Influence of Temperature upon the Diffusion Velocity of Solid Metals

(The Zinc-Copper System)

By

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Abstract

In the first part it is shown that the ratio of velocities of diffusion given by Weiss is equal to the ratio of coefficients of diffusion defined by Fick's law in the case of primary solid solutions. In the second part, the zinc-copper system being taken as an example, it is shown by means of an electrical resistance method that the velocity of diffusion can exist in the case of non-primary solid solutions and some of the states of diffusion have been examined by X-rays. In the third part it is proved that the relation between the velocity of diffusion V and the absolute temperature T is given by $V = Be^{-\frac{\alpha}{T}}$ instead of by Weiss' formula $V = Ke^{\beta T}$ with the zinc-copper system in the range of temperature $87\text{–}302°C$, where B, K, α and β are constants and $\alpha = 9.52 \times 10^3$ degrees.

Relation between Diffusion Velocity and Diffusion Coefficient

In the case of metals which do not form a perfect solid solution, we can easily see from the complexity of their equilibrium diagrams that there is no such constant as the coefficient of diffusion which is independent of the concentration and time. Nevertheless, H. Weiss[1] has found by microscopic examination that when samples which are both composed of the two kinds of metals to be tested, are heated at different temperatures, T and T', and one of them reaches a certain state (say A) after the time interval t_1 and another state (say B) after t_2, then the other of them also reaches the state A after the time

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1. H. Weiss: Ann. de Chimie, **19**, 21 (1923); and **20**, 131 (1923).

interval t_1' (which is different from t_1) and the state B after t_2', and, moreover, there exists the relation

$$t_1/t_1' = t_2/t_2'. \tag{1}$$

Since the states A and B are arbitrary, the above ratio is constant in any state, and may be put as V'/V (V corresponding to T and V' to T'). Weiss called V the velocity of diffusion at the temperature T.

Now we will consider what meaning the velocity of diffusion has in the case where there exists the coefficient of diffusion D which is defined by Fick's law[1] or by its form of differential equation

$$\frac{\partial c}{\partial t} = D\varDelta c,$$

where c is the concentration, t the time and $\varDelta$ the Laplace operator. The concentration, then, will be given by the form $c = f\,(Dt,\,x,\,y,\,z)$, where x, y and z are the space coordinates which determine the point where the concentration is considered, and f is a certain function[2] which is determined if the boundary and initial conditions are given. If we choose, as in Weiss' case, the same two samples and heat one at the temperature T and the other at T', then the first state is reached after the times t_1 and t_1' and the other state is reached after t_2 and t_2'. In order to get the same state at the different temperatures and different intervals of time, the following relations must exist :—

$$c = f\,(Dt_1,\,x,\,y,\,z) = f\,(D't_1',\,x,\,y,\,z),$$

and $\quad c = f\,(Dt_2,\,x,\,y,\,z) = f(D't_2',\,x,\,y,\,z),$

or $\quad Dt_1 = D't_1' \quad$ and $\quad Dt_2 = D't_2',$

and so $\quad D'/D = t_1/t_1' = t_2/t_2', \tag{2}$

where D and D' are the coefficients of diffusion referring to the temperatures T and T' respectively. Comparing this with (1), we have

$$D'/D = V'/V, \tag{3}$$

i. e. the ratio of the coefficients of diffusion defined by Fick's law at any two temperatures is the same as the ratio of the velocities of

1. Fick : Pogg. Ann., **94**, 59 (1855).

2. Riemann-Weber : Differentialgleichungen der Physik II S. 177 (1927).

diffusion defined by Weiss at those temperatures in the case of solid solutions.

