Determination of accurate theoretical values for thermodynamic properties in bulk metallic glasses

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Abstract Deviation values of specific heat difference ΔC_p , the Gibbs free energy difference ΔG , enthalpy difference ΔH , and entropy difference ΔS between the supercooled liquid and corresponding crystalline phase produced by the linear, hyperbolic, and Dubey's expressions of ΔC_p and the corresponding experimental values are determined for sixteen bulk metallic glasses (BMGs) from the glass transition temperature T_g to the melting temperature T_m . The calculated values produced by the hyperbolic expression for ΔC_p most closely approximate experimental values, indicating that the hyperbolic ΔC_p expression can be considered universally applicable, compared to linear and Dubey's expressions for ΔC_p , which are accurate only within a limited range of conditions. For instance, Dubey's ΔC_p expression provides a good approximation of actual experimental values within certain conditions (i.e., $\xi = \Delta C_p^g / \Delta C_p^m < 2$, where ΔC_p^g and ΔC_p^m represent the specific heat difference at temperatures T_g and T_m , respectively).

Keywords Bulk metallic glass (BMG) · Specific heat · Linear expression · Hyperbolic expression

1 Introduction

Due to the presence of a large supercooled liquid region, bulk metallic glasses (BMGs) usually exhibit high thermal stability against crystallization. As a result, a large range of experimental time and temperatures for nucleation and crystalline growth processes exist in metallic glass forming melts. Characterization of the three thermodynamic parameters including Gibbs free energy difference ΔG , entropy difference ΔS , and enthalpy difference ΔH , are important in evaluation of nucleation and crystal growth processes in BMGs between the supercooled liquid and corresponding crystalline phases [1, 2]. Nucleation rates have been shown to have an exponential dependence on ΔG [3], acting as a driving force of nucleation. When ΔG is small, the critical nucleation work is improved, and nucleation rates are reduced [4]. As a result, the glass forming ability (GFA) of these materials is improved. The values of ΔG , ΔS , and ΔH are routinely calculated by measuring changes in the specific heat difference, ΔC_p , between the supercooled liquid and corresponding crystalline phases across a range of temperatures.

The metastable nature of supercooled liquids, however, makes accurate experimental values for ΔC_p difficult to determine [5]. Thus, most ΔC_p values for the supercooled liquid regions of various BMGs are only rough approximations generated by fitting limited experimental data to the melting temperature, T_m , in the vicinity of the glass transition temperature T_g . Because the accurate specific heat data in the supercooled region are notably absent, the functional dependences of ΔG , ΔS , and ΔH on temperature are generally estimated theoretically [5]. Several models for calculating ΔG , ΔS , and ΔH values have been previously proposed based on different expressions for ΔC_p [6–14].

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In these expressions, Thompson et al. [12] and Hoffman et al. [13] assumed that ΔC_p was constant with temperature. Whereas Mondal et al. [10] and Patel et al. [11] suggested that ΔC_p value depended linearly or hyperbolically on temperature, respectively. Each of these expressions, however, is deduced strictly from experimental data [6, 10–14] without theoretical support.

Recently, Dubey et al. [7, 8] proposed a theoretical expression for ΔC_p based on the hole theory of the liquid state, thus calculating more accurate values for ΔG , ΔH , and ΔS from experimental results collected among the temperature range from T_g to T_m in the $Zr_{57}Cu_{15.4}Ni_{12.6}Al_{10}Nb_5$ BMG [8]. Furthermore, a hyperbolic expression for ΔC_p was deduced that provided an optimal mathematical model for elucidating GFA based on the theoretical expression for ΔC_p proposed by Dubey et al. [7, 8].

According to the hyperbolic expression for ΔC_p based on the hole theory of the liquid state [15], the current study further deduced a linear expression for ΔC_p . The values of ΔG , ΔH , ΔS and for BMGs in the temperature range from T_g to T_m were calculated based on the hyperbolic, linear, and Dubey's expression for ΔC_p . Sixteen BMG materials [16–26] were selected as models for using in experimental evaluation of the accuracy of these 3 expressions for ΔC_p (Dubey's, hyperbolic, linear). The deviations observed in thermodynamic parameters between experimental results and these three models [7, 8, 15] were comparatively evaluated.

