

# Nonlinear Kinetic and Thermodynamic Properties of Monomeric Organic Glasses

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Thermodynamic Kauzmann temperatures,  $T_K$ , published dielectric relaxation and viscosity Fulcher temperatures,  $T_0$ , and nonlinear enthalpic Adam–Gibbs temperatures,  $T_2^{AG}$ , are compared for three isomeric indanes that differ only by the position of an aromatic methoxy group, and for *o*-terphenyl (OTP) and tri- $\alpha$ -naphthyl benzene (TNB). All three temperatures agreed to within estimated experimental uncertainty for all glasses, with one probable exception. Adam–Gibbs “primary” activation energies  $\Delta\mu$  of 1400, 1120, and 2750 kJ mol<sup>-1</sup> were derived from the enthalpy relaxation parameters for the *o*-, *m*- and *p*-indanes, respectively, compared with the dielectric values of 900, 990, and 1040 kJ mol<sup>-1</sup>. The enthalpy relaxation values of  $\Delta\mu$  for OTP and TNB were 940 and 545 kJ mol<sup>-1</sup>, respectively.

## Introduction

The temperature dependence of relaxation and retardation times  $\tau(T)$  of supercooled liquids is often well described, over an appropriately small temperature range, by the empirical Vogel–Tamman–Fulcher<sup>1–3</sup> (VTF) or equivalent WLF<sup>4,5</sup> equation

$$\tau(T) = A \exp\left[\frac{B_F}{T - T_0}\right] = \tau(T_g) \exp\left[\frac{\ln(10)C_1C_2}{T - T_g + C_2}\right] \quad (1)$$

in which  $A$ ,  $B_F$ , and  $T_0$  are positive constants and  $C_1$  and  $C_2$  are  $T_g$ -dependent parameters. The parameter  $T_0$  has long attained a fundamental significance because it is the (extrapolated) temperature at which the relaxation time is infinite and at which some sort of ground state for amorphous materials has been suggested. The latter interpretation is reinforced by the derivations of eq 1 assuming configurational entropy  $S_c$ <sup>2</sup> (or free volume,  $V_f$ <sup>5,6</sup>) to be the factors that determine molecular mobility. These derivations imply that  $T_0$  corresponds to the temperature of zero  $V_f$  or zero  $S_c$ . The temperature of zero  $S_c$  has particular thermodynamic significance because negative values of excess entropy  $S_c$  are forbidden by the third law. This is the origin of the celebrated “paradox” first noted by Kauzmann,<sup>7</sup> who observed that the excess entropy of a liquid over that of the crystal extrapolated to zero at a temperature  $T_K$  well above zero. There are many examples of  $T_0$  and  $T_K$  being equal within estimated uncertainties,<sup>8–15</sup> especially for very “fragile” materials. It has been suggested<sup>16,17</sup> that one form of the enthalpic nonlinear Adam–Gibbs (AG) equation,<sup>16–18</sup>

$$\tau(T, T_{f,H}) = A \exp\left[\frac{B_{AGF}}{T(1 - T_2^{AGF}/T_{f,H})}\right] \quad (2)$$

in which  $T_{f,H}$  is the enthalpic fictive temperature and  $A$ ,  $B_{AGF}$ , and  $T_2^{AGF}$  are adjustable parameters, implies that the degree of nonlinearity of structural relaxation within the glass transition

region should be added to the properties associated with fragility, and that nonlinearity may also have thermodynamic roots. In this context, nonlinearity refers to the dependence of the retardation time for  $T_{f,H}$  on  $T_{f,H}$  that is exhibited in eq 2, and to the consequent absence of proportionality between excitation and response that is the basis of linear response theory (as demonstrated by the classic asymmetric approaches to equilibrium following temperature jumps of opposite sign observed by Hara and Suetosh<sup>19</sup> (plotted in ref 20) and Kovacs,<sup>21</sup> for example). Above  $T_g$ ,  $T_f(t) = T(t)$  and eq 2 is identical to the VTF equation with  $T_2^{AGF} = T_0$  and  $B_{AGF} = B_F$ . For this reason, eq 2 is referred to here as AGF (“Adam–Gibbs–Fulcher”) to distinguish it from other expressions to be derived later. As explained elsewhere,<sup>14</sup> different nomenclatures for  $T_2^{AGF}$  and  $T_0$  are used to emphasize that their numerical equivalence is to be demonstrated or refuted experimentally. Equation 2 is experimentally indistinguishable<sup>14,18,22–25</sup> from the more commonly used Narayanaswamy–Moynihan equation<sup>26,27</sup>