Determination of Diffusion Velocity by Resistance Method

General consideration of the method: Weiss[1] has determined the velocity of diffusion of various metals and N. W. Ageew and O. I. Vher[2] have determined that of aluminium and iron by microscopic means, but the velocity of diffusion can be determined from the change in the electrical resistance of the samples examined. As in the previous experiment[3] carried out in the case of primary solid solutions, take two samples made of two kinds of metals in the form of foils, and heat them at the different temperatures T and T', then measure the electrical resistance of them at the same temperature T' ($< T$). The concentration c of the one metal will be given by $c = f(x, t)$ at T, and $c = \varphi(x, t)$ at T', where f and φ are unknown functions, t the time, and x the space coordinate which is perpendicular to the flat surface of the sample. If the same state be reached at the times t and t' in the respective cases as Weiss supposed, then the relation $c = f(x, t) = \varphi(x, t')$ must exist and the electrical resistance of the samples has also the same value. Conversely, if the resistance of many kinds of samples of the same pair of metals be measured, and the time intervals which are necessary to bring the resistance to the same value be compared, and if the series of time ratios have a constant value in each case, we can say that Weiss' conception is correct and the velocity of diffusion exists.

To illustrate this method the author has chosen the system of zinc and copper, although the diffusion phenomena of this system have already been studied by Weiss[4] and S. L. Hoyt[5] by microscopic examination and by C. F. Elam[6] by the X-ray method with large single-crystals of copper, but in any case the velocity of diffusion has not yet been given.

Production of samples, method of measurement and apparatus:

1. H. Weiss, loc. cit.
2. N. W. Ageew and O. I. Vher: Jour. Inst. Metals, **44**, 83 (1931).
3. C. Matano: These Memoirs, **14**, 123 (1931).
4. H. Weiss, loc. cit.
5. S. L. Hoyt: Amer. Inst. Min. Met. Eng. Tech. Publ., **128**, 1 (1928).
6. C. F. Elam: Jour. Inst. Metals. **43**, 217 (1931).

As in the previous paper[1] the samples were made in the form of foils by alternate electroplating with copper and zinc. A wax surface covered with graphite was first plated with copper in the electroplating solution; 100 c c. of water containing 4.35 gms. of caustic soda, 2.60 gms. of copper sulphate and 13.00 gms. of Rochelle salt. Then zinc and copper layers were added alternately, but as the above solution used for copper was not suitable for zinc objects, the following solutions were used: for zinc, 100 c.c. of water containing 2.20 gms. of sodium citrate and 3.52 gms. of zinc chloride; and for copper, 100 c.c. of water containing 2.12 gms. of sodium bisulphite, 1.75 gms. of copper acetate and 2.12 gms. of potassium cyanide. After a suitable thickness had been obtained, the foils were peeled off and cut into strips about 0.1 cm. in breadth and 15 cms. in length. The time for each plating, the current density, the number of layers and the total thickness of the foils are tabulated in Table I.

Table I

Foil	Time for plating each half layer mins.		Current Density m. amp./cm².	Number of Layers	Total Thickness cm. × 10⁻³	Thickness of each layer cm. × 10⁻⁴
I	{Cu {Zn	40 10	3.5 6.7	8	3	4
II	{Cu {Zn	80 20	3.5 7.5	4	3	8
III	{Cu {Zn	180 15	3.5 6.7	2	5	25

The sample, held in the terminals as described below, was then put in a vacuum or in glycerin or castor oil which were heated by the electrical resistance furnace, and the electrical resistance of it was measured by the null method with a Wheatstone bridge made by Hartmann and Braun. The terminals are shown in Fig. 1. L_1 and L_2 are the copper lead wires whose resistance is about 0.003 ohm, and T_1 and T_2 are the brass terminals at which the sample S is fixed by screws. T is an ordinary mercury thermometer measuring up to $360°C$, C the castor oil which is contained in the glass vessel, R the rubber stopper and F the electrical resistance furnace. G is a glass tube which insulates the lead wire L_2 from the terminal T_1. Hs are glass vessels filled with mercury and at these parts the lead wires

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1. S. Tanaka and C. Matano: These Memoirs, **13**, 343 (1930).

which are connected to the terminals of the Wheatstone bridge are in contact with the lead wires L_1 and L_2. St is a stirrer.

