

the effective hydrodynamic radius of the diffusing species. Thus, while the point at which a material becomes a glass is historically defined in terms of the viscosity (i.e., $\eta > 10^{14}$ poise) (42), if the Stokes–Einstein relationship is valid, the corresponding definition of a glass could also be based on the diffusion coefficient. The translational diffusion coefficient is given in terms of the “jump distance,” x , and the diffusional correlation time, τ , or “relaxation time” by

$$D = \frac{x^2}{2\tau} \quad (2)$$

so the diffusion coefficient is inversely proportional to the diffusional relaxation time. A similar relationship holds for rotational motion. Since the electrical mobility of an ion is directly related to the diffusion coefficient (43), electrical conductance is also inversely proportional to the coefficient of viscosity, given the validity of the Stokes–Einstein equation. We use the term “mobility” in a general sense to refer to translational or rotational diffusion constant, or reciprocal of relaxation time. Assuming validity of the Stokes–Einstein equation, mobility and viscosity are inversely related.

As a liquid is cooled near the glass transition, viscosity increases sharply and the temperature dependence of viscosity becomes distinctly non-Arrhenius. That is, the apparent activation energy increases as the temperature decreases. The Adam–Gibbs equation is a theoretical result describing relaxation behavior in highly viscous systems that was developed using a statistical mechanical analysis of configurational changes in highly viscous systems (44). Configurational changes in systems close to the glass transition temperature take place by highly cooperative motions involving rearrangements in a region whose size is determined by the configurational entropy of the system. As the temperature in a highly viscous system decreases, the configurational entropy decreases, and the size of the cooperatively rearranging region increases, thereby increasing the total free energy barrier to the configurational change and slowing the process. The relationship between configurational entropy, S_c , and the relaxation time is given by

$$\tau(T) = A \exp\left(\frac{C}{TS_c}\right) \quad (3)$$

where C is a constant which is proportional to the molar (or segmental, for polymers) change in chemical potential for a transition, and A is a pre-exponential factor practically independent of temperature. The configurational entropy must vanish at some temperature, T_0 , otherwise one is faced with the “unphysical” conclusion that the configurational entropy will become negative at some low temperature. This result is based on the observation that extrapolations of configurational entropy from temperatures above T_g to lower temperatures predict negative values roughly 50° below T_g (i.e., at T_0). Thus, the temperature, T_0 , marks the temperature at which the system, at equilibrium, must undergo a second-order phase transition losing the configurational heat capacity. Below T_0 the configurational entropy is zero. With $S_c = 0$ for $T < T_0$, the configurational entropy at temperature T , $S_c(T)$, becomes

$$S_c(T) = \int_{T_0}^T \left(\frac{\Delta C_p}{T}\right) dT \quad (4)$$