$$\tau(T, T_{f,H}) = A \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_{f,H}}\right] \quad (3)$$

where  $A$  and  $x$  are adjustable parameters and  $\Delta h^*$  is the effective activation energy at  $T_g$  defined by  $|\partial \ln \tau / \partial (1/T)|_{T_g}$ . The parameters in eqs 2 and 3 are related by<sup>16,18</sup>

$$x \approx 1 - \frac{T_2^{AGF}}{T_g} = \frac{C_2}{T_g} \quad (4)$$

and

$$\frac{\Delta h^*}{R} \approx \frac{B_{AGF}}{[1 - T_2^{AGF}/T_g]^2} \approx \frac{B_{AGF}}{x^2} = \frac{\ln(10)C_1T_g^2}{C_2} \quad (5)$$

Parameters obtained from application of eq 2 to the glass transition are in principle more reliable than those obtained for eq 1 above  $T_g$ , because the glass transition temperature range is small (typically about 10 K) compared with the much wider range accessible above  $T_g$  (40 K for the dielectric studies of the indanes, for example, but typically even wider for more thermally stable inorganic compounds). Equation 2 parameters

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obtained in the glass transition range should therefore be less sensitive to any possible variation of  $T_2^{\text{AGF}}$  with temperature, as  $T_0$  is sometimes found to have. However, this potential advantage is negated by the parameters of eq 2 having large and strongly correlated uncertainties that are associated in part with its nonlinearity. In particular, the average effective activation energy  $\Delta h^*/R \approx B_{\text{AGF}}/x^2$  is determined at best to about  $\pm 20\%$  from the relation<sup>26</sup>

$$\frac{\Delta h^*}{R} = \frac{d \ln Q_c}{d(1/T_f')} \quad (6)$$

where  $T_f'$  is the fictive temperature of the glass formed immediately after cooling at a rate  $Q_c$  (without annealing). The complexity of the data analysis for enthalpy relaxation adds an additional element of uncertainty.

Equation 2 is derived from the nonlinear form of the AG relation<sup>4</sup>

$$\tau(T, T_{f,H}) = A \exp\left[\frac{B^*}{TS_c(T_{f,H})}\right] = A \exp\left[\frac{\Delta\mu(s_c^*/k_B)}{TS_c(T_{f,H})}\right] \quad (7)$$

first applied to structural relaxation by Scherer,<sup>22</sup> where  $\Delta\mu$  is a "primary" activation energy for movement of a single moiety,  $s_c^*/k_B = \ln w^*$  is the minimum entropy associated with the minimum number of rearrangeable configurations  $w^*$  (usually equated to 2, although  $2^3$  has been suggested for polymers<sup>16,18</sup>). The mathematical form of  $S_c(T_f)$  is determined by the temperature dependence of the configurational heat capacity,  $\Delta C_p(T)$ :

$$S_c(T_f) = \int_{T_{2,AG}}^{T_f} \frac{\Delta C_p(T) dT'}{T'} \quad (8)$$

For

$$\Delta C_p(T) = \frac{CT_2^{\text{AGF}}}{T} \quad (9)$$

$$S_c(T_f) = C \left(1 - \frac{T_2^{\text{AGF}}}{T_f}\right) = \Delta C_p(T_g) \left[\frac{T_g}{T_2^{\text{AGF}}}\right] \left(1 - \frac{T_2^{\text{AGF}}}{T_f}\right) \quad (10)$$

and eq 2 is obtained. The hyperbolic temperature dependence of  $\Delta C_p$  expressed in eq 9 is a mathematically convenient approximation to the commonly reported linear form

$$\Delta C_p(T) = a - bT \quad (11)$$

which is accurate when  $b/a = 1/2T_g < 10^{-3} \text{ K}^{-1}$ ,<sup>23</sup> although small inaccuracies are of little consequence because the values of  $T_2^{\text{AG}}$  are insensitive to the specific form of  $\Delta C_p(T)$  for small values of  $x$  (see below). For eq 11,

