The Glassy State, Ideal Glass Transition, and Second-Order Phase Transition

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ABSTRACT: According to Ehrenfest classification, the glass transition is a second-order phase transition. Controversy, however, remains due to the discrepancy between experiment and the Ehrenfest relations and thereby their prediction of unity of the Prigogine-Defay ratio in particular. In this article, we consider the case of ideal (equilibrium) glass and show that the glass transition may be described thermodynamically. At the transition, we obtain the following relations:

$$\frac{dT}{dP} = \frac{\Delta\beta}{\Delta\alpha}$$

and

$$\frac{dT}{dP} = \frac{TV\Delta\alpha(1-\Lambda)}{\Delta C_P - \Delta C_V}$$

with $\Lambda = (\alpha_g \beta_l - \alpha_l \beta_g)^2 / \beta_l \beta_g \Delta \alpha^2$;

$$\frac{dV}{dP} = V \frac{\alpha_g \beta_l - \alpha_l \beta_g}{\Delta \alpha}, \quad \frac{dV}{dP} = \frac{\beta_l \beta_g (\Delta C_P - \Delta C_V) (\alpha_g \beta_l - \alpha_l \beta_g)}{T \Delta \alpha (\alpha_l^2 \beta_g - \alpha_g^2 \beta_l)}; \quad \frac{dV}{dT} = V \frac{(\alpha_g \beta_l - \alpha_l \beta_g)}{\Delta \beta}$$

and

$$rac{dV}{dT} = rac{eta_leta_g(\Delta C_P - \Delta C_V)(lpha_geta_l - lpha_leta_g)}{T\Deltaeta(lpha_l^2eta_arphi - lpha_arphi^2eta_l)}\,.$$

The Prigogine-Defay ratio is

$$\Pi = \frac{1}{1 - (\Delta C_V - \Gamma) / \Delta C_P}$$

with $\Gamma = TV(\alpha_l\beta_g - \alpha_g\beta_l)^2/\beta_l\beta_g\Delta\beta$, instead of unity as predicted by the Ehrenfest relations. Dependent on the relative value of ΔC_V and Γ , the ratio may take a number equal to, larger or smaller than unity. The incorrect assumption of perfect differentiability of entropy at the transition, leading to the second Ehrenfest relation, is rectified to resolve the long-standing dilemma perplexing the nature of the glass transition. The relationships obtained in this work are in agreement with experimental findings. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 143–150, 1999

Key words: glass transition; second-order phase transition; Ehrenfest relations; Prigogine-Defay ratio; analyticity

INTRODUCTION

The glassy state is a universal phenomenon. It is observed in polymers, organic liquids, inorganic melts, biological macromolecules, colloids, super-

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conductors, spin glass, nonmetallic and metallic elements, and alloys, among others. The nature of glass and the glass transition is currently one fundamental question of great controversy in condensed matter physics, and may show practical impact and importance for exploring the modes of state in which matter can exist.¹⁻⁷

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The thermodynamic character of the glass transition has been widely revealed, well demonstrated in polymeric materials in particular.⁸ For example, the temperature characterizing the transition, glass transition temperature, displays remarkably a number-averaged molecular weight dependence. Practically, it can be calculated by the group-contribution techniques, and has been correlated to the solubility parameter or cohesive energy of the material. The findings of the correlation between the melting temperatures and glass transition temperatures further support the idea that the glass transition is thermodynamically based. In the glass transition region, many thermodynamic, physical, mechanical, electrical, and other properties of glass undergo considerable changes that may be predictable in principle.

