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**SLAB-DIFFUSION APPROXIMATION FROM
TIME-CONSTANT-LIKE CALCULATIONS**

R. W. Johnson

December 1976

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**OAK RIDGE Y-12 PLANT
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ABSTRACT

Two equations were derived which describe the quantity and any fluid diffused from a slab as a function of time. One equation is applicable to the initial stage of the process; the other to the final stage. Accuracy is 0.2% at the one point where both approximations apply and where accuracy of either approximation is the poorest.

Characterizing other rate processes might be facilitated by the use of the concept of NOLOR (normal of the logarithm of the rate) and its time dependence.

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SUMMARY

The two-stage approximation described in this report is now in routine use at the Oak Ridge Y-12 Plant for the analysis of slab diffusion data. It has proven to be extremely useful for characterizing diffusion processes, even in cases where the age of the process at the start of measurements is unknown.

During the initial stage of slab diffusion (0 to 50.74% completion), the product of the quantity diffused times the rate of diffusion is a constant, M . During the final stage of slab diffusion (from 50.74 to 100% completion), the ratio of the quantity yet to be diffused to the rate of diffusion is a constant, β_{∞} .

The final stage, β_{∞} , is the time constant equal to the square of the thickness of the slab divided by $\pi^2 D$, where D represents the diffusion coefficient. The time constant is the ratio of the rate divided by the rate at which the rate decreases with time. The name "NOLOR" (normal of the logarithm of the rate) is suggested for this ratio when it is not constant. During the initial stage, NOLOR is equal to twice the age of the diffusion process.

The slab diffusion approximation is based on a NOLOR-versus-time relationship derived from exact infinite-series expressions by numerical calculations, using a computer. It is suggested that the NOLOR-versus-time relationship should be useful in characterizing other rate processes.

INTRODUCTION

Diffusion is a process of great practical importance in many industrial situations. Frequently, such industrial processes may be defined mathematically by the equations for diffusion out of a slab, such as in the vacuum degassing of metals. However, obtaining an exact mathematical description of these processes is often a formidable task. The following presentation describes a two-stage approximation that has been developed to determine the diffusion parameters of several processes of interest at the Oak Ridge Y-12 Plant.^(a) The concept of the time dependence of the time normal of the logarithm of the rate should be useful in characterizing other rate processes.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Energy Research and Development Administration.

SLAB-DIFFUSION APPROXIMATIONS

NOLOR

NOLOR (normal of the logarithm of the rate) is a time-constant-like parameter.

Many rate processes may be described by an equation of the form:

$$R = \pm \frac{dx}{dt} = kx^N \quad (1)$$

For an exponential rate process ($N = 1$), a plot of the logarithm of the rate versus time will be a straight line. The normal to this line is positive for an exponential decay process and is usually called a "time constant". In many other rate processes that obey Equation 1, a plot of the logarithm of the rate versus time will yield a curve rather than a straight line. For these processes, the instantaneous normal, NOLOR or β , is a linear function of time. At any time, t , NOLOR (β) is the negative reciprocal of the instantaneous slope of the $\log R$ -versus-time curve, and may be evaluated by the identity:

$$\beta = \frac{-1}{\frac{d}{dt} \log R} = \frac{R}{-\frac{dR}{dt}} \quad (2)$$

Furthermore, if Equation 1 is valid or can be considered a good approximation over the time interval of interest, then:

$$\beta = + \frac{x^{1-N}}{Nk} = \frac{x}{N \left(-\frac{dx}{dt} \right)} \quad (3)$$

Using Equations 1 and 3, it is apparent that the time dependence of β , that is $d\beta/dt$, can be calculated if N for a particular rate process is known. Equally important is the observation that for rate processes where N is not known, it may be found from an experimental determination of $d\beta/dt$, using the identity:

$$\frac{d\beta}{dt} = \frac{N-1}{N} \quad (4)$$

For example, if a process is found to have a $d\beta/dt$ of zero, then $N = 1$, as in the case of radioactive decay, the discharge of an electrical capacitance through a resistance, or a simple first-order chemical reaction. An example of a negative $d\beta/dt$ is a freely falling body, where the velocity, dx/dt , is equal to the constant timer, the $\sqrt{x}$. In this case, $d\beta/dt$ is equal to a -1 and $N = 1/2$. For a parabolic process, such as the corrosion of a metal with the

formation of a protective film, the corrosion rate, dx/dt , is inversely proportional to the film thickness, x . In this case, $d\beta/dt$ is equal to $+2$ and N equals -1 . It should be noted that for every rate process which obeys Equation 1, $d\beta/dt$ is a constant, providing the value of N remains constant. Thus, if experimental results show that a plot of β versus time has a change in slope, it may be directly inferred that the order (N value) of the rate process has changed.

Slab Diffusion

A commonly encountered rate process in industry is diffusion from a slab or membrane, such as in the vacuum degassing of metal plates. Normally, the only experimental data available in this case are measurements of gas evolution rates or quantities versus time. This process can be described by the mathematical model for diffusion out of a slab, and one form of the exact solution⁽¹⁾ is:

$$Q = Q_{\infty} \left[1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} e^{-\frac{(2j+1)^2 t}{\beta_{\infty}}} \right] \quad (5)$$

where:

Q represents the quantity diffused at time, t ,

Q_{∞} the total available quantity to be diffused, and

$\beta_{\infty} = h^2/\pi^2 D$, the ultimate time constant (in this expression, h represents the slab thickness, with diffusion out both sides, and D the diffusion coefficient).

If t is large when compared to β_{∞} , all but the first term of the infinite series can be neglected. If t is very small compared to β_{∞} , then Q varies with the square root of time. Although these two facts are well known, it does not appear to have been previously demonstrated that, at the point $t = \beta_{\infty}/2$, both approximations are satisfactory for many practical purposes.