2 Expressions for the thermodynamic parameters ΔC_p , ΔG , ΔS , and ΔH

Since ΔG is vital to the study of GFA in BMGs, expressions for ΔC_p used in the calculation of ΔG values are important. The authors [15] previously proposed a hyperbolic expression for ΔC_p based on the hole theory of the liquid state [7, 8], shown as follows:

$$\begin{aligned}\Delta C_p &= \Delta C_p^m \left(\sigma_h - 1 + (2 - \sigma_h) \frac{T_m}{T} \right) \\ &= \Delta C_p^m \left(\sigma_h - 1 + (2 - \sigma_h) \frac{1}{1 - \frac{\Delta T}{T_m}} \right),\end{aligned}\quad (1)$$

where ΔC_p^m is the specific heat difference between the supercooled liquid and the corresponding crystalline phase at T_m ; σ_h is a coefficient related to the hole formation energy in the hyperbolic express; ΔT is the degree of supercooling ($\Delta T = T_m - T$, where T is the temperature). In BMG systems, the $T_m - T$ values are smaller than T_m

when T is decreased from T_m to T_g , suggesting that the value of $\Delta T/T_m$ is less than one. In this case, it is reasonable to approximate that the hyperbolic term in Eq. (1) can be expanded using a Taylor series, as follows:

$$\frac{T_m}{T} = \frac{1}{1 - \frac{\Delta T}{T_m}} = 1 + \frac{\Delta T}{T_m} + \left(\frac{\Delta T}{T_m} \right)^2 + \cdots + \left(\frac{\Delta T}{T_m} \right)^n, \quad (2)$$

thus producing the expression by neglecting a portion of the higher-order terms ($n > 1$),

$$\Delta C_p = \Delta C_p^m \left(3 - \sigma_1 - (2 - \sigma_1) \frac{T}{T_m} \right), \quad (3)$$

where σ_1 is a coefficient related to the hole formation energy in the linear expression. Since the portion of the higher-order terms ($n > 1$) in Taylor's series, i.e., Eq. (2), is neglected, which can modify the coefficient of $(2 - \sigma_h)$ in Eq. (1), σ_1 is used to replace σ_h . The linear expression of ΔC_p shown in Eq. (3) is similar to the linear form of $\Delta C_p = A + BT$, where A ($A = \frac{T_g \Delta C_p^m - T_m \Delta C_p^g}{T_g - T_m} = \Delta C_p^m (3 - \sigma_1)$) and B ($B = \frac{\Delta C_p^g - \Delta C_p^m}{T_g - T_m} = \frac{\Delta C_p^m (\sigma_1 - 2)}{T_m}$) are the coefficients for linear expression, proposed by Patel et al. [11]. Evaluation of the parameter σ_1 also results in a method similar to that proposed by Dubey et al. [7, 8]. Since experimental values of ΔC_p^g are usually measured in the vicinity of T_g , the ΔC_p^m value can be employed in conjunction with Eq. (3) to yield

$$\sigma_1 = 2 + \frac{1 - \xi}{1 - T_{rg}}, \quad (4)$$

where $T_{rg} = T_g/T_m$ is the reduced glass transition temperature; and $\xi = \Delta C_p^g/\Delta C_p^m$, where ΔC_p^g is the specific heat difference between the supercooled liquid and the corresponding crystalline phase at T_g .

ΔG , ΔH and ΔS are the differential values between the supercooled liquid and the corresponding crystalline phase, which can be expressed as

$$\Delta H = \Delta H_m - \int_T^{T_m} \Delta C_p dT, \quad (5)$$

and

$$\Delta S = \Delta S_m - \int_T^{T_m} \frac{\Delta C_p}{T} dT, \quad (6)$$

$$\Delta G = \Delta H - T \Delta S, \quad (7)$$

where ΔH_m is the enthalpy of fusion, and $\Delta S_m = \Delta H_m/T_m$ is the entropy of fusion. Substituting Eq. (3) into Eqs. (5)–(7), the novel expressions for ΔH , ΔS and ΔG can be obtained as

Table 1 Thermodynamic parameters for evaluation of ΔG , ΔH , and ΔS in the 16 BMGs

