VOLUME-TEMPERATURE RELATIONSHIPS IN SIMULATED GLASS FORMING NUCLEAR WASTE MELTS

L.D. Pye, R. Locker and M.J. Plodinec

New York State College of Ceramics
Alfred University, Alfred, N.Y.

*I.E. duPont de Nemours & Co.
Savannah River Laboratory, Aiken, S.C.

INTRODUCTION

The classical description of a melt cooling to form a solid glass is expressed by the volume-temperature behavior shown in Fig. 1. The point where a change of slope takes place in this graph is defined as the glass transition temperature, \( T_g \). Its exact value is moderately dependent on the rate of cooling, faster rates giving larger values. That the volume change at \( T_g \) is not discontinuous (as for example, during melting or crystallization), is often taken to mean that the glass transition is a quasi second-order thermodynamic transformation of the type described by Ehrenfest. In this classification, properties defined by the first derivative of free energy, i.e., enthalpy, entropy, and volume are expected to change gradually during a second-order transformation, whereas properties defined by the second derivative of free energy (heat capacity, thermal expansion), are expected to show a discontinuous change. Thus, extension of the Ehrenfest criteria to the glass transition would predict a discontinuous change of the coefficient of thermal expansion at \( T_g \). We shall examine below the extent to which this prediction is fulfilled for several simulated nuclear waste glasses.

Beyond these theoretical considerations, the change of specific volume of a glass forming melt with temperature is important in many aspects of glass manufacture: melting, annealing, sealing, tempering, and others. During melting it is this change of volume (or density) with temperature that gives rise to convention currents necessary for the satisfactory mixing.
Fig. 1. Classical volume-temperature behavior of a glass forming when cooled to a solid glass.

of a melt. In this sense it becomes an especially important parameter in the design of glass melting units. In annealing, volume-temperature relationships, expressed as the coefficient of thermal expansion, allow the prediction of cooling rates necessary to avoid fracture during cooling.

It was for these reasons, primarily, that the present investigation involving simulated glass forming nuclear wastes melts was undertaken. We also note that the number of glass forming systems for which expansivity data are available for both the molten and solid state is relatively small. At the same time, it is easier by far to measure volume (expansion) changes of a glass as it is heated from room temperature through its transition range. Since this measurement gives low temperature information on the volume-temperature behavior shown in Fig. 1, it is often inquired as to what error can be expected by extrapolating these measurements to predict melt density, e.g. density of the molten state. This question is examined in some detail below since in this work, both high and low temperature densities and expansions were measured thereby allowing a comparison to be made.