Fig. 1

From the theoretical point of view, it is best to heat the sample in a vacuum, but since the diffusion occurs very fast in some cases and although the sample and terminals have only small heat capacities, a sufficiently long duration is necessary before the sample etc. are brought to the fixed constant temperature, so the author, in many cases, rather heated the sample in some insulating liquid with such a large heat capacity that the sample (owing to the good thermal conductivity of it) reached the constant temperature of the liquid in an instant when it was put in the liquid. The lead wires are sufficiently thick so that the change of resistance owing to the change of temperature is negligible. The sample S is spiraled near the mercury in the thermometer and the temperature can be measured accurately. No effect of thermoelectricity can be detected by reversing the direction of the current in the sample when the resistance is measured.

In order to lower the temperature of the sample heated at T to $T'(< T)$ quickly, the electrical furnace was opened and the vessel was exposed to the air. The resistance of the sample at T' was measured and to elevate the temperature of the sample to T quickly, a large amount of current was sent through the furnace. But it required a fairly long time and this point is the chief drawback in this method.

Results of experiments, existence of diffusion phenomena: The results are shown in the curves in Fig. 2. The abscissa is the time interval which is measured from the instant when the sample is put in the furnace and so when the diffusion begins. The ordinate is the ratio of the resistance at the temperature and the time selected to the resistance at $15°C$. where diffusion does not occur appreciably over a long time. The thickness of the sample or rather the thickness of each layer plays an important part in every problem of diffusion and so in this case by taking the ratio of the resistances, the effect due to the difference in the length and the breadth of each sample has been removed.
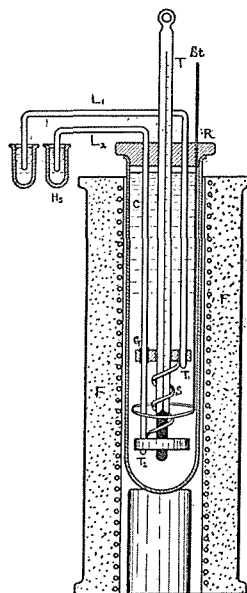
In every curve the resistance changes as the time passes and this shows that diffusion has taken place. The resistance first increases, then reaches the maximum value and finally decreases, and as every curve is of this nature, there seems to exsist such a quantity as that

Fig. 2
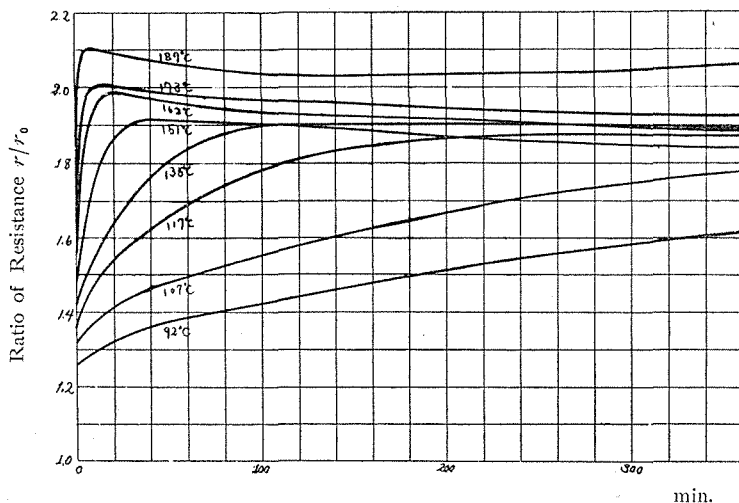
called "the velocity of diffusion". We understand that the part where the resistance increases rapidly also shows the vigorous occurrence of diffusion. But in the part where the resistance decreases slowly, we can not so easily determine whether this effect is due to diffusion or to annealing, which effect the author considers as due to the phenomena of grain growth etc. To confirm this point, X-ray photographs were taken with the Debye-Scherrer camera in the Müller spectrograph, but instead of the pin hole, the slit was used. The Shearer metal tube was used as the X-ray apparatus and the current strength was about 3 milliamp., the maximum voltage applied was 60 K. V. and the time of exposure was 7 hours in each case. Three photographs taken with the samples from foil I are shown in Plate I. The first was obtained with the sample before heating and is shown in Fig. 1a; the second was taken with a sample kept at $165°C$. for 26 minutes, when its resistance is at its maximum value, and then quenched, and is shown in Fig. 1b; and the third was obtained with a sample kept at $165°C$. for over 350 minutes, when the resistance is considerably less than the maximum value, and also quenched, and is shown in Fig. 1c. From these photographs we can say that the

