

The Gibbs free energy of formation of a glassy alloy

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A simple expression for the Gibbs free energy of formation of a pure component or a eutectic alloy glass, relative to the stable crystalline phase (or phases) at the same temperature is deduced by use of thermodynamic arguments. The expression obtained is supposed to apply to both monocomponent and multicomponent liquid alloys that might become glasses from the supercooled liquid state, irrespective of the critical cooling rate needed to avoid crystallization.

I. INTRODUCTION

The ability of molten alloys to form metastable non-crystalline structures is of significant practical and theoretical interest and is the subject of many studies.¹⁻⁸ One of the important quantities appearing in the thermodynamic prediction of glass formation is the Gibbs free energy difference between the crystallized material and the competing but metastable glassy alloy phase.⁹ From phase diagram calculations it is possible to estimate the thermodynamic properties of the liquid and crystalline phases over a wide temperature interval.¹⁰ Now, it is well known that at the glass transition temperature the supercooled liquid becomes a glass. The nature of the glass transition phenomenon is a question that remains open.^{11,12} Nevertheless, one thing is recognized to be quite general: at the glass transition temperature the heat capacity decreases sharply and takes, for the glass, a value very similar to that of the crystallized material.

One of the formulae which has proved to be very fruitful in describing the free energy difference between the supercooled liquid and the crystal was established some years ago by Hoffman,¹³ and it is currently used to estimate the rate of nucleation and growth of crystallites in supercooled liquids.¹⁴⁻¹⁷ Further expressions have been derived by Jones and Chadwick,¹⁸ Thompson and Spaepen,¹⁹ Dubey and Ramachandrarao,²⁰ and Battezzati and Garrone.²¹ However, little attention has focused on the very related concept of the free energy of formation of the glass.

In this paper we want to derive a simple expression for the Gibbs free energy of formation of a glassy alloy based on pure thermodynamic considerations. The way to achieve that purpose is defined in the following manner. First of all, we will consider the situation of a pure substance (element or compound) or a eutectic alloy. Then we will obtain an estimate of the sharp decrease of the heat capacity of the liquid at the glass transition region when it becomes a glass, in terms of the melting entropy. Further,

we will comment on the formulae already deduced in the literature to describe the Gibbs free energy difference between the supercooled liquid and the crystal. Then we will establish an approximate formula for the Gibbs free energy of formation of what we will call an "ideal" glass. Finally, we will discuss carefully the implications of the application of the concept of "ideal" glass to a eutectic alloy to obtain its free energy of formation.

II. EVALUATION OF THE GIBBS FREE ENERGY OF FORMATION

A. Estimation of the value of ΔC_p

In good glass-forming systems the heat capacity of the supercooled liquid, C_p^l , is higher than that of the crystal, C_p^c . As a consequence, the entropy of the supercooled liquid decreases more rapidly than that of the crystal with lowering the temperature. Now, at the melting point, T_m , the entropy of the crystal is lower than that of the liquid. Nevertheless, if that behavior of the heat capacity is extrapolated at low enough temperatures, at some temperature T_g (higher than the absolute zero) the entropy of the liquid will become equal to that of the crystal and, even, it will be smaller at $T < T_g$. As first stated by Kauzmann,²² it is unlikely that this will ever occur. Therefore, the heat capacity of a real glass-forming liquid has to decrease at a temperature near but higher than T_g . In practice this implies that the material should become a glass at a temperature $T_g > T_s$. Then T_s is the lower limit of the glass transition temperature, T_g .

If, for simplicity, we assume that $\Delta C_p = C_p^l - C_p^c$ is constant in the temperature interval $T_s < T < T_m$, the equality

$$S^l(T_s) = S^c(T_s) \quad (1)$$

with S^l (S^c) the entropy of the liquid (crystal) leads to

$$\Delta S_m = \frac{\Delta H_m}{T_m} = \Delta C_p \ln \frac{T_m}{T_s} \quad (2)$$

with ΔS_m (ΔH_m) the melting entropy (enthalpy).

Therefore, as previously stated by other authors,^{19,21} with the preceding assumption one obtains

$$\Delta C_p = \alpha \frac{\Delta H_m}{T_m} = \alpha \Delta S_m \quad (3)$$

where

$$\alpha = \frac{1}{\ln(T_m/T_s)} \quad (4)$$

It is well known that in general the ratio $T_g/T_m = 2/3$ for good glass-forming systems²³ and that ratio may decrease down to about $1/2$.²⁴ As in real systems $T_g > T_s$, this leads to the estimate that T_m/T_s has a value between about 1.6 and 2.2, the first value being retained for very good glass formers. With these estimates introduced in Eqs. (3) and (4) we obtain, as depicted in Fig. 1, that ΔC_p will comprise between about 1.3 and 2.1 times ΔS_m , the last value corresponding to very good glass formers. The relationship between the quotients $\Delta C_p/\Delta S_m$ and T_m/T_s will be very useful to estimate the Gibbs free energy difference between the liquid, G^l , and the crystalline material, G^c , $\Delta G = G^l - G^c$, at high supercooling.

