

Influence of Temperature upon the Diffusion Coefficient of Solid Metals

By

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Abstract

From the electrical resistance of foils composed of thin layers of two kinds of metals at various temperatures, the coefficients of diffusion D were determined successively by using the relation $Dt = \text{const.}$ for the same kind of foils, where t is a time interval which is necessary to bring their resistance to some fixed value, the portion of the resistance due to the coefficient of temperature being removed. By means of this method it was confirmed that the relations $D = Ae^{-\frac{\alpha}{\theta}}$, and $D = A\theta e^{-\frac{\alpha}{\theta}}$, where A and α are constants and θ is the absolute temperature, show equally well the experimental results for the *Ag-Au* system and for the *Ni-Cu* system between 300°C (or 330°C) and 500°C .

Method of Successive Determination of Diffusion Coefficient

Theoretical part: If the samples are composed, as in the previous experiments¹, of many thin layers of two kinds of metals, and the electrical resistance of them is measured at various constant temperatures, then it will be found that the resistance will change as the time passes owing to the occurrence of the diffusion. Hence, if Fick's law holds good, the concentration c of one of the two metals will be given by

$$c = f\left(\frac{Dt}{d^2}, \frac{a}{d}, \frac{x}{d}\right),$$

1. S. Tanaka and C. Matano: These Memoirs **13**, 343 (1930); and **14**, 59 (1931)

where f is a certain known function¹ of three variables $\frac{Dt}{d^2}$, $\frac{a}{d}$ and $\frac{x}{d}$, D being the coefficient of diffusion, t the time, d the mean thickness of each layer, a half the thickness of the one metal, and x the one of the space coordinates which is perpendicular to the flat surface of the sample and has its origin in the middle of the one metal. The electrical conductivity k which is generally an unknown function of c will be put as

$$k = \varphi(c).$$

From these the conductance will be given by

$$\begin{aligned} K &= \frac{Nl}{L} \int_0^a k \, dx = \frac{Nl}{L} \int_0^a \varphi(c) \, dx \\ &= \frac{Nl}{L} \int_0^a \varphi \left\{ f \left(\frac{Dt}{d^2}, \frac{a}{d}, \frac{x}{d} \right) \right\} dx = \frac{Ndl}{L} \psi \left(\frac{Dt}{d^2}, \frac{a}{d} \right), \end{aligned}$$

where N is the number of layers, l the breadth, and L the length of the sample. ψ is an unknown function of the variables $\frac{Dt}{d^2}$ and $\frac{a}{d}$.

In the previous paper S. Tanaka and the author² showed a method of determining the coefficient of diffusion by using the values of resistance near the saturation, but this method needs long time and, in practice, it is impossible except when the temperature is sufficiently high. To avoid this inconvenience, the author determined the coefficient D_1 at a temperature $T_1^0 C$ in comparison with the known coefficient D_0 at a temperature $T_0^0 C$, in the following way:—

Let us assume that two samples which have the same value of $\frac{a}{d}$, be used and heated at different temperatures T_1 and $T_0^0 C$, and that the resistance of both is measured at $T_1 (< T_0^0) C$. The sample at $T_0^0 C$ is cooled to $T_1^0 C$ only when the measurements are carried out. Then although the function φ is unknown, φ has the same form in both cases, and consequently ψ has the same form. So if we take $\frac{K_1 L_1}{N_1 l_1 d_1} = \frac{K_0 L_0}{N_0 l_0 d_0}$, or $\frac{R_1 l_1 d_1 N_1}{L_1} = \frac{R_0 l_0 d_0 N_0}{L_0}$ (where R is the resistance) and $\frac{a_1}{d_1} = \frac{a_0}{d_0}$, then corresponding to these, $\frac{D_1 t_1}{d_1^2} = \frac{D_0 t_0}{d_0^2}$, the suffix 1 here referring to the sample heated at $T_1^0 C$ and suffix 0 referring to that at $T_0^0 C$. Therefore

1. Riemann-Weber: Differentialgleichungen der Physik, II, p. 232

2. S. Tanaka and C. Matano: Phys. Math. Soc. Japan, Proc., 12, 279 (1930)

$$D_1 = \frac{t_0}{t_1} \left(\frac{d_1}{d_0} \right)^2 D_0,$$

and if d_1 , d_0 and D_0 are known, then from the corresponding values of t_1 and t_0 we can determine D_1 . And if we know the value of D_1 at $T_1^\circ C$, we can get the coefficient D_2 at $T_2 (< T_1)^\circ C$ in the same way as above and we can get a series of values of coefficients at successively lower temperatures, without using the values of resistance near the saturation.