three stages are different from each other, and while the diffusion
occurs in the interval when the resistance increases, it also occurs in
the interval when the resistance decreases, and as neither broadening
of spectral lines nor aggregation of Laue spots can be detected in
Fig. 1c, the grain growth has not occurred yet.

Existence of diffusion velocity: The existence of velocity of
diffusion was examined as follows :— A sample obtained from foil II
was first heated to 149°C., and its resistance was measured at that
temperature, the result being shown in Fig. 3a. Another sample from
the same foil was heated to 131°C. and its resistance was measured
at that temperature with the results shown in Figs. 3b and 4c; the
resistance of another sample at 108°C. is shown in Fig 3c. Still
another sample from the same foil was heated to 149°C. and its
resistance was measured at that temperature (results shown in Fig.
4a) and also at 131°C. (result in Fig. 4b).

As has been mentioned in the preceding section, it is difficult
to lower the temperature and again raise it to the previous tempera-
ture instanteneously, and in this experiment it took some five minutes
to do this.

On comparing the curves of Figs. 3a and 4a, the points which
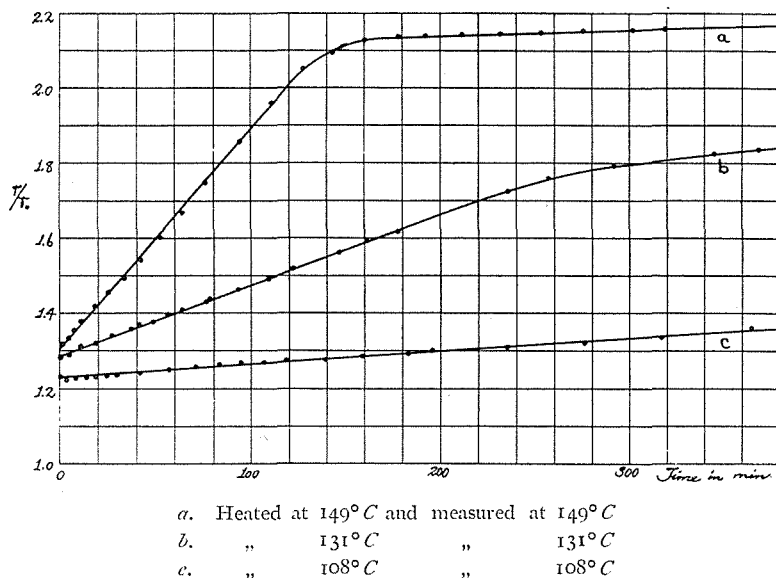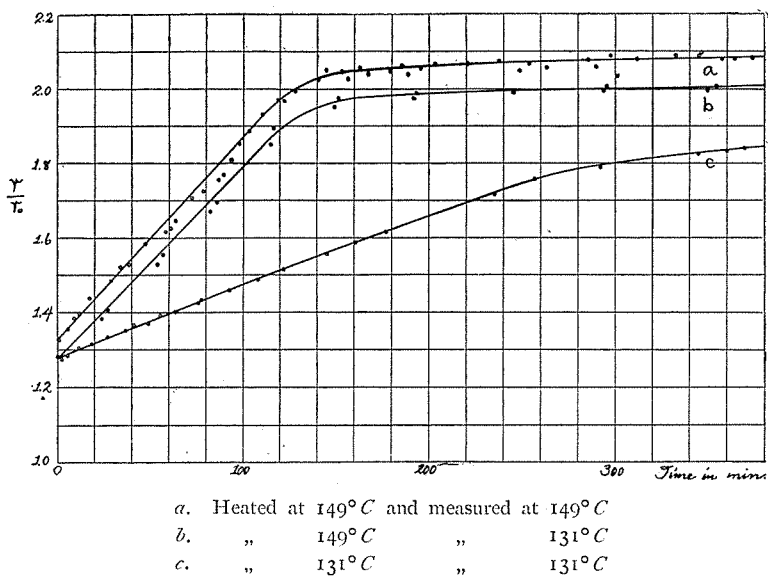
Fig. 3