Other estimates have been given in the literature. For instance, Battezzati and Garrone²¹ assume that the upper

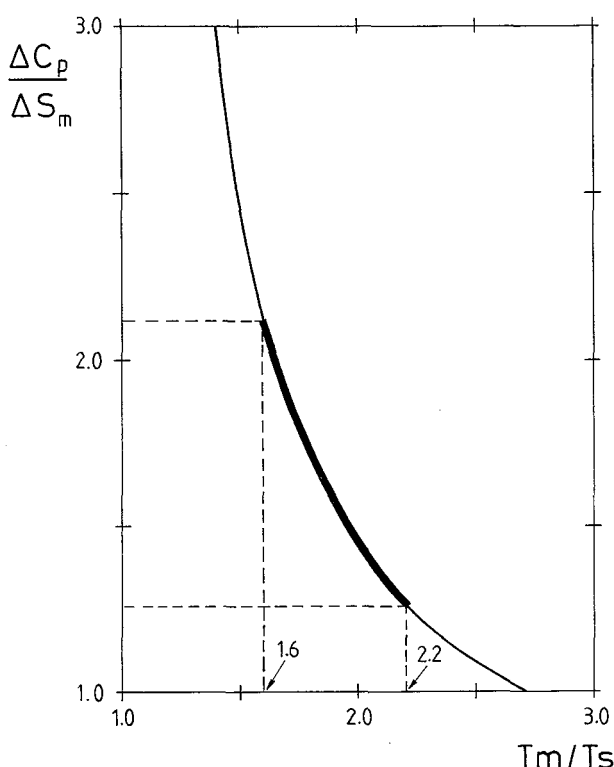


FIG. 1. Reduced representation of $\Delta C_p/\Delta S_m$ vs T_m/T_s , indicating the range of values corresponding to good glass formers.

limit of α for metallic glass-forming systems is 1.44 and the upper bound of α for nonmetallic systems is 2.46.

B. Gibbs free energy difference between a supercooled liquid and a glass

To obtain an estimate of ΔG we will follow very closely the treatment of other authors.^{13,18,19,21} The general equation for ΔG can be written as

$$\Delta G = \Delta S_m(T_m - T) - \int_T^{T_m} \Delta C_p dT + T \int_T^{T_m} \Delta C_p d(\ln T) \quad (5)$$

If, as done previously, we assume $\Delta C_p = \text{const.}$, Eq. (5) becomes

$$\Delta G = \Delta S_m(T_m - T) + \Delta C_p \left\{ T \ln \frac{T_m}{T} - (T_m - T) \right\} \quad (6)$$

As stated by Hoffman¹³

$$\ln \frac{T_m}{T} \cong 2 \frac{T_m - T}{T_m + T} \quad (7)$$

With this approximation Eq. (6) becomes

$$\Delta G = \Delta S_m(T_m - T) - \Delta C_p \frac{(T_m - T)^2}{T_m + T} \quad (8)$$

which is the expression obtained by Jones and Chadwick.¹⁸ Now, using the estimated value of ΔC_p given by Eq. (3), Eq. (6) transforms to

$$\Delta G = \Delta S_m(T_m - T) - \alpha \Delta S_m \cdot [(T_m - T) - T \ln(T_m/T)] \quad (9)$$

A wider range of possible expressions of ΔG has been proposed. Apart from the Hoffman expression¹³

$$\Delta G = \Delta S_m(T_m - T)(T/T_m) \quad (10)$$

there are, among others, the expression derived by Thompson and Spaepen¹⁹

$$\Delta G = \Delta S_m(T_m - T)(2T/T_m + T) \quad (11)$$

and the one given by Battezzati and Garrone²¹

$$\Delta G = \Delta S_m(T_m - T) - \gamma \Delta S_m \cdot [(T_m - T) - T \ln(T_m/T)] \quad (12)$$

with

$$\gamma = (1 - \Delta H_x/\Delta H_m)/(1 - T_x/T_m) \quad (13)$$

ΔH_x , T_x being the enthalpy and temperature of crystallization. The Battezzati and Garrone Eq. (13) is formally identical to our proposed Eq. (9). However, α and γ have different meanings: α is supposed to give the mean value of ΔC_p between T_m and T_s , while γ gives the mean value of ΔC_p between T_m and T_x . This can produce significant differences in the treatment of metallic glasses because

they normally have a ΔC_p which increases with decreasing temperature in the supercooled range.²⁵