Using a computer, numerical calculations were performed to find NOLOR, expressed as β/β_{∞} , as a function of time, expressed as t/β_{∞} . Values of t/β_{∞} ranging from 0.01 to 2 were used. From Equations 2 and 5, it is apparent that NOLOR (β) for this diffusion process is the ratio of dQ/dt to $-d^2Q/dt^2$. The ratio β/β_{∞} is then:

$$\frac{\beta}{\beta_{\infty}} = \frac{\sum_{j=0}^{\infty} e^{-\frac{(2j+1)^2 t}{\beta_{\infty}}}}{\sum_{j=0}^{\infty} (2j+1)^2 e^{-\frac{(2j+1)^2 t}{\beta_{\infty}}}} \quad (6)$$

The curve in Figure 1, where β/β_∞ is plotted versus t/β_∞ , shows the results of the calculations. It can be seen that the slope of the curve, $d\beta/dt$, is equal to a +2 in the early portion ($t < \beta_\infty/2$), and is equal to zero in the latter portion ($t > \beta_\infty/2$). In the examples given previously on the discussion of various rate processes, it was pointed out that a $d\beta/dt$ of +2 is characteristic of a parabolic ($N = -1$) rate process, and that a $d\beta/dt$ of zero

Figure 1. NORMAL OF THE LOGARITHM OF THE RATE (NOLOR) VERSUS TIME.

is characteristic of an exponential ($N = +1$) rate process. These observations provide the basis for the following two-stage approximation for this diffusion process: $d\beta/dt$ is +2 from zero time to $t = \beta_\infty/2$, and is zero thereafter. This thesis implies that the initial stage of slab diffusion can be approximated by an $N = -1$ process and the final stage as an $N = +1$ process. These approximations can be stated mathematically as:

$$\frac{dQ}{dt} = \frac{M}{Q} \quad (7)$$

$$Q = \sqrt{2Mt}, \text{ and} \quad (8)$$

$$\text{Rate} = \frac{dQ}{dt} = \sqrt{\frac{M}{2t}} \quad (9)$$

for the initial stage; for the final stage the mathematical statements are:

$$-\frac{d(Q_\infty - Q)}{dt} = \frac{Q_\infty - Q}{\beta_\infty} \quad (10)$$

$$Q_\infty - Q = \frac{8 Q_\infty}{\pi^2} e^{-t/\beta_\infty} \quad , \text{ and} \quad (11)$$

$$\text{Rate} = -\frac{d(Q_\infty - Q)}{dt} = \frac{8 Q_\infty}{\pi^2 \beta_\infty} e^{-t/\beta_\infty} \quad (12)$$

For the initial stage, the product of the rate times the quantity is equal to a constant, M . Reference to Equations 5 and 7 shows that M is defined mathematically as:

$$M = Q \frac{dQ}{dt} = \frac{8 Q_\infty^2}{\pi^2 \beta_\infty} \left[1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} e^{-\frac{(2j+1)^2 t}{\beta_\infty}} \right] \left[\sum_{j=0}^{\infty} e^{-\frac{(2j+1)^2 t}{\beta_\infty}} \right] \quad (13)$$

If the quantities in brackets in Equation 13 are summed to convergence, the product is found to be numerically equal to $1/\pi$ at small values of t/β_∞ . Even at $t = \beta_\infty/2$, the product is numerically equal to $0.984/\pi$. Thus, to an excellent approximation, the rate constant (M) for the initial diffusion stage may be defined as:

$$M = \frac{8 Q_\infty^2}{\pi^2 \beta_\infty} \left[\frac{1}{\pi} \right] = \frac{8 Q_\infty^2}{\pi^3 \beta_\infty} \quad (14)$$

Using this definition for M, the expression for Q (Equation 8) is accurate to better than one part in one million if t/β_∞ is 1/7 or less, and better than two parts in one thousand if $t = \beta_\infty/2$. A similar accuracy may be obtained from Equation 11 for $Q_\infty - Q$ when t equals $\beta_\infty/2$. The error in either rate expression (Equations 9 and 12) approaches a maximum of less than 2% when t equals $\beta_\infty/2$.

In practice, measurements are usually made of either incremental quantity—diffused or diffusion rate as a function of time. If an analysis of the data indicates that all measurements were made during the initial stage of the diffusion process, then the rate constant (M), the total quantity diffused both during and before the test, and the actual age of the diffusion process may be calculated. The future diffusion behavior cannot be predicted confidently since neither β_∞ nor Q_∞ can be determined. Maximum Q versus time values can be calculated by assuming that the diffusion process remains in the initial stage for the entire time of interest.

If an analysis of the data indicates that the measurements included portions of both the initial and final stages of the diffusion process, then not only M, total quantity, and real age may be determined, but also the initial quantity, Q_∞ , and the time constant, β_∞ , may be calculated. This provision makes it possible to have a complete description of both past and future diffusion behavior. Furthermore, the diffusion coefficient, D, may be determined if the thickness of the slab under study is known.

Finally, if an analysis of the data should indicate that all measurements were made during only the final stage of diffusion, then the time constant, β_∞ , and the remaining quantity to be diffused, $Q_\infty - Q$, may be found. Furthermore, future diffusion behavior may be confidently predicted. The diffusion coefficient, D, may be calculated providing the slab thickness is known. However, neither the initial total quantity to be diffused, Q_∞ , nor the actual age of the diffusion process may be determined in this case.

The two-stage approximation described here is now in routine use at Y-12 for the analysis of slab diffusion data. It has proven to be extremely useful for characterizing diffusion processes, even in cases where the age of the process at the start of measurements is unknown.

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