Alloys	$A/(J \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	$B/(J \cdot \text{mol}^{-1} \cdot \text{K}^{-3})$	$C/(J \cdot \text{mol}^{-1} \cdot \text{K}^{-2})$	T_g/K	T_m/K	T_{rg}	$\Delta H_m/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta C_p^m/(J \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$	$\Delta C_p^s/(J \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$
La ₆₂ Al ₁₄ Cu ₂₄ [16]	0.03071	4.16×10^5	-1.49×10^{-5}	401	673	0.60	6.835	14.840	12.510
La ₅₅ Al ₂₅ Ni ₂₀ [17]	0.02190	1.24×10^6	-1.01×10^{-5}	491	712	0.69	7.477	12.940	13.460
Cu ₄₇ Ti ₃₄ Zr ₁₁ Ni ₈ [18]	0.01650	2.83×10^6	-6.82×10^{-6}	673	1114	0.60	11.300	12.187	14.257
Zr ₄₆ Cu ₄₆ Al ₈ [19]	0.12850	4.61×10^6	-5.59×10^{-6}	715	979	0.73	8.035	13.490	16.410
La ₅₅ Al ₂₅ Cu ₁₀ Ni ₅ Co ₅ [17]	0.02520	1.69×10^6	-1.18×10^{-5}	466	661	0.70	6.095	12.610	15.580
La ₆₂ Al ₁₄ (Cu _{5/6} Ag _{1/6}) ₂₄ [16]	0.03340	7.54×10^5	-3.04×10^{-5}	404	656	0.62	6.118	10.600	13.160
Mg ₆₅ Cu ₂₅ Y ₁₀ [20]	0.01750	1.8×10^6	-1.02×10^{-5}	410	730	0.56	8.650	10.730	15.700
Zr ₅₇ Cu _{15.4} Ni _{12.6} Al ₁₀ Nb ₅ [18]	0.01630	6.32×10^6	-8.37×10^{-6}	682	1091	0.63	9.400	13.130	20.810
Zr ₄₆ (Cu _{4.5/5.5} Ag _{1/5.5}) ₄₆ Al ₈ [19]	0.01620	8.17×10^6	-2.08×10^{-5}	620	937	0.66	8.200	11.060	17.870
Pt _{57.3} Cu _{14.6} Ni _{5.3} P _{22.8} [21]	0.01010	5.77×10^6	-1.20×10^{-5}	488	776	0.63	11.400	10.190	26.280
Zr _{52.5} Cu _{17.9} Ni _{14.6} Al ₁₀ Ti ₅ [18]	0.00260	6.43×10^6	-16.8×10^{-6}	675	1072	0.63	8.200	7.520	19.830
Ti _{36.89} Cu _{43.87} Ni _{9.36} Zr _{9.88} [22]	0.02140	1.02×10^7	-0.97×10^{-5}	678	1093	0.62	10.949	8.400	27.920
Ti _{37.65} Cu _{43.25} Ni _{9.6} Zr _{9.5} [22]	0.00870	1.17×10^7	-9.25×10^{-6}	673	1097	0.61	11.040	8.150	27.510
Zr _{41.2} Ti _{13.8} Ni ₁₀ Cu _{12.5} Be _{22.5} [23, 24]	0.01620	8.17×10^6	-2.08×10^{-5}	620	937	0.66	8.200	6.220	23.300
Zr _{58.5} Cu _{15.6} Ni _{12.8} Al _{10.3} Nb _{2.8} [25]	0.01280	5.70×10^6	-1.37×10^{-5}	660	1083	0.61	8.700	2.655	15.550
Pd ₄₃ Ni ₁₀ Cu ₂₇ P ₂₀ [26]	0.03320	4.89×10^6	-5.00×10^{-5}	576	790	0.73	7.200	2.860	17.280

$$\Delta H = \Delta H_m - \Delta C_p^m \left((3 - \sigma_1)(T_m - T) - \left(1 - \frac{\sigma_1}{2}\right) \frac{1}{T_m} (T_m^2 - T^2) \right), \quad (8)$$

$$\Delta S = \Delta S_m - \Delta C_p^m \left(\frac{\sigma_1 - 2}{T_m} \Delta T + (3 - \sigma_1) \ln \frac{T_m}{T} \right), \quad (9)$$

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \left((\sigma_1 - 2) \frac{\Delta T^2}{2T_m} + (3 - \sigma_1) \left(\Delta T - T \ln \frac{T_m}{T} \right) \right). \quad (10)$$

Comparative studies were conducted on the expressions for ΔG , ΔS , and ΔH produced by the hyperbolic expression and Dubey's expression for ΔC_p using the framework of the hole theory of the liquid state as a basis. This technique allowed for further characterization of the thermodynamic behaviors of BMGs. Based on the hyperbolic expression for ΔC_p , the expressions for ΔG , ΔS , and ΔH , respectively, are [15]

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \left((3 - \sigma_h) \Delta T + ((3 - \sigma_h) T_m - (\sigma_h - 1) \Delta T) \ln \frac{T_m}{T} \right), \quad (11)$$

$$\Delta H = \Delta H_m - \Delta C_p^m \left((\sigma_h - 1)(T_m - T) + (2 - \sigma_h) T_m \ln \frac{T_m}{T} \right), \quad (12)$$

$$\Delta S = \Delta S_m - \Delta C_p^m \left((2 - \sigma_h) \frac{T_m - T}{T} + (\sigma_h - 1) \ln \frac{T_m}{T} \right), \quad (13)$$

and

$$\sigma_h = 1 + \frac{1 - T_{rg} \xi}{1 - T_{rg}}. \quad (14)$$

Based on the hole theory of the liquid state, Dubey et al. [7, 8] provided an expression for the ΔC_p as

$$\Delta C_p = \Delta C_p^m \left(\frac{T_m}{T} \right)^2 \exp \left(-\sigma_D \frac{\Delta T}{T} \right), \quad (15)$$

where σ_D is a coefficient related to the hole formation energy in the Dubey's expression. Substituting Eq. (15) into Eqs. (5)–(7), the simplified Dubey's expressions for ΔG , ΔH and ΔS are [7, 8]

