Energy and Entropy of Crystals, Glasses and Melts

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Abstract

The molar entropy, S, and enthalpy (energy), H, of crystals, glasses and melts of the same one-component systems have been suitably visualized including the transformation from the melt into a glass or crystallization. For the temperature $T \to 0\,K$ the enthalpy and entropy of the glass are larger by ΔH_0 and ΔS_0 as compared to the stable crystal. The S and H functions of glasses correspond to a simple continuation of these functions from the molten state to lower temperatures. Crystallization occurs as a spontaneous process under production of entropy.

Extrapolating the entropy of the molten and crystalline states from the melting range to lower temperatures, which is the basis of "Kauzmann's paradox", is ambiguous and misleading, as the extrapolated data deviate considerably from the experimental temperature dependencies of S of glasses and crystals. A proper extrapolation does not cause an entropy catastrophe as claimed in "Kauzmann's paradox", since the enthalpy difference between the undercooled melt and the corresponding crystals must be taken into account and the respective entropies in both states are not connected by an isothermal process.

The molar entropy and enthalpy are visualized as functions of temperature by numerical results of a Debye model. The molar entropy is a universal function of the ratio T/T_D, wherein T_D is the Debye temperature of the well known specific heat capacity, C_D. Between $0\,K$ and T_D the entropy increases by $1.36 \times 3R \approx 4R$ irrespective of T_D. Above T_D it increases approximately as $3R \times \ln(T/T_D)$. The entropy capacity, C_D/T, scales with $1/T_D$ and the enthalpy with T_D, both considered as functions of T/T_D. The entropy capacity shows a maximum of $2.033 \times 3R/T_D$ for $T/T_D = 0.28$.