INVESTIGATION OF THE THERMODYNAMIC STABILITY OF ULTRASTABLE GLASSES BY SOLUTION CALORIMETRY AND DSC

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An ultrastable glass is a nonequilibrium amorphous state of matter corresponding to a deep minimum on the potential energy landscape [1] and therefore exhibiting anomalously high thermodynamic stability. Quantitative assessment of this stability still relies mainly on an indirect parameter, the fictive temperature (T_f), determined by differential scanning calorimetry (DSC) [2].

In the present work, a direct approach to determining the relative thermodynamic stability of glasses at 298.15 K is proposed and experimentally implemented.

1,3,5-Tris(α-naphthyl)benzene and N,N′-diphenyl-N,N′-bis(3-methylphenyl)benzidine were selected as model compounds. The glasses were prepared by slow physical vapor deposition onto substrates held at controlled temperature and by rapid quenching of the melt.

The relative thermodynamic stability was evaluated as the difference in Gibbs free energy between the glassy states at $T_0 = 298.15$ K using the Gibbs equation. The experimental ΔH values were obtained from solution calorimetry in benzene. In addition, these results were compared with estimates based on the Kirchhoff relation. The entropy difference, ΔS, was evaluated analogously using the fictive temperature.

$$\Delta_{g,II}^{g,I}H = \Delta_{g,I}^{l}H - \Delta_{g,II}^{l}H = \Delta_{g,I}^{soln}H - \Delta_{g,II}^{soln}H = \int_{T_f(I)}^{T_0} \Delta_g^l C_{p,m} dT - \int_{T_f(II)}^{T_0} \Delta_g^l C_{p,m} dT$$

Here, ΔH is the enthalpy change, $\Delta C_{p,m}$ is the change in isobaric heat capacity, $T_0 = 298.15$ K, and (T_f) is the fictive temperature. The subscript (l) refers to the liquid, (g, II) to the vapor-deposited glass, (g, I) to the melt-quenched glass, and (soln) to the infinitely dilute solution.

A method is proposed that, for the first time, enables a quantitative comparison of the thermodynamic stability of glasses prepared by different methods at a fixed temperature. The crystallization behavior of the glasses was also studied and correlated with their structural and thermodynamic parameters.

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