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Table I

Influence of Imbibed Water on Resin Activity[a]

entry	reaction conditions	resin	imbibed toluene,[b] g/g of polymer	imbibed water,[b] g/g of polymer	hydration state[c] n	activity[d] $10^5 k_{\text{obsd}}$, s^{-1}
1	biphase stoichiometric	1a		0.0	0	30
2		1a		0.036	0.9	20
3		1a		0.150	3.7	12
4		1a		0.360	8.9	3.5
5		1a		0.750	18.5	0.9
6		1a		11.910[e]	297	0.17
7	triphase stoichiometric	1a	0.43	11.910	297	0.06
8	triphase catalytic	1a	0.37	0.440	11.0	4.4
9	biphase stoichiometric	1b		0.0	0	52
10		1b		0.019	0.9	37
11		1b		0.079	3.7	29
12		1b		0.189	8.9	11
13		1b		0.395	18.5	4.5
14		1b		0.780[e]	96	3.9
15	triphase stoichiometric	1b	0.55	0.780	96	4.2
16	triphase catalytic	1b	0.56	0.420	18.9	12

[a] Reaction of 4.0 mL of 0.005 M *n*-decyl methanesulfonate in toluene with 0.45 mequiv of polymer at 70 °C, using procedures described in the text. [b] Analytical methods used for determining imbided toluene, water, and sodium chloride are described elsewhere.[15] [c] n = mol of water/mol of phosphonium groups. [d] Observed pseudo-first-order rate constant. Biphase reactions generally showed a slight acceleration with time due to evaporation of water from the resin. In these cases, k_{obsd} was determined from the initial slope. [e] Maximum volume of water uptake.

rated aqueous sodium chloride solution was employed. In the case of **1a**, the presence of salt substantially reduced the amount of imbibed water (osmotic shrinkage)[14] and increased its activity. Of particular significance was the fact that the activity and hydration state under catalytic conditions were nearly identical with those of a biphase reaction (compare entries 4 and 8). This shows that a major role of the salt in influencing catalytic activity is to define the hydration state of the resin. While a similar comparison made for **1b** qualitatively supports this conclusion, the numbers do not closely coincide. Specifically, if entries 12 and 16 are compared, the activities are essentially the same but the apparent hydration state is higher under catalytic conditions. Quantitative analysis of the sodium chloride associated with **1a** and **1b** under catalytic conditions has yielded values of 0.02 and 0.11 g of salt/g of polymer, respectively.[15] Is seems likely, therefore, that the higher hydration state for **1b** in entry 16 is due to the presence of adsorbed sodium chloride.

References and Notes

(1) Supported by the Division of Basic Energy Sciences of the Department of Energy (Contract EG-77-S-02-4446).

(2) Triphase catalysis is a technique which normally employs insoluble polymers to catalyze reaction between substances located in aqueous and organic phases. Review: Regen, S. L., *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421.

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(8) Generally, high aqueous salt concentrations have been employed in order to maintain resins in their nucleophilic form via ion exchange.

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(10) Biphase reactions are reactions carried out with a limited volume of water plus excess toluene; i.e., only a polymer and an external aqueous phase are visible. Triphase catalytic reactions are performed with excess toluene and an excess aqueous sodium chloride solution; imbibed solvents reside within the polymer.

(11) Monitored by a Cole-Parmer Strobette stroboscope tachometer.

(12) Analytical methods have been previously described.[9]

(13) Kinetic experiments using a 20-fold excess of *n*-decyl methanesulfonate relative to **1a** and **1b** have also been carried out under triphase stoichiometric conditions at 70 °C. In both cases clean pseudo-first-order kinetics were obtained (over 3 half-lives), indicating that all of the chloride ions in each polymer are uniformly active.

(14) Osmotic shrinkage has been commonly observed for ion-exchange resins under two-phase (polymer–water) conditions: Helfferich, F. "Ion Exchange"; McGraw-Hill: New York, 1962; p 103.