a. Heated at 149°C and measured at 149°C
b. ,, 131°C ,, 131°C
c. ,, 108°C ,, 108°C

Fig. 4

a. Heated at $149^\circ C$ and measured at $149^\circ C$
b.   ,, $149^\circ C$,, $131^\circ C$
c.   ,, $131^\circ C$,, $131^\circ C$

determine the curve Fig. 4a are somewhat disorderly, but we can say that both curves have the same form, i. e. both curves are at first nearly straight and their slopes to the time axis are 5.5×10^{-3}, and 5.2×10^{-3} min.$^{-1}$ respectively; at about 140 minutes, the curves are somewhat flattened and afterwards both curves are again nearly straight and their slopes in this time take the same value, 1.25×10^{-4} min.$^{-1}$ From this fact, it is clear that the diffusion phenomenon was nearly the same whether the sample was heated at the constant temperature or heated at the constant temperature but disturbed many times by lowering its temperature for small intervals of time. On comparing the curves in Figs. 4a and 4b, we see that both curves again have the same form in many respects, viz. the inclination of the straight portion, the point where the line changes its direction, but the curve in Fig. 4a is always higher than the curve of Fig. 4b, nearly the same distance from it throughout the whole interval of the measurement. From this last fact, it is evident that the direction of the curve of Fig. 4a can be taken instead of that of Fig. 4b, if the direction of a curve of the nature of that in Fig. 4b is needed. This fact will be utilised in the latter part of this paper. Lastly, on comparing the curves in Figs. 4b and 4c, we see that both curves start from nearly the same point, and run in straight lines but have different slopes;

while the one tends to change its direction at nearly 100 minutes, the other does so at nearly 260 minutes, and as the one tends to change its direction sharply, the other does so very slowly. From these facts, it is clear that in the straight portion in the early stage where the diffusion occurs vigorously, the velocity of diffusion exists strictly, as the ratio of the velocities of diffusion at these temperatures can be given from the ratio of their slopes and this is independent of time, and so independent of the homogenisation of the component metals. The details of this are as follows:

The equation of the curve in Fig. 4b is

$$r/r_0 = 1.28 + 5.1 \times 10^{-3}t \qquad (0 \leqq t \leqq 100)$$

and the equation of the curve in Fig. 4c is

$$r/r_0 = 1.28 + 1.9 \times 10^{-3}t \qquad (0 \leqq t \leqq 260)$$

graphically, where r is the resistance at the time t, which is expressed in minutes, and r_0 is the resistance at time $t = 0$ at the temperature $15°C$. Since the state of diffusion is the same when the resistance is the same, so is in the same state in the above equations, let the two time intervals which are necessary to bring them to that state be t_{149} and t_{131}, then

$$t_{149}/t_{131} = 1.9/5.1 = 0.37 \ (= V_{131}/V_{149}),$$

where t_{149} is the time required for the sample heated to $149°C$. and t_{131} is for that heated to $131°C$., and this is the ratio of the velocities of diffusion V_{131}/V_{149}.