$$\Delta G = \Delta S_m \Delta T - \Delta C_p^m \frac{\Delta T^2}{2T} \left(1 - \sigma_D \frac{\Delta T}{3T} \right), \quad (16)$$

$$\Delta H = \Delta H_m - \Delta C_p^m T_m \frac{\Delta T}{T} \left(1 - \frac{\sigma_D \Delta T}{2T} \right), \quad (17)$$

and

$$\Delta S = \Delta S_m - \Delta C_p^m \frac{\Delta T}{T} \left(1 + \frac{\Delta T}{2T} \right) \left(1 - \frac{\sigma_D \Delta T}{2} \frac{1}{T} \frac{1 + \frac{2\Delta T}{3T}}{1 + \frac{\Delta T}{2T}} \right). \quad (18)$$

Fig. 1 Specific heat difference ΔC_p **a, b**, and the deviation values of $D - \Delta C_p$ **c, d** as functions of temperature derived for 2 of 16 representative BMGs, $Zr_{46}Cu_{46}Al_8$ and $La_{55}Al_{25}Cu_{10}Ni_5Co_5$ alloys

The value σ_D is given by [7, 8]

$$\sigma_D = \frac{T_{rg}}{1 - T_{rg}} \ln \left(\frac{1}{T_{rg}^2 \xi} \right). \quad (19)$$

The deviation percentage D , between the theoretical calculated value and the experimental value can be expressed as

$$D = \left| \frac{V(\text{mod}) - V(\text{exp})}{V(\text{exp})} \right|, \quad (20)$$

where $V(\text{mod})$ and $V(\text{exp})$ represent the calculated values and experimental values of ΔC_p , ΔG , ΔH and ΔS respectively. As shown in Eqs. (4), (14), and (19), most of the BMG materials in this study exhibit T_{rg} values that can be considered to be a constant equal to 0.65 (discussed in detail in later sections). Thus the deviation values, D , for ΔC_p , ΔG , ΔH , and ΔS occurring between temperatures from T_g to T_m correlate with the σ_l , σ_h and σ_D values as well as the ξ value.

3 Deviation between theoretical model-based calculated and experimental values of ΔC_p in BMGs

The thermodynamic behavior of BMGs is studied using expressions for thermodynamic parameters ΔC_p , ΔG , ΔS , ΔH , based on experimental results from 16 different BMGs. The values of ΔG , ΔS , and ΔH are calculated using experimentally measured ΔC_p values, which can be expressed as [16–26]

$$\Delta C_p = AT + BT^{-2} + CT^2, \quad (21)$$

where A , B , and C are constant. These constants and parameters can be found in Refs. [16–26] and are summarized in Table 1. The calculated ΔC_p value, experimental ΔC_p value, and deviation value between calculated and experimental values from T_g to T_m can be generated by Eqs. (1), (3), (15), (20), and (21). It is prolux that all figures of ΔC_p , ΔG , ΔS , ΔH are described for the 16 alloys. In consideration of the different ξ values and alloy

Fig. 2 Specific heat difference ΔC_p **a, b**, and the deviation values of $D - \Delta C_p$ **c, d** as functions of temperature derived for 2 of 16 representative BMGs, $\text{Ti}_{36.89}\text{Cu}_{43.87}\text{Ni}_{9.36}\text{Zr}_{9.88}$ and $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ alloys

compositions in the present study, the 4 BMGs $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_8$ [19], $\text{La}_{55}\text{Al}_{25}\text{Cu}_{10}\text{Ni}_5\text{Co}_5$ [17], $\text{Ti}_{36.89}\text{Cu}_{43.87}\text{Ni}_{9.36}\text{Zr}_{9.88}$ [22], and $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ [26] were representatively plotted in Figs. 1 and 2, respectively (2 materials per figure). These images are representative of results from all 16 BMGs (see Table 1).

Figures 1 and 2 show experimentally fitted ΔC_p values and calculated values deduced from the hyperbolic, Dubey's, and linear expressions. Initially, the deviations in ΔC_p for these 4 BMGs increased, followed by an immediate reduction with further temperature increased from T_g to T_m . The deviations in ΔC_p achieved a maximum deviation value, $D_{\max}$, at an uncertain temperature in the range of T_g and T_m . Notably, this value was achieved approximately at the midpoint between T_g and T_m in each sample. For $\text{Zr}_{46}\text{Cu}_{46}\text{Al}_8$ and $\text{La}_{55}\text{Al}_{25}\text{Cu}_{10}\text{Ni}_5\text{Co}_5$, the $D_{\max}$ values of ΔC_p , $D_{\max} - \Delta C_p$, from hyperbolic, linear, and Dubey's expressions were each smaller than 4 %, indicating that calculated values of ΔC_p closely approximated

experimental values, as compared with the $D_{\max} - \Delta C_p$ values for $\text{Ti}_{36.89}\text{Cu}_{43.87}\text{Ni}_{9.36}\text{Zr}_{9.88}$ and $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ BMGs (see Fig. 2).

