Free Volume Quantities and Gas Diffusion Properties at Low Temperatures

H. Higuchi† **and R. Simha***

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

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Introduction

We have recently been concerned with the connections between the thermal properties, positron annihilation experiments, stress relaxation parameters, and gas diffusion through polymer matrices.[1−4] Such connections could be established by considering the following functions: (1) the hole (or free volume) fraction, h_{ss}, derived from the volume−temperature function at atmospheric pressure by means of the Simha−Somcynsky (SS) theory; (2) the free volume fraction, h_p, extracted from orthopositronium (o-Ps) lifetimes, τ_3, and intensities, I_3; (3) the mean cavity size, $\langle v_f \rangle$, determined by the lifetimes, τ_3.

We note the close agreement between the functions h_{ss}, obtained by free energy minimization above T_g, and h_p.[1,2,5] However, in the glassy state, h_{ss} *adjusted* to satisfy the $V-T$ function gave consistently higher values than h_p.[1,2,5] Above T_g, the hole fraction, h_{ss}, can be shown to obey the following equation:[1,2]

$$h_{ss} = (V - V_s)/V, \qquad V_s = K(T/T^*)V^* \tag{1}$$

where V^* and T^* are scaling parameters, and K is a slowly varying function with $K \approx 0.955$. Equation 1, which displays the character of h_{ss} as a free volume quantity, has a theoretical foundation for $T \geq T_g$. For $T < T_g$, we have retained eq 1, which now defines a free volume fraction, h_V, where V is the *experimental* volume. The different symbols h_{ss} and h_V, although *formally* satisfying the identical eq 1, serve to distinguish the different origins of the two quantities. It was previously shown[1,2] that the close agreement of h_{ss} and h_p continues with h_V and h_p.

Recently, two sets of experimental data on Bisphenol-A polycarbonate (PC) have appeared. One is the diffusion of He.[6] The other concerns the o-Ps lifetime and intensity.[7] The range of temperatures between approximately 50 and 320 K is of particular interest to us, because of our investigations of low-temperature dilatometry ($T \geq 12$ K)[8,9] and corresponding theory.[10] The purpose of this note is to examine the sets of data in refs 6 and 7 along the lines indicated above.

Thermal Expansivity and Positron Annihilation. We begin with an evaluation of the volume−temperature curve. References 9 and 10 present the thermal expansivity as a function of temperature only in graphical form. The corresponding tabulations are found in Roe's doctoral thesis.[8] Combined with a reference volume at 320 K, provided by Zoller,[11] these data then yield the $V-T$ function displayed in Figure 1.

From these data, a free volume quantity, h_V, can be derived as long as we accept eq 1, and its relation to the h_p function can be examined. Recall that h_p is given by eq 2, viz.[5]

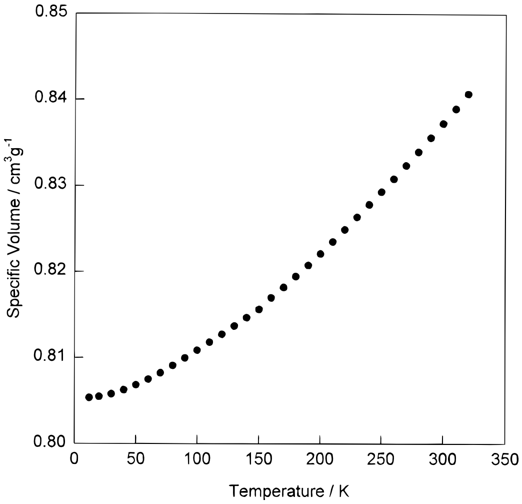

Figure 1. Volume−temperature function of Bisphenol-A polycarbonate.

$$h_p = CI_3\langle v_f \rangle \tag{2}$$

where C is a proportionality factor. Thus there are two unknown parameters, C and V_s, to be determined by means of two temperature points. Reference 7 gives linear fits in temperature to the smoothed values of τ_3 and I_3. The former yields $\langle v_f \rangle$ (see, for example, ref 1), and from the condition of coincidence of the two functions $h_p(T)$ and $h_V(T)$, C and V_s are obtained. These are employed to obtain Figure 2. For $T \geq 130$ K, a good coincidence between h_p and h_V is seen with $C = 2.38 \times 10^{-3}$ Å^{-3}, and most importantly, $V_s = 0.7886$ cm^3/g. The latter value is close to 0.7868 cm^3/g, the number obtained by the comparison of positron and thermal data in the melt and the glass at elevated temperatures.[2] These parameter values are in satisfactory agreement with the product $K(T/T^*)V^* = 0.7791$ cm^3/g.[2] This result suggests that V_s could be independently computed without recourse to positron information, analogous to the earlier findings for polystyrene.[1] Below 130 K, h_p is found to be temperature independent; the free volume is apparently frozen. Krištiak et al.[7] point to the peak in the dilatomeric derivative $d\alpha/dT$ observed at this temperature.[8,9] The minimum temperature in those experiments is approximately 12 K and a further peak at approximately 64 K is observed.[8,9] Parallel with this experimental low-temperature work, an equation of state theory was formulated.[10] It is based on a low-temperature expansion of the Lennard-Jones−Devonshire cell potential[12] with no explicit allowance for holes or (excess) free volume. In other words, whatever holes may have survived are effectively frozen. A very good agreement with experiment, in respect to the thermal expansivity, it should be emphasized, is observed up to 50−60 K. To proceed to higher temperatures, two effects would have to be introduced, namely the appearance of a temperature-dependent hole fraction and higher terms in the expansion or the full expression of the cell potential. The SS high-temperature theory, on the other hand, approximates this potential by a square well.[13] It would be of considerable interest to extend the positron experiments to still lower temperatures and to pursue the proper modifications of the theory for higher temperatures. This, incidentally, raises the question whether positron methodology can detect low-temperature subglass relaxations.