Near and below the glass transition, however, the process is greatly slowed down, and the time scale of molecular motion is so prolonged that the time scale of the experiment is comparable to or even shorter than it, as often manifested in the time and history dependence of the experiment. If the experiment done is sufficiently slow, namely, enough time is allocated for the system to relax, an ideal thermodynamic liquid–glass transition may be observable. The dynamic treatment of the glass transition paints the kinetically controlled aspect of the system near the glass transition and is actually rooted in thermodynamics.⁹

We intend to resolve the long-standing dilemma perplexing the nature of the glass transition, due to the discrepancy between experiments and the Ehrenfest relations, and thereby their prediction of unity of the Prigogine-Defay ratio. In this article, the case of ideal (equilibrium) glass transition is considered, and its extension to real glass is treated elsewhere.²⁵ The presentation is organized as follows. We first review the Ehrenfest relations and their prediction on the Prigogine-Defay ratio and then compare them with experimental results. In The New Thermodynamic Expression section we provide a simple procedure to derive a general expression for the Prigogine-Defay ratio, applying the same thermodynamic relation above and below the transition line. Then, in the next section we discuss the relationships between volume, pressure, and temperature at the transition. Such an analysis consistently leads to the same result for the Prigogine-Defay ratio. In the Nonanalytical section, we analyze the problem of perfect differentiability of entropy at the transition line, resulting in the second Ehrenfest relation. The last section highlights the nature of glassy state and sums up the

results obtained in this article. In the Appendix we discuss concrete examples in the literature.

EHRENFEST RELATIONS VS. EXPERIMENTS

It is experimentally found at the liquid-glass transition or simply the glass transition that the first derivatives of the free energy as volume, enthalpy, and entropy are continuous quantities, but the second derivatives as specific heat, compressibility, and thermal expansion coefficient manifest anomalous jumps. In light of Ehrenfest classification, the glass transition is thereby a second-order phase transition. In this article, we use the glass transition and second-order phase transition interchangeably.

Ehrenfest implicitly hypothesized further, besides the continuous changes of volume and entropy, that the volume and entropy are perfect differentiable through the glass transition line, i.e.,

Condition I
$$dV_l(T \to T_g^+) = dV_g(T \to T_g^-)$$

or $dV_l = dV_g$

and

Condition II
$$dS_l(T \to T_g^+) = dS_g(T \to T_g^-)$$

or $dS_l = dS_g$

He then obtained the following celebrated relations, 10

$$\left(\frac{dT}{dP}\right)_e = \frac{\Delta\beta}{\Delta\alpha} \tag{1}$$

$$\left(\frac{dT}{dP}\right)_e = \frac{TV\Delta\alpha}{\Delta C_P} \tag{2}$$

where P, V, and T are the pressure, temperature and volume of the system, the thermal expansion coefficient

$$lpha = rac{1}{V} \left(rac{\partial V}{\partial T}
ight)_P,$$

compressibility

$$eta = -rac{1}{V}\left(rac{\partial V}{\partial P}
ight)_T,$$

specific heat at constant pressure

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

with *H* the enthalpy, and $\Delta X \equiv X_l - X_g$ for all X (l = liquid, g = glass). The subscript *e* in

$$\left(\frac{dT}{dP}\right)_{a}$$

stresses that the expressions are originated from Ehrenfest's hypothesis.

It is widely believed that if the glass transition is a thermodynamic phase transition the Prigogine-Defay ratio¹¹ defined as

$$\Pi = \frac{\Delta C_p \Delta \beta}{T V \Delta \alpha^2} \tag{3}$$

should be 1, $\Pi = 1$, as the result of the Ehrenfest relations (1) and (2).

Experimentally, there is no consensus reached yet to confirm the Ehrenfest relations, partly due to the difficulties in obtaining relevant pressure data and the relevant parameters often obtained from different samples.¹² Nonetheless, it may be summarized that the first Ehrenfest relation of eq. (1) is inconclusive, and the second of eq. (2)applies only in the majority of materials investigated.^{2,12-15} Moreover, the prediction of the Prigogine-Defay ratio, often used as a criterion for a second-order phase transition, finds little convincing support by existing experimental results, which are usually other than $1.^{2,13-16}$ This situation questions whether the glass transition is a thermodynamic phase transition and leans to suggest nonequilibrium roots of the transition. It is thought that additional internal parameters, ordering parameters, need to be introduced into the description of the glass transition. Unfortunately, such an approach, though modifying the Ehrenfest relations, fails to alter the result of $\Pi = 1$ ^{11,17} and a more recent attempt gives a value of less than 1 for $\Pi.^{12}$

In the next two sections, we give two consistent methods in the vein of thermodynamics to derive the expression for the Prigogine-Defay ratio, not necessarily to be unity, for second-order phase transitions in general. In the second method

$$\frac{dT}{dP}, \frac{dV}{dP}$$
 and $\frac{dV}{dT}$

at the transition are derived simultaneously.