A comparison of the calculated and experimental values of ΔC_p in BMGs is provided by the $D_{\max} - \Delta C_p$ values for 16 BMGs (see Table 2). The relationship between $D_{\max} - \Delta C_p$ values and ξ values for the 16 alloys is summarized in Fig. 3. In addition, $D_{\max} - \Delta C_p$ values derived from the linear expression demonstrated a maximum value of 16 % of the initial value, and the values derived from Dubey's expression increased with increasing ξ value for $\xi > 2$. Notably, the maximum value of Dubey's expression approached 38 % of the initial value for a ξ value of 6. For the hyperbolic expression, $D_{\max} - \Delta C_p$ values were generally less than 11 % of the initial values. Cumulatively, these findings indicated that the hyperbolic expression for ΔC_p fitted well with the experimental values compared with both linear and Dubey's expressions. When $\xi < 2$, the $D_{\max} - \Delta C_p$ derived from all 3 expressions was smaller

Table 2 The maximum deviation values $D_{\max} - \Delta C_p$ of ΔC_p ; deviation values $D - \Delta G$, $D - \Delta H$, and $D - \Delta S$ at T_g ; and ξ values for 16 alloys ($D_{\max} - \Delta C_p$, $D - \Delta G$, $D - \Delta H$, and $D - \Delta S$ denote the deviation values of ΔC_p , ΔG , ΔH , and ΔS , respectively, between the calculated and experimental values)

Alloys	$D_{\max} - \Delta C_p$			Hyper-D ($T = T_g$)			Line-D ($T = T_g$)			Dubey-D ($T = T_g$)			ξ
	Hyper.	$D_{\max} - \Delta C_p$		Hyper-D	$T = T_g$		Line-D	$T = T_g$		Dubey-D	$T = T_g$		
		Line	Dubey		$D - \Delta G$	$D - \Delta H$		$D - \Delta S$	$D - \Delta G$		$D - \Delta H$	$D - \Delta S$	
La ₆₂ Al ₁₄ Cu ₂₄	2.7	0.6	9.3	0.7	2.0	3.8	0.1	0.2	0.5	4.4	32.8	74.7	0.84
La ₅₅ Al ₂₅ Ni ₂₀	1.6	1.9	5.1	0.3	0.5	0.9	0.3	0.8	1.1	0.4	4.2	6.7	1.04
Cu ₄₇ Ti ₃₄ Zr ₁₁ Ni ₈	1.3	3.2	7.5	0.3	0.8	1.4	0.8	2.1	3.9	1.0	10.8	23.8	1.17
Zr ₄₆ Cu ₄₆ Al ₈	1.1	2.7	3.1	0.3	0.7	2.0	0.6	1.7	2.3	0.2	1.3	2.3	1.22
La ₅₅ Al ₂₅ Cu ₁₀ Ni ₅ Co ₅	0.6	2.4	3.1	0.1	0.3	0.4	0.5	1.2	1.8	0.1	2.0	3.3	1.24
La ₆₂ Al ₁₄ (Cu _{5/6} Ag _{1/6}) ₂₄	2.5	0.7	3.3	0.7	1.5	2.5	0.0	0.2	0.3	1.4	9.1	18.4	1.24
Mg ₆₅ Cu ₂₅ Y ₁₀	4.2	10.3	10.8	0.9	2.3	4.5	2.4	5.9	11.3	0.5	4.1	11.2	1.46
Zr ₅₇ Cu _{15.4} Ni _{12.6} Al ₁₀ Nb ₅	1.3	6.7	4.2	0.4	1.9	7.4	2.8	10.7	41.0	0.3	4.1	21.1	1.58
Zr ₄₆ (Cu _{4.5/5.5} Ag _{1/5.5}) ₄₆ Al ₈	0.7	5.5	2.0	0.2	0.8	2.5	2.2	8.7	25.0	0.1	2.2	8.0	1.62
Pt _{57.3} Cu _{14.6} Ni _{5.3} P _{22.8}	2.4	13.8	3.5	0.4	1.2	2.0	2.7	6.6	10.7	0.6	1.5	2.4	2.58
Zr _{52.5} Cu _{17.9} Ni _{14.6} Al ₁₀ Ti ₅	5.4	9.0	11.0	1.8	5.5	14.0	2.0	7.0	18.0	3.8	12.5	32	2.64
Ti _{36.89} Cu _{43.87} Ni _{9.36} Zr _{9.88}	5.3	9.1	15.4	1.7	5.2	14.6	3.1	10.9	31.9	5.5	19.5	57.1	3.28
Ti _{37.65} Cu _{43.25} Ni _{9.6} Zr _{9.5}	1.1	15.9	11.1	0.2	0.9	2.7	5.1	16.8	45.7	3.8	13.2	36.7	3.38
Zr _{41.2} Ti _{13.8} Ni ₁₀ Cu _{12.5} Be _{22.5}	4.1	9.6	18.8	1.0	2.5	4.4	2.4	7.2	13.0	5.4	18.1	33.4	3.74
Zr _{58.5} Cu _{15.6} Ni _{12.8} Al _{10.3} Nb _{2.8}	10.5	10.4	34.0	1.7	3.9	6.4	1.9	4.9	8.4	7.1	20.4	36.0	5.85
Pd ₄₃ Ni ₁₀ Cu ₂₇ P ₂₀	10.6	2.4	37.5	1.1	2.5	3.2	0.3	0.7	0.9	5.4	15.6	20.7	6.04

