CANADA

THE USE OF PROBABILITY PAPER FOR THE DETERMINATION OF DIFFUSION COEFFICIENTS

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by

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SYNOPSIS

A graphical method using probability paper for determination of diffusion coefficients, subject to certain boundary conditions, has been investigated in detail. This method has been analysed mathematically and previously noted solutions have been extended to the additional case of constant surface concentration.

RÉSUMÉ

On a étudié en détail un procédé graphique qui comporte l'emploi du graphique de probabilités, pour déterminer les coefficients de diffusion en deçà de certaines limites. Ce procédé a été analysé de façon mathématique et les solutions déjà acquises ont été étendues au cas supplémentaire de la concentration superficielle constante.

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In view of the considerable effort currently being directed towards the determination of diffusion coefficients in the field of metals and semiconductors, it appears worthwhile to elaborate on the properties of probability paper, which have been previously noted,(1)* that make its use attractive in this connection.

Probability paper (2) is ruled in such a way that when the relative cumulative frequency of a normal distribution is plotted as the ordinate against a linear abscissa the result is a straight line. In order to show the application of this property to the determination of diffusion coefficients, we describe the manner in which the relative cumulative frequency of a normal distribution is computed.

The frequency distribution for a normal curve may be represented by

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}$$

where σ is the standard deviation.

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*The references are listed on page 4.

The cumulative frequency (CF) to any value x is given by

$$CF = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{x} e^{-\frac{x^2}{2\sigma^2}}\, dx$$

This becomes $CF = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\frac{x}{\sqrt{2}\,\sigma}} e^{-z^2} dz$ if $z^2 = \frac{x^2}{2\,\sigma^2}$,

which may be expressed as

$$CF = \frac{1}{2}\left[\frac{2}{\sqrt{\pi}} \int_{-\infty}^{0} e^{-z^2} dz \pm \frac{2}{\sqrt{\pi}} \int_{0}^{\frac{x}{\sqrt{2}\,\sigma}} e^{-z^2} dz\right]$$

$$= \frac{1}{2}\left[1 \pm \operatorname{erf} \frac{x}{\sqrt{2}\,\sigma}\right]$$

where the $\pm$ sign refers to positive or negative values of x measured from the mean.

The relative cumulative frequency (RCF) may be obtained by dividing the cumulative frequency by the sum of all frequencies, thus

$$RCF = \frac{\frac{1}{2}\left[1 \pm \operatorname{erf} \frac{x}{\sqrt{2}\,\sigma}\right]}{\frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-\frac{x^2}{2\sigma^2}} dx}$$

$$= \frac{1}{2}\left[1 \pm \operatorname{erf} \frac{x}{\sqrt{2}\,\sigma}\right] \qquad .. \ 1)$$

since the denominator is 1.

The similarity to the diffusion relations when there is an extended initial distribution is apparent.[3] In this latter case the solution of the diffusion equation may be written:

$$\frac{C}{C_o} = \frac{1}{2}\left[1 \mp \operatorname{erf}\frac{x}{\sqrt{4Dt}}\right] \qquad .. \ 2)$$

where $\frac{C}{C_o}$ is the relative concentration at distance x (measured from the initial interface) and after a time t,

D is the diffusion coefficient, and

the sign $\mp$ refers to positive and negative values of x respectively.

We see, then, that equations 1) and 2) represent curves which are the mirror image of each other. Hence, when the relative concentration is plotted as the ordinate on probability paper and the penetration as the abscissa, the result will be a straight line.

In order to illustrate this application, the relative concentration as a function of penetration is plotted on linear graph paper in Fig. 1 and the corresponding information is presented on probability paper in Fig. 2. In the latter figure, that portion of the abscissa subtended by the section of the curve lying between 16% and 50% (or 50% and 84%) is the standard deviation, which is equal to $(2Dt)^{\frac{1}{2}}$. The manner in which $(2Dt)^{\frac{1}{2}}$ is obtained is illustrated in Fig. 2, and from this quantity the diffusion coefficient may be obtained.

The extension of this graphical technique to the solution of the diffusion equation for a semi-infinite medium with a constant boundary concentration would be very desirable. The solution of the diffusion equation under these conditions is:

$$\frac{C}{C_o} = 1 - \text{erf}\,\frac{x}{\sqrt{4Dt}} \qquad ..\ 3)$$

However, the problem of determining the concentration C_o still remains, and whereas approximations may be obtained graphically this procedure is liable to serious error. If one does estimate C_o in this manner, an error in C_o would be indicated by a curve, rather than a straight line, when $\frac{1}{2}\,\frac{C}{C_o}$ is plotted against penetration on probability paper.