A NEW THERMODYNAMIC EXPRESSION FOR II

To circumvent the uncertainty of the analytic behavior of thermodynamic functions at the secondorder phase transition, we begin with the thermodynamic relation below¹⁸:

$$C_P - C_V = TV\alpha \left(\frac{\partial P}{\partial T}\right)_V \tag{4}$$

with the specific heat at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

(U = internal energy). This relation is strictly satisfied away from a phase transition point (line), and is applicable to the both sides of the transition, i.e., the respective glassy and liquid state in the present case. On inserting the relation of

$$\left(\frac{\partial T}{\partial P}\right)_{V} = \frac{\beta}{\alpha}$$

into eq. (4), we reach

$$\Delta C_P - \Delta C_V = TV\Delta \frac{\alpha^2}{\beta} \tag{5}$$

where

$$\Delta C_{V} = C_{V,l} - C_{V,g}, \ \Delta \frac{\alpha^{2}}{\beta} = \frac{\alpha_{l}^{2}}{\beta_{l}} - \frac{\alpha_{g}^{2}}{\beta_{g}}$$

and the assumption of continuous volume $V_l = V_g = V$ at the transition was applied. Equation (5) may equivalently be rewritten in the form of the Prigogine-Defay ratio:

$$\Pi = \frac{1}{1 - \frac{(\Delta C_V - \Gamma)}{\Delta C_P}} \tag{6}$$

where

$$\Gamma \equiv \frac{TV(\alpha_l\beta_g - \alpha_g\beta_l)^2}{\beta_l\beta_g\Delta\beta}$$

Equation (6) is usually not to be unity, except in the case of $\Delta C_V = \Gamma$, so the value of Π predicted from the Ehrenfest relations is a special case of eq. (6).

We point out that eq. (6) is valid for nonideal glass.²⁵ The Appendix discusses concrete examples, illustrating the influences of the isochoric heat capacity difference ΔC_V and the thermomechanical quantity Γ on the Prigogine-Defay ratio. The observation of the ratio Π other than 1, actually much larger than 1 for the samples analyzed there, is in consistency with the prediction of eq. (6), which can, dependent on the magnitude of the difference of $(\Delta C_V - \Gamma)$ to ΔC_P , take values differing from 1.

EXPRESSIONS FOR dT/dP, dV/dP, AND (dV)/(dT) AT THE TRANSITION

The variables of P, V, and T define the transition, and we assume the perfect differentiability of volume (thereby pressure and temperature) at the transition line, $dV_l = dV_g$, in addition to the continuous volume $V_l = V_g$. Then, we may take the temperature T as a thermodynamic function in terms of variables P and V. After the expansion it holds

$$\frac{dT}{dP} = \left(\frac{\partial T}{\partial P}\right)_{V} + \left(\frac{\partial T}{\partial V}\right)_{P} \frac{dV}{dP} = \frac{\beta}{\alpha} + \frac{1}{V\alpha} \frac{dV}{dP}$$
(7)

From the existence of

$$\frac{dT}{dP}, \frac{dV}{dP}$$

at the glass transition line, we are led to

$$\frac{\beta_l}{\alpha_l} + \frac{1}{V\alpha_l}\frac{dV}{dP} = \frac{\beta_g}{\alpha_g} + \frac{1}{V\alpha_g}\frac{dV}{dP}$$
(8)

or

$$\frac{dV}{dP} = V \frac{\alpha_g \beta_l - \alpha_l \beta_g}{\alpha_l - \alpha_g} = V \frac{\alpha_g \beta_l - \alpha_l \beta_g}{\Delta \alpha}$$
(9)

In terms of eq. (9), the behavior of dV/dP at the transition line is determined by the relative signs of

$$\left(\frac{\boldsymbol{\beta}_l}{\boldsymbol{\alpha}_l}-\frac{\boldsymbol{\beta}_g}{\boldsymbol{\alpha}_g}\right)$$

and $\Delta \alpha$.