Fig. 3 Relationships between the maximal deviation values $D_{\max} - \Delta C_p$ (the maximum deviation of ΔC_p between the calculated and experimental values), and the ξ values for the 16 alloys in Table 2

than 11 % of the initial value, suggesting that all 3 theoretical models were applicable.

4 Deviations, calculated values, and experimental values of ΔG , ΔS , and ΔH in BMGs

The deviation values D of parameters ΔG , ΔS , ΔH , $D - \Delta G$, $D - \Delta S$, and $D - \Delta H$, respectively, between calculated and experimental values for 4 BMGs were determined. As shown in Figs. 4–7, the values of $D - \Delta G$, $D - \Delta H$, and $D - \Delta S$ exhibited maximum deviations at T_g in the temperature range from T_g to T_m . A notable exception to this trend was the deviation value of ΔG from

Dubey's expression for ΔC_p for $Zr_{46}Cu_{46}Al_8$ (see Fig. 4d) and $Mg_{65}Cu_{25}Y_{10}$ (not shown). Thus, deviation values for ΔG , ΔS , and ΔH at T_g could reasonably denote the degree of fit between ΔG , ΔS , and ΔH values in both calculated expressions and experimental results. $D - \Delta G$, $D - \Delta H$, and $D - \Delta S$ values at T_g for all 16 metallic glasses are listed in Table 2.

The $D - \Delta G$, $D - \Delta H$, and $D - \Delta S$ values at T_g and ξ values for 16 BMGs are listed in Table 2. The maximum $D - \Delta G$ values were achieved in the hyperbolic expression, whereas Dubey's and linear expression values for ΔC_p were smaller than 8 % of initial values, indicating the accuracy of calculated values using these 3 expressions for ΔG relative to experimental values. The maximum $D - \Delta H$ and $D - \Delta S$ values achieved by the hyperbolic expression for ΔC_p in 16 BMGs were less than 10 % and 15 % of initial values (see Table 2), respectively. The maximum $D - \Delta H$ and $D - \Delta S$ values derived from linear and Dubey's expressions for ΔC_p (see Table 2) presented bigger values of 16.8 % and 45.7 %, respectively, compared with those derived from the hyperbolic expression. Thus, calculations for ΔG , ΔH , and ΔS values also suggested that the hyperbolic expression for ΔC_p was the most accurate predictor of experimental values.

Results and analysis of $D - \Delta H$ and $D - \Delta S$ derived from Dubey's expression for ΔC_p produced similar findings to those of $D - \Delta C_p$ derived from Dubey's expression. The majority of $D - \Delta H$ and $D - \Delta S$ values derived from Dubey's expression for $\xi < 2$ were very close to the $D - \Delta H$ and $D - \Delta S$ values derived from the linear and

Fig. 4 Parameters ΔG **a**, ΔH **b**, and ΔS **c** as well as deviation values $D - \Delta G$ **d**, $D - \Delta H$ **e**, and $D - \Delta S$ **f** as functions of temperature derived for the $Zr_{46}Cu_{46}Al_8$ alloy using reported experimental results and three different expressions

Fig. 5 Parameters ΔG **a**, ΔH **b**, and ΔS **c** and deviation values $D - \Delta G$ **d**, $D - \Delta H$ **e**, and $D - \Delta S$ **f** as functions of temperature derived for the $\text{La}_{55}\text{Al}_{25}\text{Cu}_{10}\text{Ni}_5\text{Co}_5$ alloy using reported experimental results and 3 different expressions

Fig. 6 Parameters ΔG **a**, ΔH **b**, and ΔS **c** and deviation values $D - \Delta G$ **d**, $D - \Delta H$ **e**, and $D - \Delta S$ **f** as functions of temperature derived for the $\text{Ti}_{36.89}\text{Cu}_{43.87}\text{Ni}_{9.36}\text{Zr}_{9.88}$ alloy using reported experimental results and 3 different expressions

hyperbolic expressions, suggesting that the difference between $D - \Delta H$ and $D - \Delta S$ values in each of the three expressions was very small for $\xi < 2$ (see Table 2). The majority of $D - \Delta H$ and $D - \Delta S$ values derived from Dubey's expression for $\xi > 2$ were much larger than the $D - \Delta H$ and $D - \Delta S$ values derived from the linear and

hyperbolic expressions, suggesting that most ΔH , and ΔS values derived from Dubey's expression did not accurately predict experimental values for $\xi > 2$.