After the straight portion stage, the direction of the curve is not independent of time, but from the similarity of the curves of Figs. 4b and 4c, even in this part, broadly speaking, the velocity of diffusion exists. The points where the direction tends to change give the ratio of the velocities as $100/260 = 0.39$ and this ratio nearly coincides with the ratio 0.37 given above.

To take another example—the sample obtained from foil II was heated to $108°C$. and its resistance was measured at that temperature, with the results shown in Fig. 5c. Next another sample from the same foil was heated to $131°C$. and its resistance was measured at $131°C$. and occasionaly at $108°C$. by lowering the temperature to that point in a small time interval (about 15 minutes). The results are shown in Figs. 5a and 5b. As in the above example, comparing the curves in Figs. 5a and 4c, we see that both curves are nearly straight in the interval of time when the measurement was made, but the

Fig. 5

a. Heated at $131^\circ C$ and measured at $131^\circ C$
b.   ,, $131^\circ C$,, $108^\circ C$
c.   ,, $108^\circ C$,, $108^\circ C$
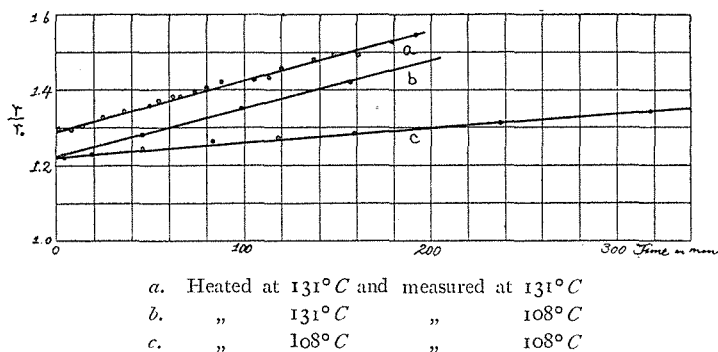
slopes are different, the curve in Fig. 4c being more inclined than the curve in Fig. 5a. This fact, however, may be explained as follows : The time interval which is needed to lower the temperature from $131^\circ C.$ to $108^\circ C.$ is so long that the diffusion occurred in this interval at a temperature below $131^\circ C.$ Next, comparing the curves in Figs. 5a and 5b, we see that the two curves have the same slope as in the former example and the explanation must be the same. Lastly, comparing the curves in Figs. 5b and 5c, we see that they are also of the same nature as that of the former example. And in this case, also, the velocity of diffusion exists strictly.

The equations of the curves in Figs. 5b and 5c are

$$r/r_0 = 1.223 + 1.27 \times 10^{-3}t$$

and

$$r/r_0 = 1.223 + 3.74 \times 10^{-4}t$$

graphically. So the ratio of the velocities of diffusion, which is the ratio of the slopes is

$$t_{131}/t_{108} = 3.74/12.7 = 0.273 \ (= V_{108}/V_{131}).$$

Relation between Diffusion Velocity and Temperature

Determination of ratio of diffusion velocities at various temperatures : In the preceding section it is shown that the velocity of diffusion exists and the ratio of the velocities at two different temperatures can be determined from the ratio of the times which are necessary to bring the samples to the same value of resistance taken as a standard, the portion of the resistance due to the temperature coefficient being removed. But in general it is difficult experimentally to remove the portion of the resistance due to the temperature

coefficient. In the case of the samples from foil II, the resistance-time curve has a straight line portion and what is needed to determine the ratio in question is the ratio of the slopes, and so from the results described in the preceding section, the slope of the straight line can be used in the resistance-time curve in which the resistance was measured at the temperature at which the diffusion has occurred and the resistance due to the temperature coefficient has not been removed. The above method can be utilised for the samples from foil III. Since the ratio of the slopes is equal to the ratio of the velocities of diffusion, the slope is itself proportional to the velocity of diffusion

