

**Extraction of Diffusion Constants from Data**

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## Introduction

The author and colleagues are studying diffusion of materials in solids. They are interested in being able to extract information about the diffusive characteristics from the data. The two characteristics of most importance are the total content of the sample and the diffusivity. Although diffusion from a number of simple one-, two-, and three-dimensional shapes can be derived from well-known analytical solutions (most of which have been available in the literature for decades if not centuries), the author is not aware of analytical solutions for more general shapes. Further, even for shapes for which a solution is known, if the only information one has is measurements of quantity change or rate from a sample, it may not be easy to determine either the original content or the diffusivity.

The objectives of the study documented here are two-fold. First, to determine how to find the total content and diffusivity from data on shapes for which the solution is known. Second, to infer a theory for more complex shapes.

## The General Solution for Time-dependent Diffusion in Regular Solids

Scientists and mathematicians have studied the problem of time-dependent diffusion in a solid and the mathematically identical problem of diffusion of heat in a solid for centuries. The standard texts by Carslaw and Jaeger<sup>i</sup> and Crank<sup>ii</sup> show numerous results that represent the tip of the iceberg in this subject. The author has examined analytical solutions for the problem in which the initial concentration of the diffusing species within the solid is constant and there is a sudden change in the concentration at the surface at some time. He has examined this situation for the infinite slab, the infinite cylinder, the cylinder of finite length, and a rectangular parallelepiped of infinite length. For all of these geometries, the solutions for quantity and rate vs time are infinite series or products of infinite series. However, there are useful approximations to the solutions for quantity and rate vs time at early and late times that will be described in the next two paragraphs.

There is an initial stage for which the change in content and the rate of change may be approximated by the simple one-dimensional solution for a semi-infinite medium multiplied by the surface area. This initial solution is as follows:

$$\Delta Q_t \approx 2C_0 A \sqrt{\frac{Dt}{p}} \quad (\text{Equation 1})$$

and

$$\dot{Q}_t \approx -C_0 A \sqrt{\frac{D}{pt}} \quad (\text{Equation 2})$$

where  $DQ$  is the change in content of the diffusing species from time zero,  $\dot{Q}$  is the rate of change of the diffusing species,  $A$  is the surface area of the object,  $C_0$  is the initial concentration of the diffusing species,  $D$  is the diffusivity (which is assumed constant in space and time), and  $t$  is time measured from when the surface concentration is changed. As has already been stated, the objectives of this work include finding the diffusivity and the total initial content of the diffusing species, which is the initial concentration multiplied by the volume of the object. Examination of Eqs. 1 and 2 indicates that the most information that can be extracted from the initial solution is the product  $C_0\sqrt{D}$ . The author sees no way to extract either  $C_0$  or  $D$  independently from this approximation.

For large values of time, there is another pair of approximations that appear. The next three equations are written to show a generalized form appropriate for all the geometries studied and perhaps also for more general geometries. These are as follows:

$$\Delta Q_F \approx Q_\infty \left\langle 1 - f \exp\left\{-\frac{t}{\mathbf{t}}\right\} \right\rangle \quad (\text{Equation 3})$$

and

$$\dot{Q}_F \approx -Q_\infty \frac{f}{\mathbf{t}} \exp\left\{-\frac{t}{\mathbf{t}}\right\} \quad (\text{Equation 4})$$

where  $Q_\infty$  is the initial content of the sample ( $C_0$  times volume) and  $\mathbf{t}$  is a time constant given by