The expression for dT/dP follows simply from eqs. (7)–(9),

$$\frac{dT}{dP} = \frac{\beta_l}{\alpha_l} + \frac{1}{V\alpha_l} V \frac{\alpha_g \beta_l - \alpha_l \beta_g}{\alpha_l - \alpha_g} = \frac{\beta_g}{\alpha_g} + \frac{1}{V\alpha_g} V \frac{\alpha_g \beta_l - \alpha_l \beta_g}{\alpha_l - \alpha_g} = \frac{\Delta\beta}{\Delta\alpha} \quad (10)$$

Equation (10) is identical with the first Ehrenfest relation of eq. (1), for both the derivation procedures have essentially made use of the same hypothesis, the perfect differentiability of volume at the transition.

Furthermore, we may expand the entropy S in terms of variable pairs of (P, T) and (T, V), respectively,

$$\frac{dS}{dT} = \left(\frac{\partial S}{\partial T}\right)_{P} + \left(\frac{\partial S}{\partial P}\right)_{T} \frac{dP}{dT} = \frac{C_{P}}{T} - V\alpha \frac{dP}{dT} \quad (11)$$
$$\frac{dS}{dT} = \left(\frac{\partial S}{\partial T}\right)_{V} + \left(\frac{\partial S}{\partial V}\right)_{T} \frac{dV}{dT} = \frac{C_{V}}{T} + \frac{\alpha}{\beta} \frac{dV}{dT} \quad (12)$$

In the above equations, we have invoked the identities of

$$\left(rac{\partial oldsymbol{S}}{\partial P}
ight)_T = - \left(rac{\partial V}{\partial T}
ight)_P = -Vlpha$$

and

$$\left(\frac{\partial S}{\partial V}\right)_{T} = \left(\frac{\partial P}{\partial T}\right)_{V} = \frac{\alpha}{\beta}.$$

Consequently, we have a second relation for dT/dP expressed in C_P and C_V from eqs. (11) and (12),

$$V\alpha \,\frac{dP}{dT} = \frac{C_P - C_V}{T} - \frac{\alpha}{\beta} \frac{dV}{dT} \tag{13}$$

Again, eq. (13) is valid on the both sides of the transition, i.e.,

$$V\alpha_l \frac{dP}{dT} = \frac{C_{P,l} - C_{V,l}}{T} - \frac{\alpha_l dV}{\beta_l dT}$$
(14)

and

$$V\alpha_g \frac{dP}{dT} = \frac{C_{P,g} - C_{V,g}}{T} - \frac{\alpha_g}{\beta_g} \frac{dV}{dT}$$
(15)

In the above, we as before supposed the existence of

$$\frac{dP}{dT}, \frac{dV}{dT}, \frac{dV}{dP}$$

and the continuous volume at the transition. Subtracting eq. (14) from eq. (15), writing

$$\frac{dV}{dT} = \frac{dV}{dP}\frac{dP}{dT}$$

and then using eq. (9), we get

$$\frac{dP}{dT} = \frac{\Delta C_P - \Delta C_V}{TV\Delta\alpha} + \frac{(\alpha_g \beta_l - \alpha_l \beta_g)^2}{\beta_l \beta_g \Delta \alpha^2} \frac{dP}{dT} \quad (16)$$

or

$$\frac{dP}{dT} = \frac{\Delta C_P - \Delta C_V}{TV\Delta\alpha(1 - \Lambda)} \tag{17}$$

where

$$\Lambda = \frac{(\alpha_g \beta_l - \alpha_l \beta_g)^2}{\beta_l \beta_g \Delta \alpha^2}$$

This formulation for (dT)/(dP) from entropy is evidently different from the second Ehrenfest relation of eq. (2), except under the specific condition of eq. (24) below, for in the derivation of the latter the perfect differentiability of entropy at the transition is incorrectly assumed $dS_g = dS_l$ at the transition (see next section). If we recall eq. (5), eq. (17) is equivalent to eq. (10).