All these expressions are plotted in reduced units in Fig. 2 together with the Turnbull²⁶ expression

$$\Delta G = \Delta S_m(T_m - T) \quad (14)$$

As can be seen in that figure, at low supercooling all formulae give ΔG values basically identical, but marked differences arise when the melt is brought to low temperature. At high supercooling, not only are the different values very dissimilar but also, and normally this is not stressed enough in the literature, all of them have a lower temperature limit of application (which is generally given by T_s). This limiting T_s value of ΔG is of real importance because it gives, as we will see, an estimate of the Gibbs free energy of formation of the glass.

C. Gibbs free energy of formation of a glass

As is well known, during the formation of a glass from a supercooled liquid the temperature of the system has to pass through the glass transition region. For the supercooled liquid, the relaxation times of the atomic or molecular movements t_r are very much shorter than the experimental measurement time t_e . Then, the supercooled liquid may also be considered to be in a metastable state. On the other hand, for a glass $t_r \gg t_e$, the system may also be considered in a metastable state.^{27,28} But in the glass transition region we have $t_e \cong t_r$ and there quantities like

the heat capacity or the molar volume are time dependent. To rid the heat capacity from its irreversible contribution in the glass transition region a fictive temperature is defined as the temperature for which the glass should be in equilibrium with the corresponding supercooled liquid.²⁹ This fictive temperature, T_f , replaces T_g and, like the latter, depends on the thermal history of the system. In any case, T_f has to be higher than T_s . Furthermore, it remains to be proved that T_s is accessible experimentally. However, it is logical to assume that if T_s was experimentally accessible, then the system below T_s should follow the same behavior, as regards the heat capacity, as the crystal. Then we will define an "ideal" glass as the one that fulfills the following requirements:

- (1) its fictive temperature is equal to T_s
- (2) its heat capacity is equal to that of the crystal in the temperature interval $0 < T < T_s$.

We are now in a condition to calculate the Gibbs free energy of formation of an ideal glass. With the aforementioned conditions we have

$$\Delta G_f = G^g - G^c = \Delta G(T_s) \quad (15)$$

where G^g is the Gibbs free energy of the glass at a given temperature, G^c is the Gibbs free energy of the crystal at the same temperature, and $\Delta G(T_s)$ is the Gibbs free energy difference between the liquid and the crystal at T_s . Using Eq. (9) and recalling Eq. (4) we obtain

$$\Delta G_f = \Delta H_m \left[(1 - T_s/T_m) \cdot \{1 + 1/\ln(T_s/T_m)\} + T_s/T_m \right] \quad (16)$$

In fact, T_m/T_s was assumed in general to vary between 1.6 and 2.2 and, consequently, calculating ΔG_f from Eq. (16) means that $\Delta G_f/\Delta H_m$ is, in general, between 0.2 and 0.3, the last value corresponding to poor glass-forming systems. The value of $\Delta G_f/\Delta H_m$ as a function of T_m/T_s is given in Fig. 3.

Two remarks are to be made about the results obtained. First, as deduced, the Gibbs free energy of formation of the "ideal" glass is independent of the temperature because it is assumed that below T_s the entropy of the "ideal" glass is equal to that of the crystal. Real glasses will have a Gibbs free energy of formation greater than the ideal one. Second, a straightforward calculation²⁹ based on a Carnot cycle using observed supercooling temperatures shows that it is generally impossible to produce a metastable crystalline phase from the melt having an excess Gibbs free energy relative to the equilibrium phase larger than about $0.3 \Delta H_m$. This calculation, extended to glasses, could be evoked to explain why the quotient T_g/T_m has a lower bound of about 1/2.