$$x \approx \frac{\left[ a \ln\left(\frac{T_g}{T_2^{\text{AGS}}}\right) - b(T_g - T_2^{\text{AGS}}) \right]}{\left[ a \ln\left(\frac{T_g}{T_2^{\text{AGS}}}\right) - b(T_g - T_2^{\text{AGS}}) \right] + (a - bT_g)} \quad (12)$$

and

$$\frac{\Delta h^*}{R} \approx \frac{B_{\text{AG}} \left[ a \ln\left(\frac{T_g}{T_2^{\text{AGS}}}\right) - b(T_g - T_2^{\text{AGS}}) \right] + (a - bT_g)}{\left[ a \ln\left(\frac{T_g}{T_2^{\text{AGS}}}\right) - b(T_g - T_2^{\text{AGS}}) \right]^2} \quad (13)$$

where the superscripts and subscripts AGS are used to acknowledge Scherer's<sup>22</sup> pioneering combination of the nonlinear AG model and eq 11 and to emphasize that it is in general not equal to  $T_2^{\text{AGF}}$ . For  $\Delta C_p = C = \text{constant}$ ,

$$\tau(T, T_{f,H}) = A \exp\left[\frac{B_{\text{AGL}}}{T \ln(T_2^{\text{AGL}}/T_{f,H})}\right] \quad (14)$$

and the parameters  $x$  and  $\Delta h^*$  are given by<sup>16,18</sup>

$$x \approx \frac{L}{1+L} L \equiv \ln\left[\frac{T_g}{T_2^{\text{AGL}}}\right] \quad (15)$$

and

$$\frac{\Delta h^*}{R} \approx B_{\text{AGL}} \left[ \frac{1}{L} + \frac{1}{L^2} \right] \quad (16)$$

where AGL denotes the logarithmic form of the nonlinear AG equation. Expansion of the logarithm in eq 14 to first order produces the AGF equation, and this approximation improves if any difference between the AGL and AGF forms is subsumed into differing values of the  $B$  and  $T_2^{\text{AG}}$  parameters. In the following discussion the parameters  $T_2^{\text{AGF}}$ ,  $T_2^{\text{AGS}}$ , and  $T_2^{\text{AGL}}$  will be referred to generically as  $T_2^{\text{AG}}$ , and similarly for the  $B$  parameters.

The generalized AG expression for  $x$  in terms of the generic AG eq 8 is<sup>16,28</sup>

$$x \approx \left[ 1 + \frac{T_g}{S_c(T_g)} \left( \frac{dS_c}{dT} \right)_{T_g} \right]^{-1} \quad (17)$$

which when combined with the relation

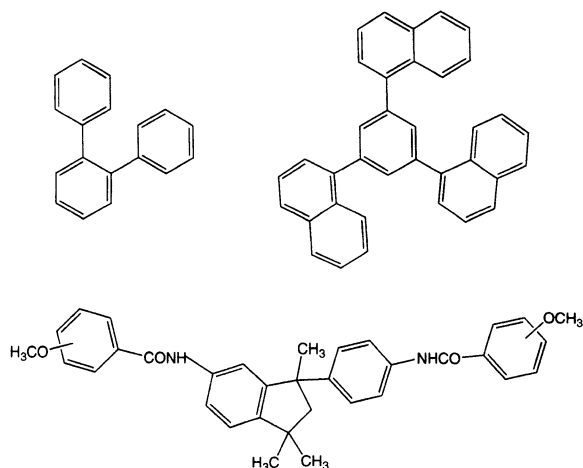
$$\left( \frac{dS_c}{dT} \right)_{T_g} \approx \frac{\Delta C_p(T_g)}{T_g} \quad (18)$$

yields the thermodynamic relation

$$x \approx \frac{S_c(T_g)}{S_c(T_g) + \Delta C_p(T_g)} \quad (19)$$

Equation 19 does not appear to have been derived before and reinforces the suggestion made above that nonlinearity and thermodynamics may be linked. In particular, it provides a basis for comparing thermodynamically and kinetically derived values of  $x$  that can be tested experimentally.<sup>29</sup> Note that eq 19 implies high values of  $x$  when  $S_c(T_g)$  is large compared with  $\Delta C_p$ , consistent with the high values  $T_g/T_2$  predicted by eqs 4, 12, and 15.