Now it is straightforward to obtain the expression for dV/dT at the transition, just by inserting dV/dP of eq. (9) and dP/dT of eq. (17) into

$$\frac{dV}{dT} = \frac{dV}{dP}\frac{dP}{dT},$$

$$\frac{dV}{dT} = \frac{\beta_l\beta_g(\Delta C_P - \Delta C_V)(\alpha_g\beta_l - \alpha_l\beta_g)}{T\Delta\beta(\alpha_l^2\beta_g - \alpha_g^2\beta_l)} \quad (18)$$

Replacing $(\Delta C_P - \Delta C_V)$ by eq. (5), the above equation is simplified to

$$\frac{dV}{dT} = V \frac{(\alpha_g \beta_l - \alpha_l \beta_g)}{\Delta \beta}$$
(19)

which can be conveniently worked out by combining eqs. (9) and (10) as well. This expression may be used to describe the volume at the transition as a function of temperature and the behavior relies on the relative signs of

$$\left(\frac{\beta_l}{\alpha_l}-\frac{\beta_g}{\alpha_g}\right)$$

and $\Delta\beta$.

Equating eqs. (10) and (17), the same expression as eq. (6) for the Prigogine-Defay ratio is obtained once more. It indicates that the assumption of perfect differentiability of volume at the transition is established from the viewpoint of thermodynamics, besides experimental verifications. We stress that in our approach the perfect differentiability of entropy at the transition is not hypothesized, which necessarily accounts for the second Ehrenfest relation. The temperature and pressure play similar roles in the glass transition.

NONANALYTICITY OF ENTROPY AT THE TRANSITION LINE

We come to discuss the invalidity of part of the entropy assumption in deriving the second Ehrenfest relation, i.e., $dS_l(T \rightarrow T_g^+) = dS_g(T \rightarrow T_g^-)$. This relation states that entropy is a perfect differentiable at the transition line. However, the assertion may be untrue, due to the fact that its analyticity at the transition is actually ignored, though the entropy itself is continuous at the transition.

Physically, ordering takes place through a second-order phase transition, as observed in phenomena as zero-field superconducting transition, superfluity transition, magnetic transition, ordering of alloys, and others,¹⁹ indicating a possible singularity of entropy at the transition point. Mathematically, we prove below that the inequality is the general case,

$$dS_l(T \to T_{\sigma}^+) \neq dS_{\sigma}(T \to T_{\sigma}^-)$$

or simply

$$dS_l \neq dS_g \tag{20}$$

Actually, we may write dS_l and dS_g in difference as

$$dS_l - dS_g = \left(\frac{\Delta C_P}{T} - V \frac{\Delta \alpha^2}{\Delta \beta}\right) dT$$
 (21)

if eqs. (10) and (11) are recalled. Or alternatively expressed in the Prigogine-Defay ratio,

$$dS_l - dS_g = (\Pi - 1)V \frac{\Delta \alpha^2}{\Delta \beta} dT \qquad (22)$$

It is clear from the above relation $(\Delta \beta > 0)$ that

$$\begin{aligned} &\frac{dS_{l}(T_{g})}{dT} > \frac{dS_{g}(T_{g})}{dT} & \Pi > 1 \\ &\frac{dS_{l}(T_{g})}{dT} = \frac{dS_{g}(T_{g})}{dT} & \text{if} & \Pi = 1 \\ &\frac{dS_{l}(T_{g})}{dT} < \frac{dS_{g}(T_{g})}{dT} & \Pi < 1 \end{aligned}$$

or vice versa. For we may write dT in

$$\left(\frac{dT}{dX}\right) \, dX \, (X=P, \, V)$$

similar relations as eq. (23) hold for

$$\frac{dS_{l}(T_{g})}{dX} \sim \frac{dS_{g}(T_{g})}{dX},$$

dependent on the sign of dT/dX.