$$\mathbf{t} = 1/\{D\mathbf{g}\} \quad (\text{Equation 5})$$

The author refers to this late time set of approximations as the “declining exponential tail” of the diffusion process. The factor  $f$  is a constant dependent on the geometry. Each of the geometries the author has studied has a different value for this. No doubt, there would be yet other values of  $f$  for more complex geometries. The value of  $f$  for the finite length cylinder is that for the infinite length cylinder multiplied by that for the 1-D slab. The value for the rectangular parallelepiped of infinite length is the square of that for the 1-D slab. The factor  $\mathbf{g}$  is dependent on both the geometry and the characteristic lengths of the respective elements (the characteristic lengths are the thickness for the 1-D slab and the radius for the cylinder). The factor  $\mathbf{g}$  for 1-D geometries (1-D slab and infinite length cylinder) has the form of a constant that is dependent on the geometry divided by the square of the characteristic length. The factor  $\mathbf{g}$  for the 2-D geometries is the sum of the two values for the 1-D geometries that make up the 2-D geometries. It is worth noting that, for two objects that are geometrically similar (i.e. have the same shape and the same ratios of characteristic lengths, but have different sizes), the values of  $\mathbf{g}$  are therefore dependent on the reciprocals of the squares of the respective characteristic lengths.

## Extraction of Diffusion Parameters from Data

In principle, one can extract both  $D$  and  $Q_\infty$  from outgas rate data using the declining exponential approximations from Eqs. 4 and 5. In practice, there are difficulties to overcome. First, one would expect that much data will be quantity change data, not rate data. The author has not found a way of extracting  $Q_\infty$  and  $\mathbf{t}$  directly from the declining exponential fit for quantity change, Eq. 3, except by using curve fit algorithms. However, using a spreadsheet, he has

demonstrated that one can do this extraction using a finite difference form of the rate calculated from successive points of quantity change data. Suppose one has a set of  $N$  values of quantity change at  $N$  times. The individual data values are  $DQ_n$  ( $1 \leq n \leq N$ ) and  $t_n$ . The rate and average time for the interval between  $t_{n+1}$  and  $t_n$  are approximated by finite differences as follows:

$$\left. \frac{dQ}{dt} \right|_{n+1/2} \approx - \frac{\Delta Q_{n+1} - \Delta Q_n}{t_{n+1} - t_n} \quad (\text{Equation 6})$$

and

$$\bar{t}_{n+1/2} \approx \frac{t_{n+1} + t_n}{2} \quad (\text{Equation 7})$$

There are  $N-1$  values of finite difference rate and average time. From Eq. 4, it may be seen that a plot of  $\ln(|rate|)$  vs  $t$  will asymptote to a straight line as time grows large. This is demonstrated in Fig. 1, which is a semi-log plot of the rate (normalized by dividing by  $Q_{\infty}/t$ ) for a cylinder of finite length (length/diameter  $\approx 1$ ) vs the time (normalized by dividing by  $t$ )\*. The slope of this line is  $-1/t$ . Using quantity change values calculated from the product of infinite series solution for this cylinder, the author has demonstrated that the plot of  $\ln(|dQ/dt|_{n+1/2})$  vs  $\bar{t}_{n+1/2}$  will follow the plot of  $\ln(|rate|)$  as calculated from the infinite series vs  $t$  to an accuracy that is smaller than the width of the plotting line on the graph (an error of a few percent). Therefore, from a least squares fit of  $\ln(|dQ/dt|_{n+1/2})$  vs  $\bar{t}_{n+1/2}$ , one can also extract  $t$ . If one knows  $t$  and  $g$ , one can extract  $D$ . The multiplier for the fit of  $\ln(|rate|)$  vs  $t$  will give the product  $Q_{\infty}f/t$ . Therefore, given an extracted value of  $t$  and knowing the value of  $f$  for the geometry, one can calculate  $Q_{\infty}$ .