In such a simple case as when the same two samples are used,

$$\frac{N_1 l_1 d_1}{L_1} = \frac{N_0 l_0 d_0}{L_0}, \quad d_1 = d_0 \quad \text{and} \quad a_1 = a_0,$$

consequently

$$D_1 = \frac{t_0}{t_1} D_0.$$

Experimental part: If we take the value of R far from its saturation, then in the first approximation we can take the temperature coefficient of resistance as that of pure component metals, and the results of our preceding paper¹ can be used at once without farther experiments, and the results are reproduced here again in Fig. 1a, 1b.

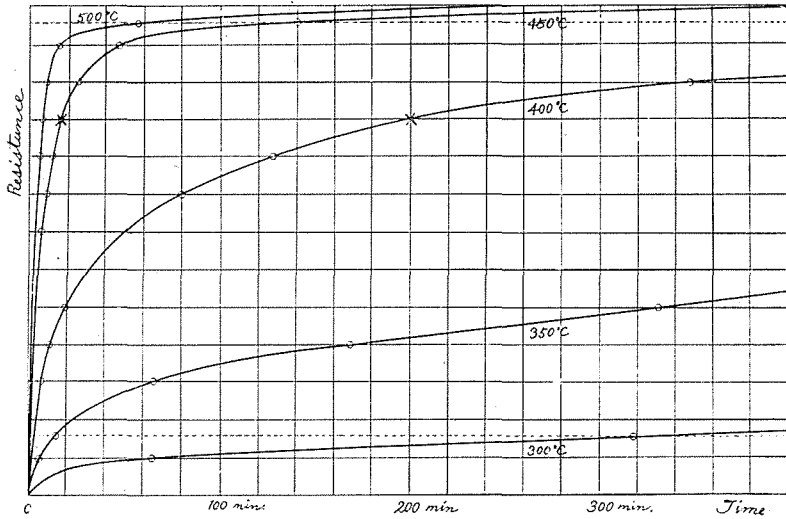


Fig. 1a Ni-Cu.

1. S. Tanaka and C. Matano: These Memoirs, 14, 59 (1931)

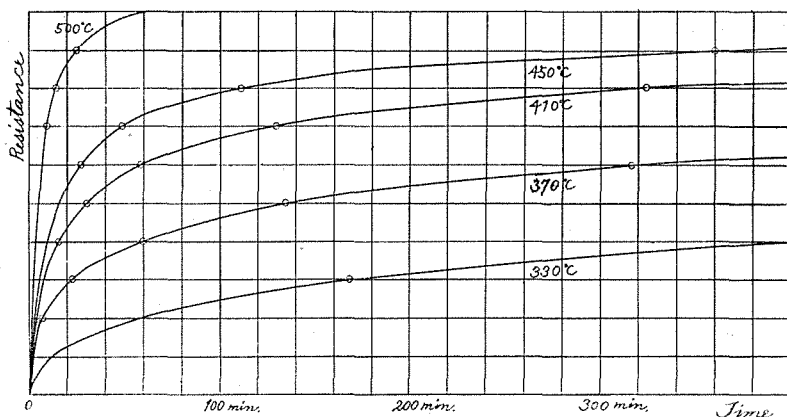


Fig. 1b Ag-Au

Here the portion of resistance due to the temperature coefficient is removed in each curve. The ordinates represent the resistance and the abscissae the time. Fig. 1a is for the *Ni-Cu* system and Fig. 1b is for the *Ag-Au* system.