Obviously, the criterion for

$$dS_l = dS_g ext{ is } \Pi = 1 ext{ or } \Delta C_p = rac{TV\Delta lpha^2}{\Delta eta},$$

which is equivalent to

$$\Delta C_{V} - \Gamma = 0 \quad \text{or} \quad \Delta C_{V} - \frac{TV(\alpha_{l}\beta_{g} - \alpha_{g}\beta_{l})^{2}}{\beta_{l}\beta_{g}\Delta\beta} = 0$$
(24)

which, in turn, leads to the correspondence between the quantities Π and $(\Delta C_V~-~\Gamma)$

$$\begin{split} \Pi > 1 & \Delta C_V - \Gamma > 0 \\ \Pi = 1 & \text{if} & \Delta C_V - \Gamma = 0 \\ \Pi < 1 & \Delta C_V - \Gamma < 0 \quad (25) \end{split}$$

or vice versa $\Delta C_p > 0$. As the consequence, the Prigogine-Defay ratio may take a number equal to, larger, or smaller than unity, depending on the relative value of ΔC_V and Γ .

According to the above analysis, the analyticity (perfect differentiability) of entropy at the transition line is a restrictive, experimentally unverified assumption, only valid under the condition of $\Pi = 1$, and disregards of the continuity of entropy itself at the transition line. Alternatively stated, entropy is nonanalytic at the transition line. Hence, that the second Ehrenfest relation of eq. (2) and the corresponding prediction of unity of the Prigogine-Defay ratio, $\Pi = 1$, is generally incorrect, only a specific result of the more general treatment in our approach.

NATURE OF THE GLASSY STATE AND SUMMARY

Glass is a crystal-like short-range ordered, liquidlike long-range disordered solid.^{4,5,20,21} It is a special condensation state of matter, sharing both local crystalline characteristics and long-range liquid features. Like other second-order transitions,¹⁹ the glass transition is an ordering process, and there is a further reduction of symmetry in the transition from the liquid phase to the glass phase. The onset of the glassy state begins at the transition and proceeds further with lowering temperature. Experimental findings indicate microheterogeneity of glass. As the glass transition is a second-order phase transition, the apparent paradox of Kauzmann²³ is naturally removed. It may be concluded that the glass transition of ideal glass is a thermodynamic second-order phase transition, while the counterpart of real glass, which is a thermodynamically rooted, experimental time scale disguised second-order phase transition.²⁵ The glass transition in both the cases may be analyzed under the general theory of second-order phase transitions.²²

In this article, we show that the additional assumption of perfect differentiability of entropy at the transition, necessary for the derivation of the second Ehrenfest relation, is incorrect and the problem is solved to remove the dilemma perplexing the nature of the glass transition. The two thermodynamic methods of self-consistence give the expression for the Prigogine-Defay ratio,

$$\Pi = \frac{1}{1 - (\Delta C_V - \Gamma) / \Delta C_P}$$

with $\Gamma = TV(\alpha_l\beta_g - \alpha_g\beta_l)^2/\beta_l\beta_g\Delta\beta$, which has been applied to reanalyze experimental results in the Appendix. Dependent on the relative value of ΔC_V and Γ , the ratio may take a number equal to, larger, or smaller than unity. In particular, we recapitulate the following relations at the transition:

$$\frac{dT}{dP} = \frac{\Delta\beta}{\Delta\alpha}$$

and

$$rac{dT}{dP} = rac{TV\Deltalpha(1-\Lambda)}{\Delta C_P - \Delta C_V}$$

with
$$\Lambda = (\alpha_g \beta_l - \alpha_l \beta_g)^2 / \beta_l \beta_g \Delta \alpha^2;$$

 $rac{dV}{dP} = V \, rac{lpha_g eta_l - lpha_l eta_g}{\Delta lpha}$

and

$$rac{dV}{dT} = V \, rac{(lpha_g eta_l - lpha_l eta_g)}{\Delta eta} \, .$$

These relations may be properly used to discuss experimental observations as recently reported by Colucci et al.¹⁶ on the change of the volume at the transition line as a function of pressure and temperature.