No experiment is ever run to completion. Furthermore, at some level of quantity change, the rates begin to lose a significant level of accuracy because the measuring apparatus has only so much sensitivity. For that matter, if one is measuring rate directly, one must still contend with limited sensitivity of the instruments. So, it is necessary to examine how close to completion (i.e., removal of all the diffusing species) one must run the diffusion experiment before one can get reliable estimates of  $D$  and  $Q_{\infty}$ . Figure 2 shows the normalized rate vs the fraction of the outgas completed for the last 30% of the run for the cylinder of finite length (length/diameter  $\approx 1$ ). As one can see, there begins to be a visible deviation of the late time rate given by Eq. 4 from the rate given by the infinite series for  $Q/Q_{\infty} < \sim 0.8$ . As one may also see, by  $Q/Q_{\infty} \approx 0.999$ , the rate is down  $\sim 2$  orders of magnitude from what it was for  $Q/Q_{\infty} = 0.7$ . If the precision of the quantity change measurement is 1 part in 10,000, then some significant scatter should start entering the rate calculation by  $Q/Q_{\infty} \approx 0.999$ . The author has done numerical experiments using the regression analysis tool of EXCEL to do a least squares fit on  $\ln(|dQ/dt|_{n+1/2})$  vs  $\bar{t}_{n+1/2}$  to find the estimates for  $Q_{\infty}f/t$  and  $1/t$  if one has data for  $Q/Q_{\infty} = 0.9-0.999$ ,  $0.8-0.9$ , and  $0.7-0.8$ . For the range  $0.9-0.999$ , the errors in  $Q_{\infty}$  and  $t$  are 0.6% and 0.5% respectively. For the range  $0.8-$

\* There is quite a bit of information to be had from this plot. One thing to note is that the curve of initial rate vs time never crosses the curve of late time rate vs time. This is true for all geometries for which the author has derived analytical solutions. It can be show that, for the 1-D slab, the smallest difference between the two different approximations for the rate is  $\sim 3\%$ . The difference is larger for more complex geometries. On semi-log plots, the curves for the two different approximations are tangent to one another at  $t=\bar{t}$ . This has been proven for all the geometries for which the author has derived analytical solutions.

0.9, the errors are 10.9% and 6.3%. For 0.7-0.8, the errors are 28.3% and 26.3%. While the errors in 0.8-0.9 are acceptable, for any value lower than 0.8, the errors become too large.

Experiments rarely start at the mathematical initial condition. Instead, there has usually been some diffusion before the beginning of the experiment. Among the things motivating this study is a desire to be able to extract the solubility of the diffusing species in the solid and also to be able to determine how much diffusing material was in the sample at the beginning of the experiment. If the experiment starts when the previous diffusion has progressed a small enough amount that the quantity change and rate follow the initial root(time) forms and continues to the declining exponential stage, then it should be possible to recover the solubility. Using a method described in the next paragraph, it should also be possible to estimate the total quantity present at the beginning of the experiment. However, if the experiment starts after enough diffusion has taken place that the initial solution is no longer applicable, matters are more difficult. Space does not allow the author to show the details of his study of this situation. However, he has been able to demonstrate that, for an experiment that starts after the solution begins to deviate from the root(time) approximations (for the finite cylinder of  $L/D \approx 1$ , the deviation of a log-log plot of rate vs time from a slope of  $-1/2$  becomes noticeable after  $t \approx 0.005t$ ), it does not seem to be possible to recover the solubility from the declining exponential approximations. In fact, under such conditions, the value of  $Q_{\infty}$  inferred from the late time fit represents neither the value from the mathematical initial condition (solubility multiplied by sample volume) nor the content at the beginning of the experiment. The inferred value of  $Q_{\infty}$  is lower than the mathematical initial value, but higher than the amount of diffusing material present at the beginning of the experiment.

There is a viable and quite straightforward alternate approach to calculating the amount of diffusing material present in the sample at the beginning of the experiment. Simply extrapolate the declining exponential outgas rate to infinite time, integrate the result, and add the quantity change measured during the experiment. The details are as follows: Suppose that for some time  $t_M$ , one has a measured value of quantity change since the beginning of the experiment that is  $\Delta Q_M$ . Suppose one also has a value of outgas rate at  $t_M$  that I will call  $\dot{Q}_M$  together with a value for  $t$ . One calculates the total amount of diffusing material, which I will call  $\Delta Q_{max}$  as follows:

$$\Delta Q_{max} = \Delta Q_M + \int_{t_M}^{\infty} \dot{Q}_M \exp[-(t - t_M)/t] dt = \Delta Q_M + \dot{Q}_M t \quad (\text{Equation 8})$$

## Extension to More General Shapes

For objects for which there is no analytical solution, one needs to find the geometric factors  $g$  and  $f$ , particularly  $g$  which is necessary to extract  $D$  from the estimated value of  $t$ . One way to extract these factors is to do an experiment on the object of interest under conditions for which the diffusivity is known. An alternate is to do a finite difference calculation of diffusion in this object. It is not necessary to have the test or calculated object have the same dimensions as that of interest as long as they are geometrically similar. As was noted earlier,  $f$  is independent of the dimensions and  $g$  is proportional to the reciprocal of the square of the characteristic dimension.