D. Implications in the Gibbs free energy of formation of an ideal eutectic alloy glass

To illustrate the implications of these ideas to a eutectic alloy we will consider a simple eutectic system where the

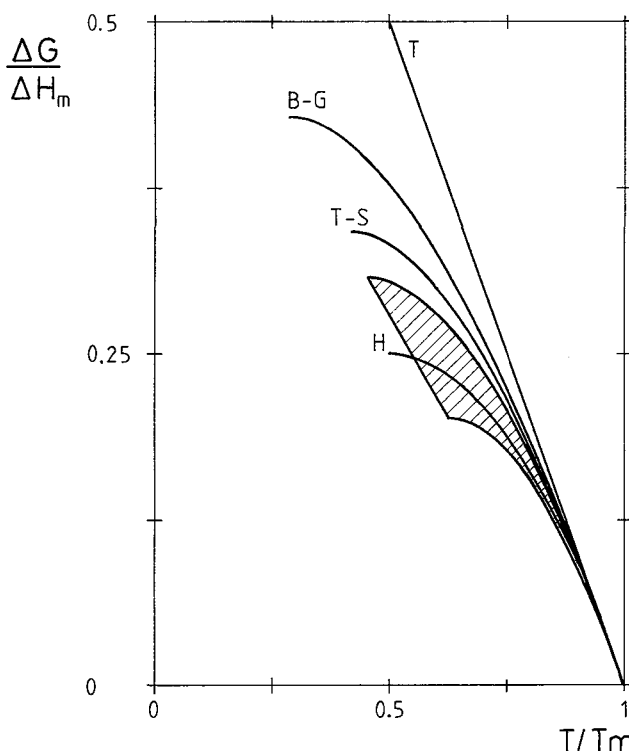


FIG. 2. Reduced representation of $\Delta G/\Delta H_m$ vs T/T_m for several theoretical expressions: (T) Turnbull,²⁶ (B-G) Battezzati and Garrone,²¹ (T-S) Thompson and Spaepen,¹⁹ (H) Hoffman.¹³ The dashed zone is the region covered by our estimate.

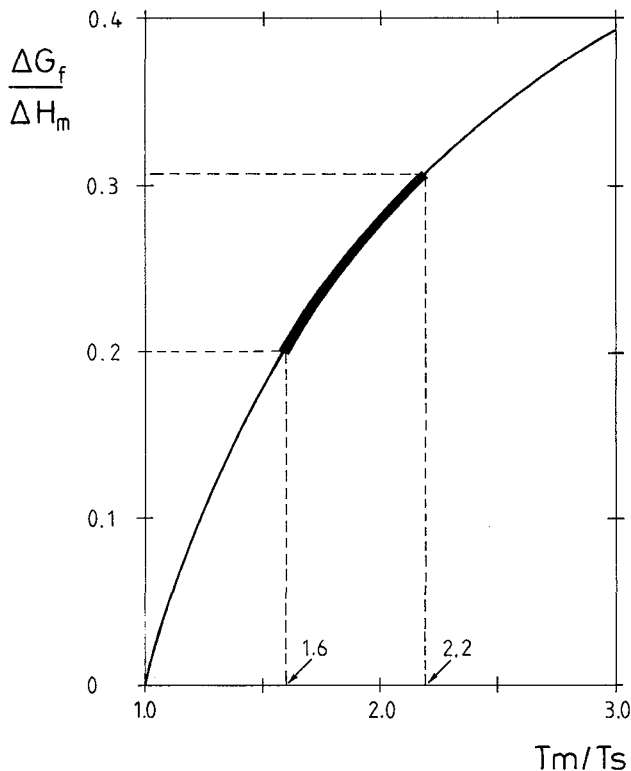


FIG. 3. Reduced representation of $\Delta G_f/\Delta H_m$ vs T_m/T_s , indicating the range of values corresponding to good glass formers.

liquid follows an ideal behavior. In that case, for a eutectic alloy A_xB_{1-x} Eqs. (3), (4), (9), and (16) may be applied by replacing T_m by the eutectic temperature. Furthermore, we have

$$\Delta C_p = x\Delta C_p^A + (1-x)\Delta C_p^B \quad (17)$$

and

$$\begin{aligned} \Delta S_m = & x\Delta S_m^A + (1-x)\Delta S_m^B \\ & - x \left[\Delta C_p^A \ln \frac{T_m^A}{T_E} + R \ln x \right] \\ & - (1-x) \left[\Delta C_p^B \ln \frac{T_m^B}{T_E} + R \ln(1-x) \right] \quad (18) \end{aligned}$$

where the superscripts A, B refer to the value of the quantities $\Delta C_p, \Delta S_m, T_m$ for pure components A, B , respectively.