Thus, the hyperbolic expression for ΔC_p represents are relatively universal expression, compared to the linear expression and Dubey's expression for ΔC_p which are only

Fig. 7 Parameters ΔG **a**, ΔH **b**, and ΔS **c** and deviation values $D - \Delta G$ **d**, $D - \Delta H$ **e**, and $D - \Delta S$ **f** as functions of temperature derived for the $\text{Pd}_{43}\text{Ni}_{10}\text{Cu}_{27}\text{P}_{20}$ alloy using reported experimental results and 3 different expressions

Fig. 8 Relationship between T_{rg} and ξ values

accurate under certain conditions. Notably, experimental values more closely fit values produced by the linear expression for ΔC_p than values produced by Dubey's expression for ΔC_p . Dubey's expression for ΔC_p was, however, a good approximation of experimental values for $\xi < 2$, though not for $\xi > 2$.

5 Discussion

$D_{\max}$ between the calculated and experimental values for ΔC_p , ΔG , ΔH , and ΔS from T_g to T_m was found to be associated with the ξ parameter according to Fig. 3 and Table 2. Equations (4), (14), and (19) showed that in addition to the effects of the ξ parameter, D values were

also influenced by the T_{rg} values, which ranged from 0.56 to 0.73 and could be expressed as a function of the ξ value (see Fig. 8). Thus, equidistant low, medium, and high T_{rg} values of 0.56, 0.65, and 0.73 were selected to further characterize the effect of T_{rg} on the value of D (or $D_{\max}$). Figure 9a shows the relationship between the σ_h , σ_D , and σ_l values and the ξ values for T_{rg} values of 0.56, 0.65, and 0.73.

For $\xi < 2$, the change in the 3 σ_h , σ_D , and σ_l values with T_{rg} was negligible, suggesting that ΔC_p , ΔG , ΔH , and ΔS values calculated using different models were virtually identical (see Fig. 3 and Table 2). For $\xi > 2$, however, the values of σ_h , σ_D , and σ_l at the 3 different T_{rg} values revealed a decreasing trend. As ξ values increased from 0.5 to 7, σ_D values exhibited only small decreases, while larger decreases were exhibited by σ_h values. Moderate decreases in σ_l values were observed in between those of σ_D and σ_h compared with σ_h , σ_D , and σ_l values at $T_{rg} = 0.65$. Notably, this change can be neglected to simplify analysis.

Thus the majority of BMGs T_{rg} can be considered constant ($T_{rg} = 0.65$). Figure 9b demonstrates the relationship between σ_h , σ_D , and σ_l values and the ξ parameter at $T_{rg} = 0.65$. When $T_{rg} = 0.65$, the changes in σ_h , σ_D , and σ_l values are revealed to be very large, leading to variation in the deviation values for ΔC_p , ΔG , ΔH , and ΔS between calculated and experimental values. As shown in Fig. 3 and Table 2, the $D_{\max} - \Delta C_p$ values can be used to reveal the fit of ΔG , ΔH , and ΔS between the calculated and experimental values (see Fig. 3 and Table 2). Due to this observation, only $D_{\max} - \Delta C_p$ values are discussed.

Fig. 9 Relationship between σ_h , σ_D , and σ_l , and ξ values for different T_{rg} **a** and $T_{rg} = 0.65$ **b**

Graphs of C_p as a function of temperature when ξ values equal to 2 and 3 ($\xi = 2$, $\xi = 3$) are shown in Fig. 10a, in which C_p^l and C_p^s represent the heat capacity of the supercooled liquid and crystal, respectively. C_p^l and C_p^s values were derived by fitting the experimental data. Figure 10b shows the ΔC_p value evolution and temperature increases for ξ values of 2 and 3, where the ξ parameter is the change rate of ΔC_p^s and ΔC_p^m . In order to characterize the difference in D_{max} values produced by Dubey's expression and the hyperbolic expressions for ΔC_p from T_g to T_m , corresponding temperatures for $D_{max} - \Delta C_p$ values can be inferred.