In the present report, experimental values of  $T_K$ ,  $T_0$  from published dielectric relaxation and viscosity data, and  $T_2^{\text{AG}}$  from enthalpy relaxation, are compared for identical preparations of the three isomers of indane and of *o*-terphenyl (OTP) and tri- $\alpha$ -naphthylbenzene (TNB) (see Figure 1 for chemical structures). These compounds were chosen because of their well-defined



**Figure 1.** *Ortho*-terphenyl (top left); tri- $\alpha$ -naphthyl benzene (top right); indane (bottom).

chemical structures and the absence of complications due to partial crystallinity and tacticity that plague the analyses of many polymers.

## Experimental Section

Dielectric methods and analysis have been described previously.<sup>30,31</sup> Heat capacities were measured on a Perkin-Elmer DSC7. Low heating rates, 2 and 5 K min<sup>-1</sup>, were employed to minimize heat transfer effects<sup>32</sup> for each of six cooling rates between 0.1 and 5 K min<sup>-1</sup>. The automated experimental protocols have been described elsewhere.<sup>33,34</sup>

Enthalpy relaxation parameters were obtained from nonlinear least-squares regression fits to normalized heat capacities, using eq 3 and the reduced time form of the stretched exponential function,<sup>26,27</sup>

$$\phi(t) = \exp[-\xi(t)^\beta] = \exp\left[-\left(\int_0^t \frac{dt'}{\tau[T(t'), T_f(t')]\right)^\beta\right] \quad (20)$$

The activation energy,  $\Delta h^*$ , was calculated from the change in fictive temperature with cooling rate using eq 6. The parameters  $A$ ,  $x$ , and  $\beta$  were obtained from Marquardt optimized fits to normalized heat capacities, as described elsewhere.<sup>16</sup> Values of  $T_2^{AG}$  were computed from  $\Delta h^*$ ,  $x$ , and the onset values of  $T_g$  using eqs 4, 12, and 15. The entropy and Kauzmann temperature were calculated by integration of the specific heat curves using the methods applied to polymers.<sup>35,36</sup> Although  $dC_p/dT$  is not accurately defined experimentally, it is shown later that the value of  $T_K$  is determined principally by the magnitude of  $\Delta C_p(T_g)$ .

## Assessments of Experimental Uncertainties

Error estimation in the enthalpy relaxation parameters is not straightforward because of the strong correlations between them, and is accordingly more approximate than usual. The known uncertainties in  $\Delta C_p(T_g)$  and  $\Delta H_m$  are  $\pm 5\%$ , both these values corresponding to high confidence levels that are taken to be greater than 90%. The estimated uncertainty in  $\Delta h^*$  is  $\pm 20\%$ , and the observed [90% confidence] uncertainty in  $x$  is  $(33 \pm 13\%)$  (Table 2 *vide infra*) that implies a 33% uncertainty in  $(1 - T_2/T_g)$ , 11% in  $T_2/T_g$  for  $T_2/T_g \approx 0.75$ , and about  $\pm 30$  K in  $T_2$  ( $\approx 300$  K) if the uncertainty in  $T_g$  is assumed to be

**TABLE 1: Thermal Properties of Monomeric Organics**

compound	$\Delta S_m^a$	$T_m^b$	$T_g^b$	$\Delta C_p(T_g)^a$	$a^c$	$b^c$
<i>o</i> -indane	77	445	357	161	488	0.91
<i>m</i> -indane	55	423	359	198	467	0.75
<i>p</i> -indane	102	476	385	182	429	0.64
OTP	52	329	240	113	158	0.21
TNB	73	456	340	150	392	0.78

<sup>a</sup> J K<sup>-1</sup> mol<sup>-1</sup>,  $\pm 5\%$ . <sup>b</sup> K. <sup>c</sup> Coefficient in  $\Delta C_p(T) = a - bT$ .