For example, in Fig. 1a, let two corresponding points marked \times on the curve at 450°C and on the curve at 400°C be taken, then graphically

$$\frac{D_{400}}{D_{450}} = \frac{17.0}{200} = 8.5 \times 10^{-2},$$

where D_{450} and D_{400} show the coefficients of diffusion at 450°C and

Table I

Material	Temperature		Ratio of Diffusion Coefficients at two succes. Temps.	Ratio of Diffusion Coefficients at $T^{\circ}\text{C}$ to 500°C	Diffusion Coefficient D . cm^2/min .
	$T^{\circ}\text{C}$	$\theta^{\circ}\text{abs.}$			
Ni-Cu	500	773	3.7×10^{-1}	1	0.7×10^{-12}
	450	723	9.3×10^{-2}	3.7×10^{-1}	2.6×10^{-13}
	400	673	7.2×10^{-2}	3.4×10^{-2}	2.4×10^{-14}
	350	623	5.4×10^{-2}	2.5×10^{-3}	1.8×10^{-15}
	300	573		1.3×10^{-4}	0.9×10^{-11}
Ag-Au	500	773	1.5×10^{-1}	1	0.8×10^{-12}
	450	723	3.8×10^{-1}	1.5×10^{-1}	1.2×10^{-13}
	410	683	2.2×10^{-1}	5.7×10^{-2}	4.6×10^{-14}
	370	643	1.4×10^{-1}	1.25×10^{-2}	1.0×10^{-14}
	330	603		1.75×10^{-3}	1.4×10^{-15}

400°C. In the same way the other corresponding points marked o on the curves are taken and the values at each temperature are tabulated in Table I.

As the values¹ of D_0 at 500°C, 0.7×10^{-12} cm²./min. for the Ni-Cu system and 0.8×10^{-12} cm²./min. for the Ag-Au system are taken, then the coefficients of diffusion at lower temperatures can be obtained. They are shown in Table I in the fifth column.

Relations between Temperature and Diffusion Coefficient

J. Frenkel², from his theory of the thermal agitation in solid bodies, has shown that the absolute temperature θ is related to the coefficient of self-diffusion D in the following way,

$$D = Ae^{-\frac{a}{\theta}}, \dots\dots\dots (1)$$

where A and a are constants independent of θ , and e the base of natural logarithms. After him, W. Braunbek³, from his theory of electrolytic conduction in solid bodies, got the relation

$$D = A\theta e^{-\frac{a}{\theta}}; \dots\dots\dots (2)$$

here also A , a and e are constants. Recently W. Jost⁴ has confirmed by the chemical method that Frenkel's law (1) holds in the case of the Ag-Au system.

The author has tried to verify these laws for the Ni-Cu system and for the Ag-Au system.

Let D_0, D_1, \dots, D_n be the coefficients of diffusion at $\theta_0, \theta_1, \dots, \theta_n$ abs. and the times for determining these successively be $t'_0, t_1; t'_1, t_2; \dots; t'_{n-1}, t_n$; then

$$\begin{aligned} \frac{D_n}{D_0} &= \frac{D_1}{D_0} \frac{D_2}{D_1} \dots \frac{D_n}{D_{n-1}} = \frac{t'_0}{t_1} \frac{t'_1}{t_2} \dots \frac{t'_{n-1}}{t_n} \\ &\equiv \prod_{m=1}^n \frac{t'_{m-1}}{t_m}, \end{aligned}$$

and $\prod_{m=1}^n \frac{t'_{m-1}}{t_m}$ can be determined experimentally as shown in the

1. S. Tanaka and C. Matano, loc. cit.
 2. J. Frenkel: Zs. f. Phys., **35**, 652 (1926)
 3. W. Braunbek: Zs. f. Phys., **44**, 684 (1927)
 4. W. Jost: Zs. f. phys. Chem., **9**, 73 (1930)

preceding section. (See Table I, 4th column). If we trace curves between

$$\log_{10}\left(\frac{D}{D_0}\right) \text{ and } \frac{1}{\theta}, \text{ or } \log_{10}\left(\frac{D}{D_0}\right) - \log_{10}\theta \text{ and } \frac{1}{\theta},$$

then in both cases we get nearly straight lines as shown in Fig. 2 a, 2 b and Fig. 3 a, 3 b.