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† Visiting Scholar. Permanent address: Central Research Laboratories, Idemitsu Kosan Co., Ltd., Chiba, Japan.

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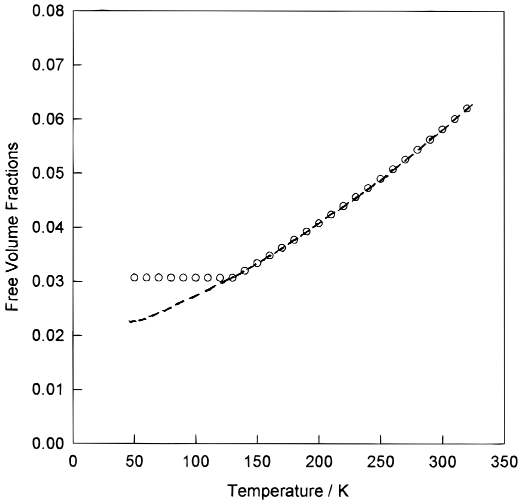

Figure 2. Free volume fractions h_p (circles) and h_V (line, eq 1). For explanation, see text.

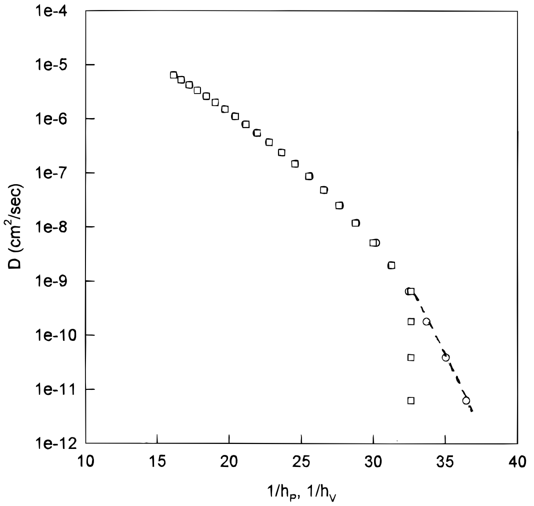

Figure 3. Diffusion coefficient of He in PC vs the two free volume quantities. Circles refer to h_V and are indistinguishable from squares (h_p) in the upper range.

Returning to Figure 2 and eq 1, we have the agreement between h_p and h_V all the way down to 130 K. A breakdown of eq 1 with a constant value of V_s is not unexpected. We have extended eq 1 to $T < 130$ K to display the magnitude of the difference. *Formal* retention of eq 1 would require V_s to change with temperature at the same rate as V.

Gas Diffusion and Free Volume Quantities. Next we turn to the diffusion experiments. We have previously considered the relation of the gas diffusion coefficient, D, to several free volume functions.[4] Figure 3 shows D as a function of $1/h_p$ and of $1/h_V$, with an identical plot for $T > 130$ K. Significant deviations from Doolittle's relation[14] are noted. Such deviations are seen in melt viscosity[15] and viscoelastic studies.[2,3]

Figure 4 illustrates the dependence of log D on the mean cavity volume $\langle v_f \rangle$, derived from τ_3. Again, a satisfactory but not linear correlation is noted. Relations between transport functions and average free volume quantities have been interpreted in terms of the Cohen–Turnbull theory,[16] which operates with a characteristic minimum free volume parameter, v_m, and rationalizes the Doolittle relation. Figure 4 shows an increase in slope with decreasing temperature or $\langle v_f \rangle$, even above 130 K. This would formally require an increase of v_m with decreasing temperature, contrary to physical expectation.

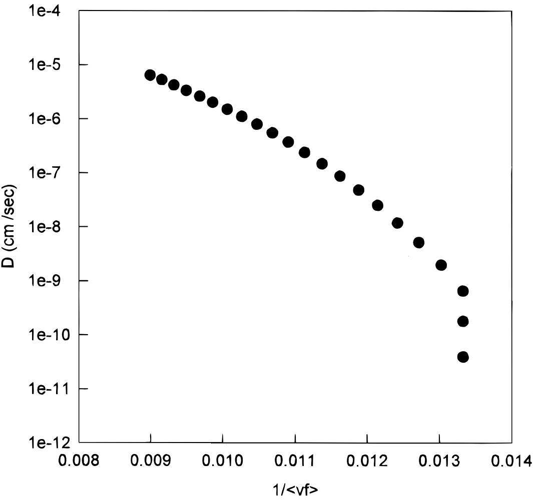

Figure 4. Semilogarithmic plot of diffusion coefficient vs reciprocal of mean cavity volume (Å^{-3}).

Our diffusion studies of Ar and CO_2 in polycarbonates of varying structures at room temperature[4] showed the Cohen–Turnbull relation[16] to be valid. That is, the characteristic minimum free volume, v_m, is a constant for a given penetrant. The properties of the matrix appear only in the free volume quantities. Thus, the elastic vibrations of the solid play at best a minor role, as they affect the free volume. Actually, in the melt the theoretical K function, eq 1, is a measure of the vibration contribution.[17] This is in contrast to the low-temperature observations, suggesting the important contribution of elastic vibrations.[6] We have computed the elastic frequencies for PC as a function of temperature,[10] but, as noted in the previous section, those expressions are not applicable at $T > 50$–60 K. It would be of interest to explore possible connections between gas diffusion properties and thermoelastic characteristic in terms of the model at hand,[10] which requires an extension of diffusion measurements to still lower temperatures.

References and Notes

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