

where  $\Delta C_p$  is the configurational part of the heat capacity, frequently taken to be the difference in heat capacity between the equilibrium melt and the glass. In cases where the heat capacity of the glass is significantly larger than the heat capacity of the crystalline phase,  $\Delta C_p$  should perhaps be taken as the difference between the heat capacity of the melt and the crystal.

Angell (45) takes the configurational heat capacity as inversely proportional to absolute temperature,  $\Delta C_p = K/T$ , where  $K$  is a constant of the material. With this relationship, the relaxation time in equation (3) becomes

$$\tau(T) = A \exp\left(\frac{DT_0}{T - T_0}\right) \quad (5)$$

where  $D$  is a constant characteristic of the material ( $D = C/K$ ). Since " $C$ " is directly proportional to the molar change in chemical potential for a transition, so also is " $D$ ." This result is of the same form as another empirical equation known to represent the behavior of highly viscous systems, commonly referred to as the VTF equation (Vogel-Tammann-Fulcher equation). If one insists that the relaxation time for all glasses is (roughly) the same at the glass transition temperature,  $\approx 100$  seconds, and further insists that  $\tau$  is the same for all materials at the extreme high-temperature limit (16 orders of magnitude change between  $T_g$  and the high-temperature limit), a relationship between  $D$  and  $T_0$  results<sup>a</sup> (45):

$$\frac{T_g}{T_0} = 1 + \frac{D}{36.85} \quad (6)$$

Thus, a large value of  $D$  means a larger difference between the glass transition temperature and the zero mobility temperature (i.e., larger ratio of  $T_g/T_0$ ). From equation (5), it is apparent that a larger difference between  $T_g$  and  $T_0$  means that as  $T \rightarrow T_g$ , the temperature dependence of relaxation time is smaller. That is, the effective activation energy is smaller, and the deviation from Arrhenius behavior is less for large  $D$ . Depending on the nature of the amorphous material, values of  $D$  do vary (45). Amorphous materials with large values of  $D$  are denoted "strong glasses" while materials with small values of  $D$  as "fragile glasses" (45). In short, not all glasses are equivalent in the temperature dependence of relaxation time and therefore are not equivalent in the deviation from Arrhenius behavior.

The traditional "derivation" of the Adam-Gibbs equation as given above assumes the configurations are always in thermal equilibrium, and therefore the results given by equations (4) and (5) do not apply below the glass transition, as the configurations in a glass are *not* in thermal equilibrium. If one assumes that the configurational heat capacity,  $\Delta C_p$ , is equal to the difference in heat capacity between the melt and the glass at  $T_g$  (i.e., no configurational contribution to the heat capacity of a glass), the configurational enthalpy and entropy do not change as the temperature is decreased below the glass transition region. Thus, the configurational entropy of the glass is equal to the configurational entropy of

<sup>a</sup>When using the VTF equation in viscosity form, one assumes a difference between the viscosity at  $T_g$  and the high-temperature limit of 17 orders of magnitude (43), which changes the numerical value of 36.85 to 39.14.