III. DISCUSSION AND CONCLUSIONS

The Gibbs free energy of formation of what here we call an ideal glassy alloy was estimated by using the following two assumptions: (i) the fictive temperature of the glass is equal to the temperature at which the supercooled liquid will have the same entropy as the stable crystalline phase (or phases); and (ii) the heat capacity of the glass is equal to that of the crystalline phases in the temperature interval $0 \leq T \leq T_s$. Both assumptions are related to the fact that the entropy of the liquid alloy cannot become lower than that of the stable crystalline phases, and, there-

fore, this ideal glass is the one with the smallest entropy at any temperature among those that can be prepared from the liquid at the same composition with different thermal treatments. As a consequence, the Gibbs free energy of formation of the ideal glass is exactly equal to its enthalpy of formation. Real glasses will have a positive entropy of formation and so a higher enthalpy of formation than the ideal glass. However, the Gibbs free energy of formation of real glasses at the glass transition temperature will not exceed significantly that of the ideal glass because the excess enthalpy term almost cancels with the excess entropy term at the glass transition, which is always higher than T_s . With regard to the crystallization enthalpy, it is normally higher than the Gibbs free energy of formation because crystallization occurs at temperatures above T_s ; however, the value of the crystallization enthalpy can be used, as stated by Battezzati and Garrone,²¹ to evaluate ΔC_p .

As there is no excess enthalpy in the ideal glass relative to the stable crystalline phases we can also call it a fully relaxed glass. It remains to be proved that the ideal glass is different from what may be called an ideal supercooled liquid, this last considered as being in a metastable state, not because the relaxation times are too long compared to the experimental time-scale, but because enough time has been accorded to the system to allow the molecular or atomic movements to bring it to a totally relaxed state.

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REFERENCES

- ¹B. Predel, *Physica* **103B**, 113 (1981).
- ²J. Hafner, *Phys. Rev. B* **28**, 1734 (1983).
- ³T. B. Massalski, C. G. Woychik, and J. L. Murray, *Mater. Res. Symp. Proc.* **19**, 241 (1983).
- ⁴N. Saunders and A. P. Miodownik, *Ber. Bunsenges. Phys. Chem.* **87**, 830 (1983).
- ⁵I. Schmidt, *Z. Metallkd.* **74**, 561 (1983).
- ⁶J. L. Murray, *Metall. Trans. A* **15A**, 261 (1983).
- ⁷F. Sommer, *Ber. Bunsenges. Phys. Chem.* **87**, 749 (1983).
- ⁸R. B. Schwarz, P. Nash, and D. Turnbull, *J. Mater. Res.* **2**, 456 (1987).
- ⁹H. Jones, *Rapid Solidification Processing in Metals and Alloys* (Institution of Metallurgists, U.K., 1982).
- ¹⁰L. Kaufman and H. Bernstein, *Computer Calculations of Phase Diagrams* (Academic Press, New York, 1970).
- ¹¹J. Jackle, *Rep. Prog. Phys.* **49**, 171 (1986).
- ¹²J. Jackle, *Phil. Mag. B* **56**, 113 (1987).
- ¹³J. D. Hoffman, *J. Chem. Phys.* **29**, 1192 (1958).
- ¹⁴D. R. Uhlmann, in *Materials Science Research*, edited by T. J. Gray (Plenum Press, New York, 1969), Vol. 4, p. 172.
- ¹⁵H. Miura, S. Isa, and K. Omuro, *J. Non-Cryst. Solids* **61 & 62**, 163 (1984).
- ¹⁶S. Suriñach, M. D. Baró, M. T. Clavaguera-Mora, and N. Clavaguera, *Thermochimica Acta* **85**, 175 (1985).
- ¹⁷J. H. Perepezko and J. S. Paik, *J. Non-Cryst. Solids* **61 & 62**, 113 (1984).

- ¹⁸D. R. H. Jones and G. A. Chadwick, *Phil. Mag.* **24**, 995 (1971).
¹⁹C. V. Thompson and F. Spaepen, *Acta Metall.* **27**, 1855 (1979).
²⁰K. S. Dubey and P. Ramachandrarao, *Acta Metall.* **32**, 91 (1984).
²¹L. Battezzati and E. Garrone, *Z. Metallkd.* **75**, 305 (1984).
²²W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).
²³S. Sakka and J. D. Mackenzie, *J. Non-Cryst. Solids* **6**, 145 (1971).
²⁴D. Turnbull, *Contemp. Phys.* **10**, 473 (1969); *J. Non-Cryst. Solids* **102**, 117 (1988).
²⁵H. S. Chen and D. Turnbull, *J. Appl. Phys.* **38**, 3646 (1967).
²⁶D. Turnbull, *J. Appl. Phys.* **21**, 1022 (1950).
²⁷J. Jackle, *Phil. Mag. B* **44**, 533 (1981).
²⁸J. Jackle, *Physica* **127B**, 79 (1984).
²⁹R. O. Davies and G. O. Jones, *Adv. Phys.* **2**, 370 (1953).
³⁰J. C. Baker and J. W. Cahn, in *Solidification* (American Society for Metals, Metals Park, OH, 1971), p. 23.