Temperatures corresponding to the $D_{max} - \Delta C_p$ values for $Zr_{46}Cu_{46}Al_8$, $La_{55}Al_{25}Cu_{10}Ni_5Co_5$, $Ti_{36.89}Cu_{43.87}Ni_{9.36}Zr_{9.88}$, and $Pd_{43}Ni_{10}Cu_{27}P_{20}$ BMGs are generally between T_g and T_m (see Figs. 1 and 2). Thus $T_{max} = 0.5(T_g + T_m)$, where T_{max} is the hypothetical maximum temperature of $D_{max} - \Delta C_p$. All 16 studied BMGs also exhibit trends similar to those of the 4 representative materials shown (data not shown). ΔC_p values calculated using the linear

Fig. 10 Graphs of C_p **a** and ΔC_p **b** for $\xi = 2$ and $\xi = 3$, respectively (The inset shows the fit of the linear expression for ΔC_p at different ξ values in the temperature range from T_g to T_m)

expression closely approximate experimental values for ΔC_p (see Fig. 3). Thus, for temperature of $0.5(T_g + T_m)$, a calculated value closely fits to the experimental ΔC_p , $\Delta C_p^{0.5(T_g+T_m)}(\text{exp.})$, can be expressed as (see Fig. 10b)

$$\Delta C_p^{0.5(T_g+T_m)}(\text{exp.}) = \frac{\Delta C_p^g + \Delta C_p^m}{2} = \frac{1 + \xi}{2} \Delta C_p^m. \quad (22)$$

Substitution of T_{max} into Eqs. (1) and (15), the hyperbolic expression and Dubey's expression for ΔC_p , $\Delta C_p^{0.5(T_g+T_m)}(\text{hyper.})$ and $\Delta C_p^{0.5(T_g+T_m)}(\text{Dubey})$ can be deduced as

$$\Delta C_p^{0.5(T_g+T_m)}(\text{hyper.}) = \left(\sigma_h - 1 + \frac{2 - \sigma_h}{0.5(1 + T_{rg})} \right) \Delta C_p^m, \quad (23)$$

$$\Delta C_p^{0.5(T_g+T_m)}(\text{Dubey}) = \frac{\Delta C_p^m}{(0.5(1 + T_{rg}))^2} \exp \left(-\sigma_D \frac{1 - T_{rg}}{1 + T_{rg}} \right). \quad (24)$$

Fig. 11 Relationship between $D_{\max}$ from the hyperbolic expression and Dubey's expression for ΔC_p and the ξ parameter for $T_{rg} = 0.65$ using Eqs. (25) and (26)

Thus, expressions of $D_{\max}$ (hyper.) and $D_{\max}$ (Dubey) generated by the hyperbolic expression and Dubey's expression for ΔC_p between the calculated and experimental values, respectively, can be written as

$$D_{\max}(\text{hyper.}) = \left| \frac{\sigma_h - 1 + \frac{2 - \sigma_h}{0.5(1 + T_{rg})}}{0.5(1 + \xi)} - 1 \right|, \quad (25)$$

$$D_{\max}(\text{Dubey}) = \left| \frac{\frac{1}{(0.5(1 + T_{rg}))^2} \exp\left(-\sigma_D \frac{1 - T_{rg}}{1 + T_{rg}}\right)}{0.5(1 + \xi)} - 1 \right|, \quad (26)$$

where T_{rg} is treated as a constant with a value of 0.65. Figure 11 shows the relationship between $D_{\max}$ from the hyperbolic expression and Dubey's expression for ΔC_p as well as the ξ parameter based on Eqs. (25) and (26). When $\xi < 2$, the majority of $D_{\max}$ (Dubey) and $D_{\max}$ (hyper.) values are less than 10 %, indicating that these values closely approximate the $D_{\max} - \Delta C_p$ values in Fig. 3. When $2 < \xi < 7$, the $D_{\max}$ (Dubey) values dramatically increase from 10 % to 43.7 %, and the $D_{\max}$ (hyper.) values gradually increase from 8 % to 16 %. These findings suggest that the accuracy of values calculated using the hyperbolic expression for ΔC_p are higher than those calculated using Dubey's expression for ΔC_p . Thus, calculated $D_{\max}$ values (see Fig. 11) from the hyperbolic expression and Dubey's expression vary according to trends very similar to those of experimental $D_{\max}$ values (see Fig. 3). Based on the error scale determined by these findings, the expressions of $D_{\max}$ (hyper.) and $D_{\max}$ (Dubey) can be used to indicate changes in $D_{\max} - \Delta C_p$ according to the ξ parameter values shown in Fig. 3 and Table 2 for all 16 examined BMGs in the current study.

6 Conclusions

A linear expression for ΔC_p derived from the hyperbolic expression for ΔC_p was deduced and used to obtain a novel expression for ΔG , ΔH , and ΔS . According to the experimentally determined thermodynamic parameters of the 16 examined BMGs in the current study, more accurate calculations of ΔC_p , ΔG , ΔH , and ΔS were obtained using the linear, hyperbolic, and Dubey's expression for ΔC_p . These results suggest that the hyperbolic expression for ΔC_p can be applied as a universal expression for ΔC_p , while linear and Dubey's expressions for ΔC_p are condition-dependent. Notably, Dubey's expression for ΔC_p also closely approximated experimental values when $\xi < 2$, though values were shown to deviate from experimental values for $\xi > 2$.

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