rapid rise of the rate of zinc evolution and the diffusion coefficient with increasing zinc content is remarkable and indicates that the solid solution of zinc in copper deviates very considerably from ideal conditions. The square of the rate of zinc loss or the diffusion coefficient may be taken as a measure of the activity or thermodynamic concentration of the zinc in solid solution.

According to the equation proposed by Rideal and Dushman (*J. Amer. Chem. Soc.*, 1921, **43**, 397; *Physical Rev.*, 1922, **20**, 113), it should be possible to calculate the value of Q in equation (1) from one observation of the diffusion coefficient, for if $\kappa \cdot dt$ is the probability that an atom of zinc will move from one layer into the adjacent layer in time dt, then $D = \kappa S^2$, where S is the distance between the layers. Further, $\kappa = (Q/Nh) \cdot e^{-Q/RT}$, where N and h are the Avogadro number and Planck's constant, respectively. S^2 is calculated to be $5 \cdot 23 \times 10^{-16}$ cm.; at $1157°$ Abs. the diffusion coefficient is $6 \cdot 35 \times 10^{-12}$ cm.; therefore $\kappa = 1 \cdot 209 \times 10^4$, and $1 \cdot 209 \times 10^4 = \dfrac{Q}{6 \cdot 06 \times 10^{23} \times 6 \cdot 55 \times 10^{-27}} \cdot e^{-\frac{Q}{1 \cdot 98 \times 1157}}$. This gives by trial, $Q = 12{,}800$ cals., which is in only fair agreement with the experimentally determined value of 10,750 cals.

The method now described opens up a new field for research. The diffusion of zinc and cadmium in metals such as copper, silver, and gold may be studied in circumstances of exceptional experimental facility up to temperatures well within the range of the ordinary resistance furnace. By working at much higher temperatures, Langmuir has shown it to be possible to evaporate a number of metals from electrically-heated tungsten and molybdenum alloys, and a complete survey of this field would undoubtedly be of great theoretical interest. The method may be applied to single crystals of zinc and cadmium alloys as soon as these have been produced and may then, with the aid of the microscope and suitable etching reagents, be used for a study of the directional diffusive properties of metallic crystals.

Summary.

The loss of zinc from a heated brass surface in a vacuum has been studied with reference to the influence of temperature, time, and composition.

It has been shown that measurements of the diffusion coefficient

of zinc in the α-ranges of solid solution in copper can readily be made by observing the rate of loss of zinc.

The diffusion coefficient has been shown to vary exponentially with zinc content and with temperature.

The temperature coefficient of diffusion has been shown to be in fair agreement with the Rideal–Dushman unimolecular reaction equation.

The possibility of using this method for a general survey of the question of diffusion in solid solution has been emphasised.