APPENDIX

To illustrate the effects of the terms ΔC_V and Γ in eq. (6) on the Prigogine-Defay ratio Π , we used the

Table I Thermodynamic Parameters for Three Glass-Formers at the Glass Transition Domains

	B_2O_3	$\begin{array}{l} 40 \ mol \ \% \ Ca(NO_3)_2 \\ -60 \ mol \ \% \ KNO_3 \end{array}$	Poly(vinylacetate)
T (K)	550	340	303.8
$10^3 V (m^3/kg)$	0.558	0.456	0.843
$10^4 \alpha_l (\mathrm{K}^{-1})$	4.0	3.5	7.12
$10^4 \alpha_g ({\rm K}^{-1})$	0.5	1.2	2.80
$10^{11} \bar{\beta}_l \ (m^2/N)$	40	13.2	49.81
$10^{11} \beta_g (m^2/N)$	12	6.3	28.96
$\Gamma = \frac{(\alpha_g \beta_l - \alpha_l \beta_g)^2)}{\beta_l \beta_g \Delta \alpha^2}$	0.13	0.09	0.17
$10^{-2} \ TV rac{lpha_l^2}{eta_l} (\mathrm{J/K}\cdot\mathrm{kg})$	1.23	1.44	2.61
$10^{-2} TV \frac{\alpha_g^2}{\beta} (J/K \cdot kg)$	0.06	0.35	0.69
$10^{-2} C_{P,l} (J/K \cdot kg)$	19.3	14.9	18.0
$10^{-2} C_{P_{g}} (J/K \cdot kg)$	13.0	9.5	13.0
$10^{-2} \Delta C_P (J/K \cdot kg)$	6.3	5.4	5.0
$10^{-2} C_{V,l} (J/K \cdot kg)$	18.1	13.5	15.4
$10^{-2} C_{V,g} (J/K \cdot kg)$	12.9	9.1	12.3
$10^{-2} \Delta C_V (\text{J/K} \cdot \text{kg})$	5.2	4.4	3.1
$\Gamma (J/K \cdot kg)$	17.9	10.4	38.1
$rac{\Gamma}{\Delta C_V}$ (%)	3.4	2.4	12.3
$ \frac{\Delta C_V}{\Delta C_P} (\%) $ $ \frac{\Gamma}{\Delta C_P} (\%) $	82.5	81.5	62
$rac{\Gamma}{\Delta C_P}\left(\% ight)$	2.8	1.9	7.6
Π (omission of Σ) by eq. (6)	5.7	5.4	2.6
Π (including Σ) by eq. (6)	4.9	4.7	2.2
$\Pi = \Delta C_p \Delta \beta / TV \Delta \alpha^2 \text{ (as defined)}$	4.7	4.5	2.2

Underlined experimental data in ref. 24 are selected here.

experimental data collected by Gupta and Moynihan (see Table I).²⁴ The values of C_V are calculated based on eq. (4). From Table I we find that in the glass transition domains the isothermal specific heats are comparable to the isobaric specific heats in the strong glasses of B_2O_3 and 40 mol % $Ca(NO_3)_2$ -60 mol % KNO₃, in contrast to that of the fragile glass poly(vinylacetate). This may account for the fact that the Prigogine-Defay ratio II of the strong glasses is much larger than 1, whereas it approaches unity for the fragile glass (also see ref. 15). Comparing the differences of

$$TV \, rac{lpha^2}{eta}, \, rac{\Gamma}{\Delta C_V} \, ext{and} \, rac{\Gamma}{\Delta C_P}$$

between the strong and fragile glasses, the tendency is evident that the quantities are larger for the fragile glass than for the strong glasses, which may energetically and structurally shed light on the fragility of glass.⁷

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