## Conclusion

A method for extracting diffusivity and total diffusing material content from quantity change and/or rate data has been outlined. The accuracy of the method has been examined for one particular geometry for which an analytical, product of infinite series solution is known. A method has been suggested for extending this process to geometries for which no analytical solution is known.

## References

- <sup>i</sup> Carslaw, H. S., and J. C. Jaeger, *Conduction of Heat in Solids*, Second Edition, Oxford University Press, 1959.
- <sup>ii</sup> Crank, J., *The Mathematics of Diffusion*, Oxford University Press, 1956.

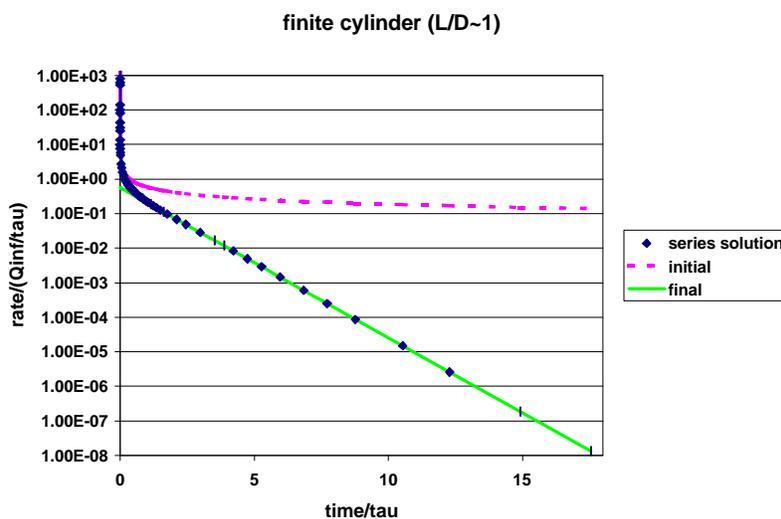


Figure 1. Normalized Outgas Rate vs Normalized Time for Finite Length Cylinder

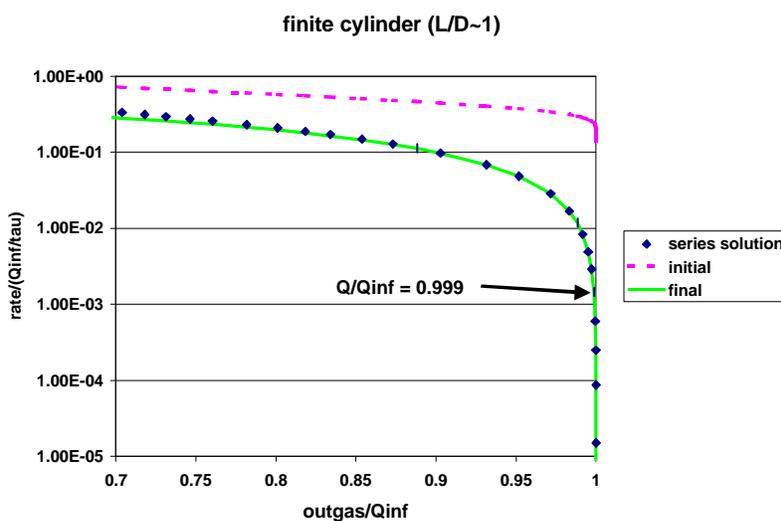


Figure 2. Normalized Outgas Rate vs Normalized Outgas for Finite Length Cylinder