**TABLE 2: Enthalpy Relaxation Parameters**

compound	$Q_h^a$	$\Delta h^*/R^b$	$x$	$\beta$
<i>o</i> -indane	2.5	88	0.23 $\pm$ 0.09	0.53 $\pm$ 0.09
<i>m</i> -indane	2.5	129	0.16 $\pm$ 0.08	0.41 $\pm$ 0.07
<i>p</i> -indane	2.5	96	0.28 $\pm$ 0.09	0.53 $\pm$ 0.05
OTP	2.5	58	0.28 $\pm$ 0.03	0.54 $\pm$ 0.03
TNB	2.5	66	0.25 $\pm$ 0.08	0.52 $\pm$ 0.11

<sup>a</sup> K min<sup>-1</sup>. <sup>b</sup> kK,  $\pm 20\%$ .

insignificant. The uncertainty in  $T_K$  is dominated by that in  $\Delta C_p(T_g)$  and is found to be about  $\pm 20$  K, so that the numerical equivalence of  $T_2^{AG}$  and  $T_K$  cannot be established to better than about  $\pm(30^2 + 20^2)^{1/2} \approx \pm 35$  K (assuming  $T_K$  and  $T_2^{AG}$  to be statistically independent). The propagated uncertainties in the Adam–Gibbs  $B$  values are particularly difficult to estimate because of the correlations and only best case and worse case values are reported here. For  $B_{AGF} \approx x^2 \Delta h^*$ , the minimum uncertainty is assumed to be that in  $\Delta h^*$  (20%), and the maximum uncertainty is estimated by assuming that the respective uncertainties of 20% and 30% in  $\Delta h^*$  and  $x$  are statistically independent,  $(2(30)^2 + 20^2)^{1/2} \approx 45\%$ . For the dielectric experiments on the indanes,<sup>30,31</sup> data were acquired over a temperature of about 40 K for all three isomers, and the reproducibility in  $C_2$  was found to be  $\pm 5$  K (surprisingly small but consistent with the VTF parameter being much better defined than the nonlinear enthalpic  $T_2$ ).

## Results and Discussion

The thermal properties of the three indane isomers, OTP,<sup>39</sup> and TNB<sup>40</sup> are summarized in Table 1, and the enthalpy relaxation parameters are listed in Table 2. The values of  $x$  computed from eq 19 and the measured values of  $S_c(T_g)$  and  $\Delta C_p(T_g)$  were 0.20, 0.10, 0.26, 0.13, and 0.16 for the *o*-, *m*-, *p*-isomers of indane, OTP, and TNB, respectively. These are within uncertainties of the best-fit values for the indanes but are about 0.10 lower than the best-fit values for OTP and TNB and are at the edge of uncertainties for these two compounds.

Because of the importance of the uncertainties in  $T_K$  and  $T_2^{AG}$  in establishing or refuting their equality, their values for three temperature dependences of  $\Delta C_p(T)$  were computed:

(a)  $\Delta C_p = \Delta C_p(T_g) = \text{constant}$ , (b)  $\Delta C_p(T) = a - bT$ , and (c)  $\Delta C_p(T) = \Delta C_p(T_g)(T_g/T)$ . The values of  $T_K$  for these three dependences, as well those computed for typical uncertainties of ca.  $\pm 5\%$  in  $\Delta C_p(T_g)$ , are shown in Table 3. The uncertainties in  $\Delta C_p(T_g)$  are seen to be more significant than the functional form of  $\Delta C_p(T)$ .

The Adam–Gibbs enthalpy relaxation temperatures  $T_2^{AG}$ ,  $T_2^{AGS}$ , and  $T_2^{AGL}$  are given in Table 4, together with  $B_{AGF}$  obtained from  $\Delta h^*/R$  and  $x$  using eqs 4 and 5. The other  $B$  parameters are not exhibited because only  $B_{AGF}$  is equal to  $\ln(10)C_1C_2$  and comparable with the Fulcher/WLF parameters (that were obtained by dielectric relaxation for the indanes and by viscosity for OTP and TNB). As noted above, the values of  $T_2^{AG}$  are insensitive to the assumed form of  $\Delta C_p(T)$ , a known

**TABLE 3: Kauzmann Temperatures for Indanes<sup>a</sup>**

isomer	$\Delta C_p(T_g)$	$\Delta C_p = \Delta C_p(T_g)$	$\Delta C_p(T_g) = a - bT$	$\Delta C_p(T) = T_g \Delta C_p / T$
ortho	0.28	267	273	272
	0.30	276	279	279
	0.32	285	285	286
meta	0.35	315	312	314
	0.37	320	317	318
	0.39	325	321	323
para	0.32	263	274	274
	0.34	280	280	282
	0.36	286	286	288