Table II				Table III	
Foil II		Foil III		Foil I	
Absolute Temp.	Slope of Curve, min.$^{-1}$	Absolute Temp.	Slope of Curve, min.$^{-1}$	Absolute Temp.	t_m min.
361	1.65×10^{-4}	453	7.16×10^{-3}	408	120
366	1.8×10^{-4}	478	1.34×10^{-2}		
381	3.6×10^{-4}	497	3.03×10^{-2}	424	44
404	$\begin{cases} 1.27 \times 10^{-3} & * \\ 1.8 \times 10^{-3} \end{cases}$	511	4.23×10^{-2}		
422	$\begin{cases} 5.1 \times 10^{-3} & * \\ 5.5 \times 10^{-3} \end{cases}$	531	1.11×10^{-1}	435	21
		546	1.62×10^{-1}	446	14
440	1.7×10^{-2}	575	4.20×10^{-1}		
462	4.5×10^{-2}			462	7
488	1.3×10^{-1}	* See Figs. 5 and 4.			

and the constant of this ratio is the same when the temperature is varied, if only the samples are of the same kind. The slopes of the lines are shown in Table II.

Now, in the case of the curves in Fig. 2, there is no straight line portion, and since any state can be taken as a standard, it is very satisfactory to find that there is a corresponding point on each curve, if a special position, such as the point where the resistance is maximum, be taken as a standard. For there are many reasons for considering that the point where the resistance is maximum corresponds at each temperature, since the resistance-concentration curves have nearly the same aspect within a moderate range of temperature. The ratio of the velocities of diffusion can thus be measured. The results obtained with the samples from foil I are shown in Table III. t_m, the time interval which is required for the samples to attain the maximum resistance, is inversely proportional to the velocity of diffusion.

Formulae which express the relation between diffusion velocity and temperature : The empirical formula which combines temperature and the velocity of diffusion given by Weiss[1] is

$$V = 1/t = K(e^{\beta T} - 1),$$

where V is the velocity of diffusion, t the time interval which is necessary to bring the sample to a certain state of diffusion, K and β constants independent of temperature, e the base of natural logarithms and T the absolute temperature. But usually 1 is small in comparison with the first term in the brackets and can be neglected, so the above formula becomes

$$V = K e^{\beta T}. \qquad\qquad (4)$$

Any state can be taken as a standard; only the ratio of the velocities of diffusion has an important meaning and so K is not important and what is important is β.

In the case where the coefficient of diffusion exists, first S. Dushman and I. Langmuir[2] and afterwards J. Frenkel[3] and others deduced from the theoretical consideration the following formula,

$$D = A e^{-\frac{\alpha}{T}}, \qquad\qquad (5)$$

where D is the coefficient of diffusion, A that of $T \to \infty$, α the constant, e the base of natural logarithms and T the absolute temperature. This formula was confirmed experimentally by many investigators[4] in the case of solid solutions, although the results of A. Obrutsheva and G. Hevesy's experiments[5] on the self diffusion of lead have confirmed rather the formula with two similar terms derived by A. Smekal[6].

Now between the coefficient of diffusion and the velocity of diffusion there exists the relation (3) in the case of solid solutions and so from (5) there must be the relation

$$V = B e^{-\frac{\alpha}{T}}, \qquad\qquad (6)$$

where B is a constant independent of temperature, and depending upon the state of diffusion which is taken as a standard. In the case

1. H. Weiss, loc. cit.

2. S. Dushman and I. Langmuir: Phys. Rev., **20**, 113 (1922).

3. J. Frenkel: Zeits. f. Phys., **35**, 652 (1926).

4. H. Braune: Zeits. phys. Chem., **110**, 147 (1924); W. Jost: Zeits. phys. Chem., **9**, 73 (1930); C. Matano, loc. cit.

5. A. Obrutsheva and G. v. Hevesy: Nature, **115**, 674 (1925).

6. A. Smekal: Zeits. f. Electrochem., **34**, 472 (1928).

of non solid solutions, in some cases[1] formula (4) does not express the results of experiments exactly, so we shall consider whether formula (4) or (6) expresses the result of this experiment more satisfactorily.

