

Energy and entropy of crystals, glasses and melts

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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 $T \rightarrow 0$ 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 $T/T_D = 0.28$.

1. Kauzmann’s paradox

At the melting temperature, T_m , of one-component systems the entropy of the melt, $S_l(T_m)$, is larger than that of the corresponding crystal, $S_s(T_m)$, due to the melting entropy, $\Delta S_m(T_m) \geq 0$. In [1] Kauzmann extrapolated S_l and S_s to lower temperatures. From the extrapolation he concluded that the entropy of melts, S_l , decreases faster as a function of the temperature than the entropy of the respective (stable) crystalline solid, S_s . The temperature for which the entropy of the undercooled melt becomes smaller than that of the stable crystalline material is called Kauzmann’s temperature, T_K , (see [2 and 3], e. g.). This occurs for lactic acid at about $T/T_m \approx 0.66$ as is seen in figure 1, which has been copied from Kauzmann’s paper [1]. In that figure, the difference between the entropy of the undercooled melt and that of the stable crystalline material, $\Delta S \equiv S_l - S_s$, is shown as a function of temperature, $T \cdot \Delta S = S_l - S_s$ is normalized to the melting entropy at atmospheric pressure, ΔS_m , and the temperature to the melting temperature, T_m . This normalization has been chosen for consistent representation and to show that different materials (in [1] predominantly organic substances) behave similarly. Extrapolating further to 0 K, the entropy difference could even reach negative values. As shown in section 2, the entropy difference and thus the entropy of the undercooled melt could even tend to $(-\infty)$ depending on the kind of extrapolation. Kauzmann himself made the statement that such an extrapolation is not allowed. He assumed that $\Delta S \equiv S_l - S_s$ should become

about constant near the glass transformation temperature, T_g . Kauzmann’s paper has provoked many subsequent papers ([2 to 10] is just a short and arbitrary selection) without convincing solution of the paradox and without comparison to experimental data. This is quite surprising since Kauzmann used already experimental data of the molar entropy and enthalpy as a function of temperature from the literature both for the crystalline and the glassy states and an extrapolation was not necessary.

In the following, it is shown that Kauzmann’s representation and extrapolation are inappropriate for entropic and energetic considerations of solids and melts. Instead, a different representation is developed to be compared with experimental results for quartz and vitreous silica as an example from the literature [11]. It seems that the confusion about the entropy and energy can be avoided for various reasons. Furthermore, the glass transformation of an inorganic structural glass is apparently not a phase transformation. It is just an extension of the molten state. From the glassy state, however, a phase transition into the stable crystalline state is possible. On its way to the crystalline state the material is in a two-phase state similar to crystals in a melt.

2. Thermodynamic considerations

Melting and glass formation occur under atmospheric pressure and under entropy flowing in or out of the system under consideration. Therefore, it is appropriate to consider

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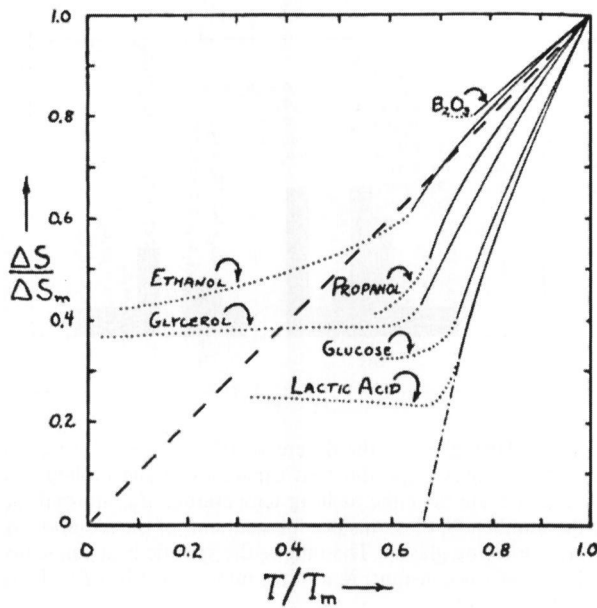


Figure 1. Difference between the entropy of the undercooled melt and that of the crystalline material, $\Delta S = S_l - S_s$, normalized to the melting entropy, ΔS_m , as a function of the temperature, T , normalized to the melting temperature, T_m , for different one-component systems according to [1].

the enthalpy, which is a thermodynamic potential or Gibbs function in the variables entropy, S , pressure, p , and particle number, N_A . It is given in its differential form

$$dH(S,p,N_A) = T dS + V dp + \mu dN_A \quad (1)$$

with the partial derivatives:

– temperature:

$$T = \left. \frac{\partial H}{\partial S} \right|_{p, N_A = \text{constant}}, \quad (2)$$

– volume:

$$V = \left. \frac{\partial H}{\partial p} \right|_{S, N_A = \text{constant}}, \quad (3)$$

– chemical potential:

$$\mu = \left. \frac{\partial H}{\partial N_A} \right|_{S, p = \text{constant}}. \quad (4)$$