<sup>a</sup> ±20 K.

result for low values of  $x$ .<sup>16</sup> The values of  $T_2^{AG}$ ,  $T_0$ , and  $T_K$  are equal within uncertainties for all five compounds, except for  $T_0$  for the viscosity of TNB, which is 81 K below  $T_K$  and probably outside any reasonable uncertainty estimate. The reported Fulcher temperature for the viscosity of OTP,<sup>41</sup> 231 K, is probably in error since it is only 20 K below  $T_g$  and the effective activation energy is not especially large: a failure of the Fulcher equation to this extent is unlikely. However, a WLF fit using the (now generally disavowed) "universal values" for  $C_1$  and  $C_2$  yielded  $T_0 = 199$  K, which was noted to be in excellent agreement with  $T_K$  although no information on the quality of fit was provided for the modified parameters.

The relative values of  $T_2^{AG}$  and  $T_K$  for the monomeric glasses discussed here are consistent with those tabulated in ref 14, namely that  $T_2^{AG} \leq T_K$  for all known materials.<sup>57</sup> In order for  $T_K$  to decrease to  $T_2^{AG}$ , either  $\Delta C_p(T)$  would have to be only partly configurational (as suggested by Goldstein<sup>43</sup>) or the entropy extrapolation is systematically in error (or even physically unjustifiable, as suggested by Stillinger<sup>44</sup>). For the latter to hold, the temperature dependence of the configurational entropy would need to exhibit an inflection close to  $T_g$ , corresponding to an unlikely maximum in  $\Delta C_p(T)$ . If  $T_K$  is a complete artifact of extrapolation, on the other hand, its near equality to  $T_2^{AG}$  and  $T_0$  in so many materials must be dismissed as fortuitous. Assuming the Kauzmann extrapolation to be reasonable, and that  $T_0$  and  $T_2^{AG}$  are experimentally unambiguous, it appears that for the handful of materials for which  $T_2^{AG} \ll T_K$  (polystyrene in particular<sup>16</sup>) either some degrees of configurational freedom that contribute to  $\Delta C_p$  do not contribute to relaxation properties in the manner suggested by Adam and Gibbs, or  $\Delta C_p$  is not entirely configurational.

The enthalpic value of  $\beta$  (0.53) for TNB is consistent with that found for orientation of tetracene in TNB (0.47), observed by optical techniques.<sup>45</sup> Larger probes yielded larger  $\beta$  values (ca. 0.7–0.9) but, since these probes were larger than TNB itself, their orientation dynamics were probably affected by stochastic averaging of the TNB environment to produce more exponential orientation correlation functions. For OTP, the enthalpic value of  $\beta$  (0.53) is broadly consistent with the range reported for the smallest probes in OTP,<sup>46</sup>  $\beta = 0.4$ –0.6.

The Adam–Gibbs "primary" activation energy  $\Delta\mu$  was computed from the experimentally derived quantities  $\Delta h^*/R$ ,

$\Delta C_p(T_g)$ , and  $x$  using an expression that is independent of the temperature dependence of  $\Delta C_p(T)$ . Eliminating  $B^*$  and  $S_c(T_g)$  from eq 19 and the relation

$$\frac{x\Delta h^*}{R} \approx \frac{B^*}{S_c(T_g)} = \frac{\Delta\mu(s_c^*/k_B)}{S_c(T_g)} \quad (21)$$

yields

$$\Delta\mu \approx \frac{\Delta h^* \Delta C_p(T_g)}{R(s_c^*/k_B)} \left[ \frac{x^2}{1-x} \right] \quad (22)$$

Although the dependence of  $\Delta\mu$  on  $x$  and  $\Delta h^*$  in eq 22 is independent of the temperature dependence of  $\Delta C_p(T)$ , the dependences on  $T_g$  and  $T_2^{AG}$  are not. For example, insertion of  $x$  and  $\Delta h^*/R$  from eqs 15 and 16, that are appropriate for  $\Delta C_p(T_g) = \text{constant}$ , yields

$$\Delta\mu \approx \frac{B_{AGL} \Delta C_p(T_g)}{(s_c^*/k_B)} \quad (23)$$

the same as eq 21 in ref 4, eqs 5–7 in ref 41, and eq 3.53 in ref 42. For  $\Delta C_p(T) = (T_g \Delta C_p(T_g)/T)$ , on the other hand,

$$\Delta\mu \approx \frac{B_{AGF} \Delta C_p(T_g)}{(s_c^*/k_B)} \left[ \frac{T_g}{T_2^{AGF}} \right] = \frac{\ln(10) C_1 C_2 \Delta C_p(T_g)}{(s_c^*/k_B)} \left[ \frac{T_g}{T_g - C_2} \right] \quad (24)$$