REFERENCES

1. W.A. Johnson, Diffusion Experiments on a Gold-Silver Alloy by Chemical and Radioactive Tracer Methods. Transactions A.I.M.E. 147, 331 (1942).

2. Keuffel and Esser Company No. 359-23, for example.

3. J. Crank, The Mathematics of Diffusion (Oxford University Press, London, 1956), p. 12.

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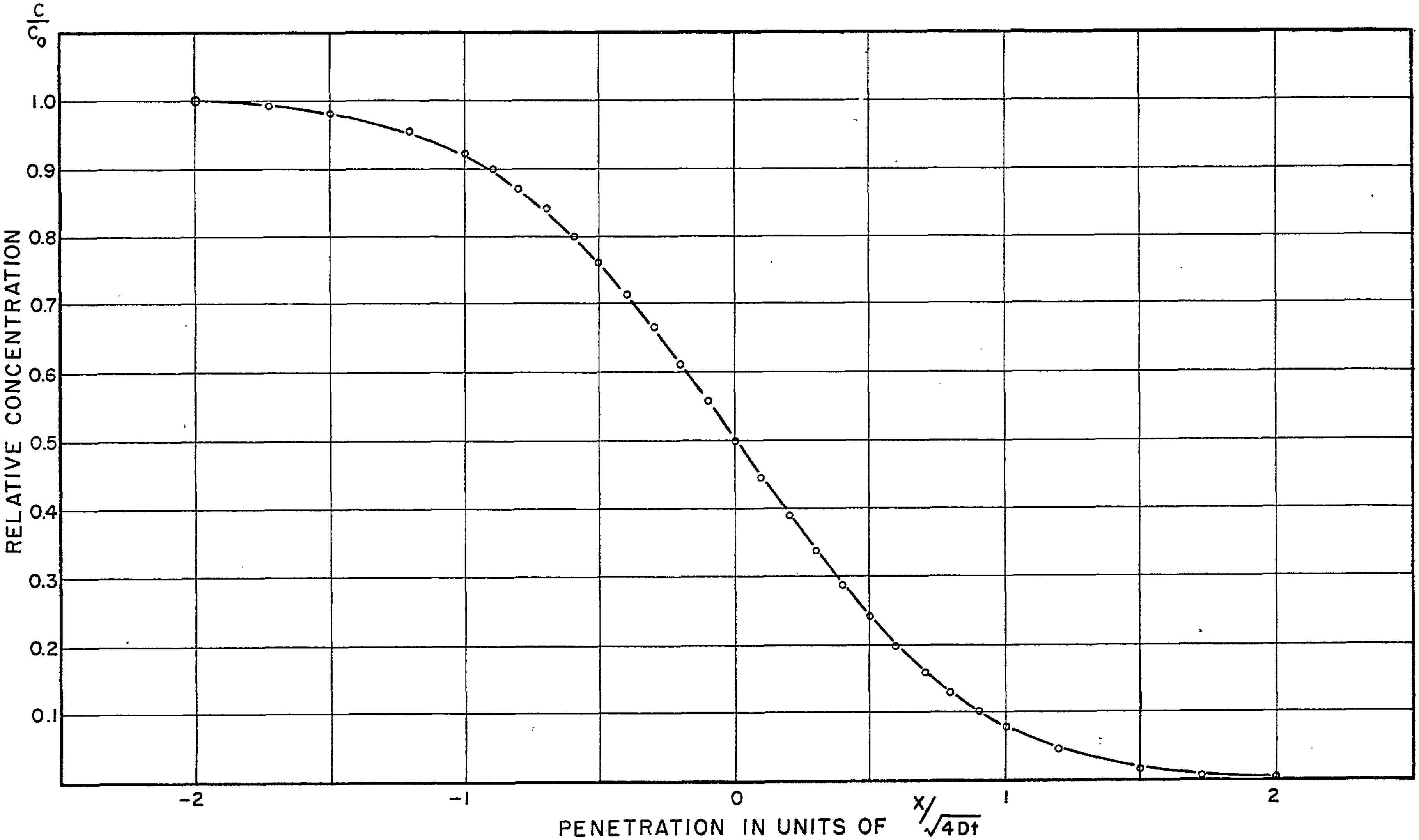

Figure 1. Normalized penetration curve plotted on square section graph paper. The zero on the abscissa corresponds to the initial interface.