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Concept of Order Parameters in the Glass Transition. Nonequilibrium State of Glass along the Transition Line

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When an equilibrium liquid solidifies to a glass, the first derivatives of the Gibbs free energy, G, with respect to temperature, T (i.e., entropy, S), and pressure, P (i.e., volume, V), remain continuous whereas the second derivatives, the isobaric heat capacity, C_p, the coefficient of thermal expansion, α, and the isothermal compressibility, β, show a final discontinuity. The behavior of these thermodynamic quantities along the line of transition $T_{\text{tr}} = T_{\text{tr}}(P)$ is usually considered from the point of view of Ehrenfest relations,[1] originally derived for a second-order phase transition:

$$\mathrm{d}T_{\text{tr}}/\mathrm{d}P = \Delta\beta/\Delta\alpha \tag{1a}$$

$$\mathrm{d}T_{\text{tr}}/\mathrm{d}P = TV\Delta\alpha/\Delta C_p \tag{1b}$$

where the symbol Δ represents the discontinuity.

A more realistic model of the glass transition is a freezing-in process where the order parameters in the

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equilibrium liquid are assumed to change in accordance with the conditions of thermodynamic equilibrium, whereas everywhere in the glassy state they retain values corresponding to the transition point. In the case of a single order parameter, the Prigogine–Defay ratio,[2] r, is given by

$$r \equiv \Delta C_p \Delta\beta / TV(\Delta\alpha)^2 = 1 \qquad (2)$$

However, experimental evidence shows that in most cases[3-7] $r > 1$ and this leads to the following important conclusions: (i) the glass transition is governed by at least two order parameters;[8-10] (ii) either one or none of the Ehrenfest relations (1) can be valid; (iii) surfaces of the Gibbs free energy of the liquid and glass are not tangential along the transition line $T_{tr}(P)$;[6,11] (iv) contour lines along which the surfaces of the volumes or entropies of the liquid and glass contact each other are not identical;[6] and hence (v) along the contour line corresponding to one quantity the discontinuity of the other quantity appears, and vice versa.[11]

In this note we suggest a relation for $\mathrm{d}T_{tr}/\mathrm{d}P$ ensuing from a view that the states of the glass are closest to states of thermodynamic equilibrium along the transition line $T_{tr}(P)$. The discontinuities in the Gibbs free energy, entropy, and volume along the transition line will be estimated quantitatively together with their dependence on the distance from the original point of transition. Within the model of time-independent order parameters, the existence of these discontinuities is equivalent to the inequality $r > 1$. This equivalence makes possible an alternative test of the order-parameter description of the glass transition.

Theory

We shall use the concept of order parameters for the description of the above phenomenon. The isothermal–isobaric state of the glass-forming compound in the liquid is described by the Gibbs free energy, G_e, which is a function of temperature, pressure, and a number n of order parameters z_i that in turn also depend on temperature and pressure; i.e.

$$G_e = G_e[T,P,z_1(T,P),...,z_n(T,P)] = G_e(T,P) \qquad (3)$$

As soon as the liquid solidifies to a glass, the functions z_i freeze at values corresponding to the point of transition $[T_g,P_g]$ and retain these values everywhere in that part of the T–P plane which corresponds to the glassy state. Thus, we can write

$$G_g = G_g[T,P|z_{1g}(T_g,P_g),...] \qquad (4)$$

Following Gupta and Moynihan[6] we define a function g as the difference between the values of the Gibbs free energy in the glassy state and in the equilibrium liquid

$$g[T,P,z_1(T,P),...] = G_g(T,P|z_{1g},...) - G_e(T,P) \qquad (5)$$

We shall now examine the function g by expanding into a Taylor series in T and P in the vicinity of the point $[T_g,P_g]$:

$$g(T_g + \delta T, P_g + \delta P) = g|_{T_g,P_g} + \left(\delta T \frac{\partial}{\partial T} + \delta P \frac{\partial}{\partial P}\right) g|_{T_g,P_g} + \frac{1}{2}\left(\delta T \frac{\partial}{\partial T} + \delta P \frac{\partial}{\partial P}\right)^2 g|_{T_g,P_g} + ... \qquad (6)$$

where δT and δP are small but finite differences in temperature and pressure, respectively. The first and second terms on the right in eq 6 vanish. Substituting in the third term of eq 6 for the partial derivatives of g and omitting all terms of higher order, we have

$$g(T_g + \delta T, P_g + \delta P) = \tfrac{1}{2}[\delta T^2(\Delta C_p/T) - 2\delta T \delta P V \Delta\alpha + \delta P^2 V \Delta\beta] \qquad (7)$$