Equation 22 indicates a strong dependence of  $\Delta\mu$  on (the experimentally uncertain) nonlinearity parameter  $x$ . The correspondingly uncertain values of  $\Delta\mu$  obtained for the indanes, assuming  $s_c^*/k_B = \ln 2$ , are 1400, 1120, and 2750 kJ mol<sup>-1</sup> for the *o*-, *m*-, and *p*-isomers, respectively. Using Wunderlich's suggestion<sup>49</sup> that  $\Delta C_p(T_g) = 11.3$  J (mol beads)<sup>-1</sup>, the numbers of beads for the *o*-, *m*-, and *p*-isomers are 14, 17, and 16, respectively, compared with about 11 rotatable bonds in the molecule (the exact number depending on chemical intuition about what bonds are rotatable). Taking the number of bonds as 11, the values of  $\Delta\mu$  for the same sequence of isomers are found to be 127, 102, and 250 kJ (mol bonds)<sup>-1</sup>, compared with the dielectric value of about 980 kJ mol<sup>-1</sup> = 85 kJ (mol bonds)<sup>-1</sup> observed for all isomers.<sup>34</sup> It is difficult to understand why enthalpy relaxation is affected by isomeric differences whereas dielectric relaxation is not. Accordingly, because the enthalpy relaxation parameters are far more uncertain than the dielectric ones, it was of interest to force all three enthalpic values for  $B_{AGF}$  equal to the dielectric value while retaining the best fit enthalpic values of  $\Delta h^* \approx B_{AGF}/x^2$ , to produce modified values of  $x$ . This resulted in values of  $x$  of 0.19, 0.17, and 0.18 for the *o*-, *m*-, and *p*-isomers, respectively, that are within probable experimental uncertainties of the best-fit values. Insertion of these values into eq 22 yields  $\Delta\mu$  values that are similar for all isomers and comparable with the dielectric values, 83, 116, and 91 kJ (mol bonds)<sup>-1</sup>. The values of  $T_2^{AGF}$  computed

**TABLE 4: Adam–Gibbs and Fulcher Parameters<sup>a</sup>**

compound	$T_K$	$T_0$	$B_F$	$B_{AG}$	$T_2^{AG}(AGL)$	$T_2^{AG}(a - bT)$	$T_2^{AG}(AGF)$
<i>o</i> -indane	279	279 ( $\epsilon^*$ )	3090	4500	265	280	275
<i>m</i> -indane	317	287 ( $\epsilon^*$ )	2788	2630	297	303	302
<i>p</i> -indane	280	308 ( $\epsilon^*$ )	3150	7370	261	278	277
OTP	207	231 ( $\eta$ )	689	4348	166	168	175
TNB	281	200 ( $\eta$ )	4100	2063	244	262	255

<sup>a</sup> All parameters in K.

from the modified values of  $x$  are not significantly different from the best-fit values, 284, 295, and 274 K.

