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CHARACTERIZATION OF THE "SHORT TIME" IN GASEOUS DIFFUSION ANALYSES

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The diffusion of gases in glasses has been studied extensively over the past half century. The diffusion process is expressed by Fick's Second Law

$$\frac{dC}{dt} = DV^2C \quad (1)$$

where C is the concentration of gas molecules in the glass. The saturation concentration of gas in glass can be expressed by

$$C = SP_e \quad (2)$$

where S = solubility, C = concentration, P_e = external pressure. The solution to Fick's Second Law for finite solids of thickness d and pressure differential ΔP is ¹

$$\frac{dP}{dt} = \frac{ADS}{Vd} \Delta P \left\{ 1 + \sum_{m=1}^{\infty} 2 \cos m\pi \exp (-m^2\pi^2Dt/d^2) \right\} \quad (3)$$

where P = pressure at the low pressure side of the membrane, A = membrane area, S = solubility, V = volume, D = diffusivity. Rogers et al.¹ have discussed the application of a transformation formula to the right side

of the above equation which results in

$$\frac{dP}{dt} = \frac{2AS\Delta P}{V} (D/\pi t)^{1/2} \sum_{m=0}^{\infty} \exp[-(d^2/4Dt)(2m+1)^2]. \quad (4)$$

The inverted placement of t causes the exponential to converge rapidly for small values of t . At small values of t all but the first term in the series can be neglected and Eq. (4) can alternatively be expressed by multiplying by $t^{1/2}$ and taking the natural logarithm of both sides

$$\ln \left(t^{1/2} \frac{dF}{dt} \right) = \ln \left[\left(\frac{2AS\Delta P}{V} \right) \left(\frac{D}{\pi} \right)^{1/2} \right] - d^2/4Dt \quad (5)$$

By plotting the quantity on the left hand side versus $1/t$ a straight line is obtained for small values of t , thus enabling the calculation of D , the diffusion coefficient. In methods where a mass spectrometer is used instead of monitoring the pressure change with time, Eq. (5) can be modified to²

$$\ln \left(t^{1/2} \frac{dQ}{dt} \right) = \ln \left[2AS\Delta P \left(\frac{D}{\pi} \right)^{1/2} \right] - d^2/4Dt \quad (6)$$

since

$$\frac{dQ}{dt} = V \left(\frac{dP}{dt} \right), \text{ where } \frac{dQ}{dt} = \text{flow rate}. \quad (7)$$

For this type of analysis it will be necessary to characterize the "relative time-frame" in which the short time solution produces reliable results with respect to the diffusion coefficient.

Let

$$\frac{d^2}{4Dt} = x \quad (8)$$

then Eq. (4) can be expressed as

$$\frac{dP}{dt} = \frac{2AS\Delta P}{V} \left(\frac{D}{\pi t} \right)^{1/2} \left(e^{-x} + e^{-9x} + e^{-25x} + e^{-49x} \dots \right).$$

The problem is to find the point in time, t , where the second term in the series contribution is small ($<1\%$) compared to that of the first term to the total flow. The limit of 1% as the tolerance where the short time solution would produce a straight line was chosen arbitrarily. This figure of 1% was considered as a reasonable limit because it is well below the level of experimental error and limit of resolution of most equipment in these types of experiments. In other words it would be considered legitimate to truncate the series if the contribution of the 2nd through ∞ terms in the series was less than 1% that of the first.

Assume that the contribution of those terms after the 2nd is negligible (this will be shown valid, later), thus

$$e^{-9x} < .01e^{-x} \quad (10)$$

for less than 1% contribution by the $2 \rightarrow \infty$ terms in the series. Then

$$x > .575 \quad (11)$$

substituting into Eq. (8)

$$\frac{d^2}{4Dt} > .575 \quad (12)$$

When

$$t < \frac{d^2}{2.3D} \quad (13)$$

(time interval of experiment = t , d = sample thickness, D = diffusivity) the contribution of the second term in the series will be less than 1% that of the first. A check back on the assumption that the rest of the terms in the series are negligible shows (using the same type of analysis) that when the second term is 1% of the first, the third is .0001% of the first. In diffusion experiments of this type, one can now determine the range of validity of the short time approximation.

In applying this analysis to diffusion coefficient determinations, one must know, D , in order to determine the valid time range of the analysis. Since D and t in Eq. (13) are both unknowns, an iterative method has been devised in order to apply the analysis in determining D 's. If one obtains a plot (at constant temperature) for "long times," the contribution of the second through ∞ terms becomes noticeable and the linear plot required by Eq.(6) becomes curved, Fig. 1. To find which data points are in the "short-time" range, one can fit all the data points to a least squares line and determine D , then obtain t by using Eq. (13). All data points which are greater than t are discarded and the

remaining are fit to another least squares line. This process is repeated until all data points are less than t when fitted with that least squares line to obtain D . This will then indicate that the proper D has been obtained for a particular temperature. It must be emphasized that, for a given sample (diffusion membrane), the maximum time limit for the validity of short time analysis, decreases with increasing temperature, $D \propto T$ (temperature):

$$t \propto \frac{1}{T}.$$

This analysis has been applied to the diffusion of He in SiO_2 (Fictive Temp. 1200°C , Water (OH) Content = zero, $T = 158^\circ\text{C}$. Flow rate measured as a function of time.

1st Iteration 25 data points, 9 secs to 249 secs

(Fig. 2) $D = 2.32 \times 10^{-7} \text{ cm}^2/\text{sec}$, $t = 94 \text{ secs}$

2nd Iteration 14 data points (exclude those above 94 secs), 9 secs to 84 secs

(Fig. 3) $D = 2.97 \times 10^{-7} \text{ cm}^2/\text{sec}$, $t = 73 \text{ secs}$

3rd Iteration 13 data points from 9 secs to 69 secs

(Fig. 4) $D = 3.08 \times 10^{-7} \text{ cm}^2/\text{sec}$, $t = 71 \text{ secs}$

The D from the 3rd iteration is the correct value because $t > t_{\text{experiment}}$ (69 secs).

Thus it can be seen that care must be taken in applying the "short time" analysis because erroneous values for diffusivities are obtained if experimental data beyond the range of validity are included.

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1. W. A. Rogers, R. S. Buritz and D. Alpert, "Diffusion Ccefficient, Solubility and Permeability for Helium in Glass," J. Appl. Phys. 25 [7] 868 (1954).
2. V. O. Altemose, "Helium Diffusion Through Glass," J. Appl. Phys. 32 [7] 1309 (1961).

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FIGURE CAPTIONS

- Fig. 1. Plot of the $\ln (t^{1/2} \frac{dQ}{dt})$ vs $\frac{1}{t}$ for long times where t = time and $\frac{dQ}{dt}$ is the flow rate in atoms/sec.
- Fig. 2. Plot of $\log (t^{1/2} \frac{dQ}{dt})$ vs $\frac{1}{t}$ for He in SiO_2 at 158°C , first iteration.
- Fig. 3. Plot of $\log (t^{1/2} \frac{dQ}{dt})$ vs $\frac{1}{t}$ for He in SiO_2 at 158°C , second iteration.
- Fig. 4. Plot of $\log (t^{1/2} \frac{dQ}{dt})$ vs $\frac{1}{t}$ for He in SiO_2 at 158°C , third iteration.

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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