Let the quantity which is proportional to the velocity of diffusion V, such as the slope or the reciprocal of t_m, be U, then $V = U/C$, where C is a constant; and from (4) taking logarithms we have

$$\log_{10} U = \log_{10} V + \log_{10} C = \log_{10} K + \beta \cdot \log_{10} e \cdot T + \log_{10} C$$
$$= \text{const.} + \beta \cdot \log_{10} e \cdot T, \qquad (7)$$

and from (6) we have

$$\log_{10} U = \text{const.} - (a \cdot \log_{10} e)/T. \qquad (8)$$

Plot the curve as $\log_{10} U$ in one coordinate and T or $1/T$ in the other coordinate on a graph using the results shown in Tables II and III. Then in each case the curve seems to be a straight line and both formulae (7) and (8), and consequently (4) and (6) seem to express the results nearly satisfactorily in the range of temperatures at which the measurement is carried out for each sample of the same kind. The slope of the line determines the constants, the values of which are summarized in Table IV.

Table IV

Foil	$\beta. \log_{10} e$ (degrees)$^{-1} \times 10^{-2}$	$\alpha. \log_{10} e$ degrees $\times 10^3$	Range of Temperature
I	2.3	4.3	408—462
II	2.4	4.3	361—488
III	1.8	4.1	453—575

α and β must not depend on the kind of the foils or in other words these are constants which depend only upon the nature of the metals in which the diffusion occurs. In this sense it seems from Table IV that formula (6) expresses the results more satisfactorily. To show this more clearly, the following curves will be drawn: Since what is important is α or β and not the initial value of the straight line, we will shift the line to its proper place by moving the temperature axis upwards or downwards and plot the curve in one figure, then the curves in Figs. 6 and 7 will be obtained. In these figures it is clear

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1. N. W. Ageew and O. I. Vher, loc. cit.
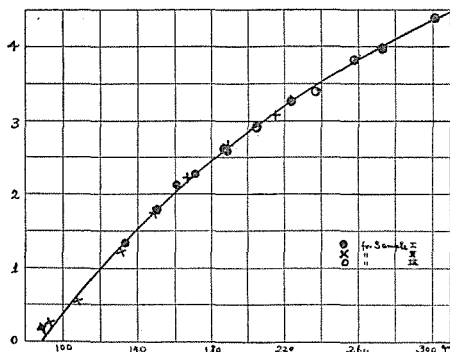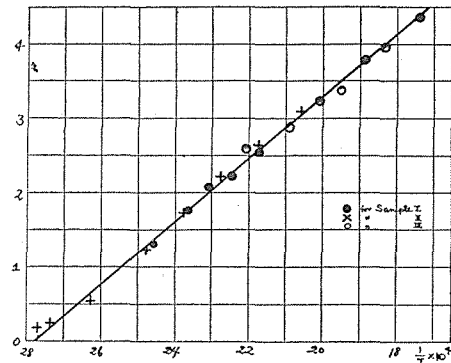
Fig. 6   Fig. 7

that the curve corresponding to formula (6) is much straighter than
the curve corresponding to formula (4) which deviates systematically
from a straight line. From this α can be determined graphically and
is equal to 9.52×10^3 degrees in the range of temperature $87 - 302°C$.
(Weiss' result with the tin-copper system gives $\beta \cdot \log_{10} e = 1.6 \times 10^{-2}$
per degree, which value is comparable to the above results in Table
IV with the zinc-copper system).

The conclusion is as follows: The formulae $V = B e^{-\frac{\alpha}{T}}$ and $V = K e^{\beta T}$ both represent nearly the experimental facts, but strictly speaking,
the former expresses the results more satisfactorily in the range of
temperature $87 - 302°C$. with the zinc-copper system. The constant α
is equal to 9.52×10^3 degrees in this case.

Fig. 1 a

Fig. 1 b

Fig. 1 c