For TNB, an evaluation of  $\Delta\mu$  is especially pertinent because rotational energy barriers have been determined by NMR to be 54 kJ mol<sup>-1</sup> (albeit in a low-viscosity solvent).<sup>50</sup> The best-fit enthalpy value of  $\Delta\mu$  is 1189 kJ mol<sup>-1</sup> = 400 kJ (mol rotatable bonds)<sup>-1</sup>, a factor of 1.6 smaller than the value for viscosity (1.87 × 10<sup>3</sup> kJ mol<sup>-1</sup>).<sup>47</sup> The value of  $\Delta\mu$  per bond is a factor of 7 larger than the NMR derived rotational energy barriers. This is qualitatively consistent with rotation of the naphthalene rings requiring significant accommodation by surrounding molecules, but it implies the unreasonable value for  $w^*$  of 2<sup>7</sup> = 128. If the NMR values are arbitrarily multiplied by 2 to account for intermolecular effects,  $w^*$  is reduced to the more reasonable value of 2<sup>3.5</sup> = 11 and the enthalpic value of  $\Delta\mu$  becomes more sensible. For OTP,  $\Delta\mu$  is found to be 940 kJ mol<sup>-1</sup> = 470 kJ (mol rotatable bonds)<sup>-1</sup>, close to the viscosity value of 990 kJ mol<sup>-1</sup> estimated at  $T_g$  from published Fulcher parameters<sup>41</sup> but about twice the value of  $\Delta h^*$ . If  $x$  from eq 17 is inserted into eq 22,  $\Delta\mu$  reduces to 340 kJ mol<sup>-1</sup>, comparable with and a little less than  $\Delta h^*$ . These Adam–Gibbs  $\Delta\mu$  values are unreasonably large, suggesting that the Adam–Gibbs model is missing an essential feature of relaxation in these two materials.

The numbers of rearranging groups at  $T_g$ ,  $z^*(T_g)$ , can be evaluated as  $s_c^*/S_c = R \ln(w^*/S_c(T_g))$ . As is frequently observed for other materials,  $z^*(T_g) \leq 1$  is found for all five compounds if  $w^* = 2$  is assumed. This result has been interpreted by others to mean that the AG model, which is acknowledged to be idealized and heuristic<sup>51</sup> rather than theoretically rigorous (in the sense that the Gibbs–DiMarzio theory<sup>52</sup> is, for example), is deeply flawed. However, the interpretive problem of  $z^*(T_g) \leq 1$  can usually be resolved by assuming that  $w^* > 2$ . For polymers, for example,  $w^* = 2^3$  can be rationalized in terms of the fundamental crankshaft motion<sup>18</sup> (although evidence against such motions has been reported<sup>53</sup>), yielding sensible values of  $\Delta\mu$  that are comparable with rotational energy barriers, and for a series of phosphate glass compositions<sup>20</sup>  $\Delta\mu$  has been equated to the P–O bond energy and  $w^* > 2$  interpreted in terms of known molecular connectivity and structural topology. The ambiguity of separating  $w^*$  and  $\Delta\mu$  probably reflects the simplified and idealized nature of the AG model, although as suggested above the large values of  $\Delta\mu$  for OTP and TNB may reflect a more serious deficiency. Nonetheless, as has been noted elsewhere,<sup>54</sup> it is surprising that such a simple model can account so well for many of the complexities of the enigmatic glass transition<sup>55,56</sup> and of the dynamics of supercooled liquids, with generally sensible values of  $\Delta\mu$  and  $T_2^{AG} \approx T_K$ .

### Concluding Remarks

The present results indicate that the remarkable success of the Adam–Gibbs model extends to the isomeric indanes but not to OTP and TNB. The fact that  $T_2^{AG} \approx T_K$  for OTP and TNB but that the values of  $\Delta\mu$  are unphysical suggests that, although relaxation in these materials is apparently not properly captured by the AG model, the link between thermodynamics and kinetics is unaffected by this failure. This cryptic message has yet to be deciphered. Equation 22, which does not appear to have been derived before, permits facile calculations of  $\Delta\mu$  from published  $x$  and  $\Delta h^*$  parameters that are independent of any assumed form for  $\Delta C_p(T)$  and should allow a broader database to be developed for evaluating the physical significance of  $\Delta\mu$ . Equation 19, which also seems to have been derived

here for the first time, provides a direct test of the putative link between nonlinear kinetics and thermodynamics that AG predicts.

### References and Notes

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(57) Comparisons of  $x$  and  $T_K$  can also be made for isotactic PMMA and PS. For PMMA,  $T_K = 285$  K (corresponding to  $x = 0.11$  for the AGF equation), and  $T_2^{AG} = 256-288$  K (corresponding to the observed values of  $x = 0.1-0.2$ ).<sup>36</sup> For PS,  $T_K = 282$  K and  $x = 0.22$  compared with the experimental values of  $T_2^{AG} = 256$  K and  $x = 0.4$ . These results for iPMMA are comparable with those for the Indane glasses but  $T_2^{AG} < T_K$  for PS (see also ref 14) and this polymer more closely resembles TNB.