This is the equation of an elliptic paraboloid (in T–P–g space). Sections parallel to the T–P plane are ellipses and give equidistant points of the surfaces G_e and G_g. Taking into consideration that $V\Delta\alpha \neq 0$, we see that the axes of these ellipses are not parallel to the coordinate axes T and P. The minima of functional values $g(T,P)$ at a given distance of the argument $[T,P]$ from $[T_g,P_g]$ correspond to points along the longer axis of the ellipses. Physically, this means that the states along the longer axis of the ellipses are closest to thermodynamic equilibrium. Let it be assumed that the direction of the longer axis of the ellipses is just that in which the transition line $T_{tr}(P)$ is passing. This hypothesis is in agreement with the limit $r \rightarrow 1$ because then the elliptic paraboloid becomes a parabolic cylinder with an axis lying in the plane $g = 0$ and forming the transition line, the direction of which is given by eq 1.

In order to find a relation for $\mathrm{d}T_{tr}/\mathrm{d}P$, the variables δT and δP are replaced by dimensionless variables $\delta T/t$ and $\delta P/p$, in which t and p are, respectively, the unit temperature and the unit pressure. In this case, the transformation formula for the rotation of the ellipse about the center gives

$$\left.\frac{\mathrm{d}T_{tr}}{\mathrm{d}P}\right|_{T_g} = \frac{\kappa}{2}\left\{\frac{\Delta\beta}{\kappa\Delta\alpha} - \frac{\kappa\Delta C_p}{T_g V_g \Delta\alpha} + \left[\left(\frac{\Delta\beta}{\kappa\Delta\alpha} - \frac{\kappa\Delta C_p}{T_g V_g \Delta\alpha}\right)^2 + 4\right]^{1/2}\right\} \qquad (8)$$

where $\kappa = t/p$.

By analyzing this equation, one can reach the following conclusions: (i) if either of the two relations (1) is satisfied, the other must be satisfied too, and so must eq 2; (ii) if one of the equations (1) is not valid, then

$$\frac{\Delta\beta}{\Delta\alpha} > \left.\frac{\mathrm{d}T_{tr}}{\mathrm{d}P}\right|_{T_g} > \frac{TV\Delta\alpha}{\Delta C_p} \qquad (9)$$

where the direction of inequalities follows from the property $r > 1$; and (iii)

if

$$\frac{\kappa\Delta C_p}{T_g V_g \Delta\alpha} \gg \frac{\Delta\beta}{\kappa\Delta\alpha}$$

then

$$\frac{\mathrm{d}T_{tr}}{\mathrm{d}P} \approx \frac{T_g V_g \Delta\alpha}{\Delta C_p} \qquad (10a)$$

if

$$\frac{\kappa\Delta C_p}{T_g V_g \Delta\alpha} \ll \frac{\Delta\beta}{\kappa\Delta\alpha}$$

then

$$\frac{\mathrm{d}T_{tr}}{\mathrm{d}P} \approx \frac{\Delta\beta}{\Delta\alpha} \qquad (10b)$$

In order to examine the discontinuity in entropy along the transition line, we define similarly a function $\mathscr{S}$

$$\mathscr{S}[T,P,z_1(T,P),...] = S_g(T,P|z_{1g},...) - S_e(T,P) \quad (11)$$

The Taylor series for $\mathscr{S}$ in the vicinity of $[T_g,P_g]$ along the transition line, truncated after the first-order term, gives

$$\mathscr{S}(T_g + \delta T, P_g + \delta P) = -\delta P[(\mathrm{d}T_{tr}/\mathrm{d}P)(\Delta C_p/T) - V\Delta\alpha] \quad (12)$$

The surfaces S_e and S_g cross each other along the line with the slope $T_g V_g \Delta\alpha/\Delta C_p$. If $r > 1$, then along $T_{tr}(P)$ the surface S_g lies below the surface S_e for $P > P_g$, and vice versa.