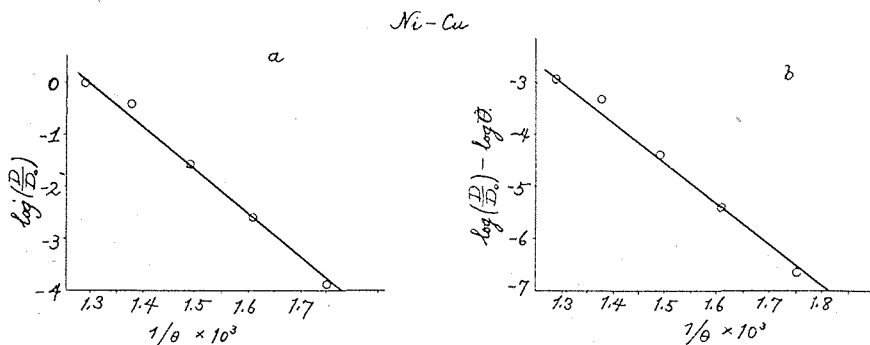


Fig. 2

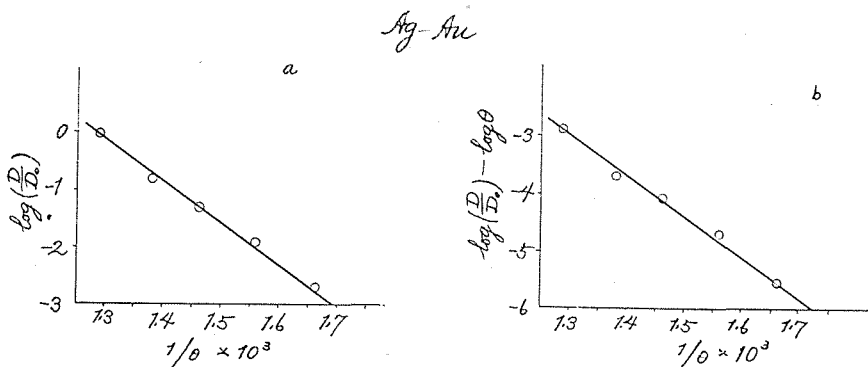


Fig. 3

So from the figures, for the *Ni-Cu* system

$$\log_{10}\left(\frac{D}{D_0}\right) = 10.50 - \frac{8.16 \times 10^3}{\theta},$$

or

$$\log_{10}\left(\frac{D}{D_0}\right) - \log_{10}\theta = 7.29 - \frac{7.19 \times 10^3}{\theta}.$$

and for the *Ag-Au* system

$$\log_{10}\left(\frac{D}{D_0}\right) = 9.70 - \frac{7.51 \times 10^3}{\theta},$$

or

$$\log_{10}\left(\frac{D}{D_0}\right) - \log_{10}\theta = 6.44 - \frac{7.24 \times 10^3}{\theta}.$$

And if the relations in the forms

$$\log_{10}\left(\frac{D}{D_0}\right) = B - \frac{a \log_{10} c}{\theta}, \quad \text{and}$$

$$\log_{10}\left(\frac{D}{D_0}\right) - \log_{10}\theta = B - \frac{a \log_{10} c}{\theta}$$

exist, then

$$\frac{D_0}{e^{-\frac{\alpha}{\theta_0}}} = \frac{D}{e^{-\frac{\alpha}{\theta}}} = A, \quad \text{and} \quad \frac{D_0}{\theta_0 e^{-\frac{\alpha}{\theta_0}}} = \frac{D}{\theta e^{-\frac{\alpha}{\theta}}} = A,$$

where A , B and a are constants independent of θ , and the formulae (1) and (2) show the results of experiments equally well.

So far the value of D_0 has not been used, but if we want to get the value of A , the value of D_0 is needed. If we use the value of D_0 which is shown in the preceding section, the formulae (1) and (2) in their logarithmic forms are given by

$$\log_e D = -3.78 - \frac{1.88 \times 10^4}{\theta}, \quad \text{and}$$

$$\log_e D = -11.2 + \log_e \theta - \frac{1.82 \times 10^4}{\theta}$$

for the *Ni-Cu* system, and

$$\log_e D = -5.54 - \frac{1.73 \times 10^4}{\theta}, \quad \text{and}$$

$$\log_e D = -12.8 + \log_e \theta - \frac{1.67 \times 10^4}{\theta}$$

for the *Ag-Au* system. Comparing these results with W. Jost's, we can see at once though the values of D are somewhat different, in each case formula (1) is confirmed.

In conclusion the author wishes to express his sincere thanks to Prof. S. Tanaka for his kind advice on this work.

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