The same procedure can be repeated also for the volume. The function

$$v[T,P,z_1(T,P),...] = V_g(T,P|z_{1g},...) - V_e(T,P) \quad (13)$$

can be also expanded into a series

$$v(T_g + \delta T, P_g + \delta P) = -\delta P[(\mathrm{d}T_{tr}/\mathrm{d}P)V\Delta\alpha - V\Delta\beta] \quad (14)$$

The contour line $v = 0$ has the slope $\Delta\beta/\Delta\alpha$ at the point $[T_g,P_g]$. For $r > 1$, the right-hand side of eq 14 is negative for $\delta P < 0$ and along $T_{tr}(P)$ the surface V_e lies above the surface V_g, while just the opposite holds for $\delta P > 0$.

Discussion

So far, the order-parameter description of the glass transition has not yielded any information on $\mathrm{d}T_{tr}/\mathrm{d}P$ because the glass transition has no other criterion of stability[12] except the requirement of a minimum G_e for an equilibrium liquid. Equation 7 maps the surface g in the vicinity of the point of transition, and its shape allows us to propose the following hypothesis instead of the criterion of stability: The direction of the transition line coincides with that of the smallest increase in $G(T,P)$, i.e., with the direction of the "least nonequilibrium" states. Equation 8 is a consequence of such an assumption.

An analysis of eq 8 shows that for $r > 1$ the hypothetical transition line lies between extremes corresponding to the Ehrenfest relations. Hence it follows, necessarily,[11] that along the transition line the excess entropy $\mathscr{S}$ and the excess volume v are not zero. The magnitudes of the thermodynamic quantities of the glass-forming material in the vicinity and in the point of transition favor inequality which leads to approximative relation (10a). Also, experimental data on many glass-forming materials[4,6,7] show that implication (10a) is quite adequate. This is in accord with the finding that both for polymers and for inorganic glasses eq 1b is often satisfied, while eq 1a is virtually never valid.[13]

Equation 1b governs the relationship between the surfaces S_e and S_g, which are continuous along the whole part of the line $T_{tr}(P)$ where eq 1b is satisfied. The discontinuity of surfaces S_g and S_e, if any, could be, in principle, observed on a calorimetric curve measured across the transition. Unfortunately, DSC traces obtained by Yourtree and Cooper[14] on densified polystyrene glasses are inconclusive in this respect.

The fact that the measured values do not satisfy eq 1a indicates that the surfaces V_g and V_e are not tangential along $T_{tr}(P)$. As $\Delta\beta/\Delta\alpha > \mathrm{d}T_{tr}/\mathrm{d}P|_{T_g}$, V_g increases in comparison to V_e toward pressures higher than P_g and, on the other hand, $V_g < V_e$ along $T_{tr}(P)$ for $P < P_g$. This finding is in agreement with a thought experiment of Goldstein:[11] a glass prepared at a pressure P_1 shows a negative discontinuity in volume when transformed back to a liquid at a pressure $P_2 > P_1$. Some experiments with polystyrene[14] and polysulfone[15] confirm this expectation.

The concept of the ordering parameters proves that glass-forming materials with $r = 1$ are thermodynamically (but not kinetically) history independent. On the other hand, materials with $r > 1$ are thermodynamically history dependent. Equations 7, 8, 12, and 14, which contain only measurable properties, offer quantitative predictions of the behavior of glasses, for example, formed by cooling under one pressure and then reheating under some another pressure. A comparison of these predictions with experiment will make possible a more complete evaluation of the suitability of the order-parameter description for the glass transition than a mere check of validity of eq 1 and 2.

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