Considering processes at atmospheric pressure, $p_0 = 101325 \text{ Pa} = \text{constant}$ (or approximately $1 \text{ bar} = 10^5 \text{ Pa} = \text{constant}$), and one mole of particles or formula units, $N_{A0} = 1 \text{ mole} = \text{constant}$, equation (1) is reduced to

$$dH(S, p_0, N_{A0}) = T dS. \quad (5)$$

Thus, entropy can be considered as the carrier of the energy or enthalpy. Entropy dS flowing into the system increases the enthalpy (or energy) with T being the factor of proportionality. For the following considerations, the slope of the molar enthalpy is considered as a function of the temperature, T , which corresponds to the molar specific heat capacity at constant pressure

$$C_p(T) = \frac{dH(S(T), p_0, N_{A0})}{dT} \quad (6)$$

$$= \frac{dH(S(T), p_0, N_{A0})}{dS} \frac{dS(T)}{dT} = T \frac{dS(T)}{dT}$$

either in the solid or in the liquid state. From (6) the molar specific entropy capacity is given by

$$\frac{dS(T)}{dT} = \frac{C_p(T)}{T}. \quad (7)$$

As a consequence, one can determine from the molar specific heat and entropy capacities the molar enthalpy (or energy at constant pressure) and the molar entropy (at constant pressure) as a function of the temperature by

$$H(T, T_{st}) = \int_{T_{st}}^T C_p(T) dT + H(T_{st}) \quad (8)$$

and

$$S(T) = \int_{0 \text{ K}}^T \frac{C_p(T)}{T} dT. \quad (9)$$

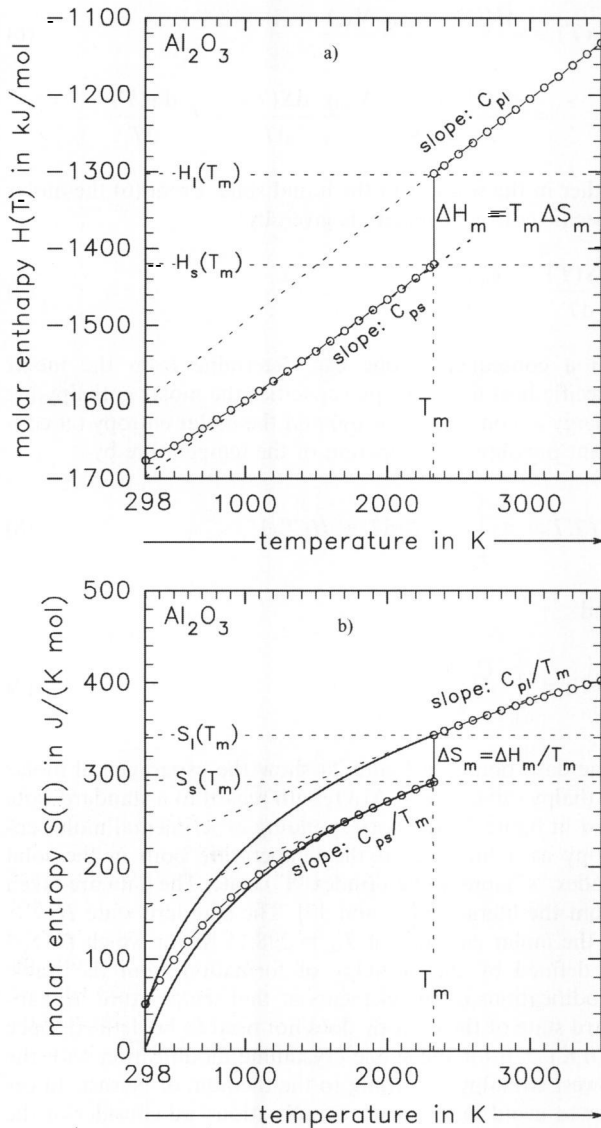
The data points in figure 2a show the experimental molar enthalpy difference of Al_2O_3 with regard to a standard state and in figure 2b the corresponding experimental molar entropy as a function of the temperature both in the solid (index “s”) and molten (index “l”) state. The data are taken from the literature [12 and 13]. The standard state $H(T_{st})$ is the molar enthalpy at $T_{st} = 298.15 \text{ K}$, for which $H(T_{st})$ is defined by the enthalpy of formation from the stable modifications of the elements at that temperature. A standard state of the entropy does not need to be defined, since $S(0 \text{ K}) = 0$ for the stable crystalline modification with the lowest enthalpy according to the theorem of Nernst. In order to avoid unnecessary complications we consider in the following only systems with one (stable) crystalline modification. Then, it is more appropriate to select $H(0 \text{ K}) = \theta$ as the standard state for the stable crystals. This is easily achieved by a shift of the vertical axis. Then, in (8) the lower integration limit of the integral is set $T_{st} = 0 \text{ K}$ and the constant $H(T_{st}) = 0$.

If a phase transition of first order at temperature T_m has to be taken into account (such as the melting transition), the molar enthalpy, $H(T)$, and entropy, $S(T)$, show steps of the height $\Delta H_m(T_m)$ and

$$\Delta S_m(T_m) = \Delta H_m(T_m)/T_m \quad (10)$$

at T_m , where $\Delta H_m(T_m)$ and $\Delta S_m(T_m)$ are the respective “latent” heat and corresponding entropy to induce that transition.

From figure 2b one realizes the difficulty in extrapolating the entropy from the molten state and the solid (crystalline) state from T_m to lower temperature. There are two obvious procedures: a linear extrapolation by tangents to $S_l(T_m)$ and $S_s(T_m)$ with the slopes $C_{pl}(T_m)/T_m$ and $C_{ps}(T_m)/T_m$, respectively, (shown in figure 2b by the dashed lines) or an extrapolation via equation (9) using the approximations $C_{pl}(T_m)/T$ and $C_{ps}(T_m)/T$ for the molar entropy capacities (examples are shown in figure 2b by the bold



Figures 2a and b. Molar enthalpy (figure a) and molar entropy (figure b) of Al_2O_3 as a function of the temperature in the solid and molten state. Circles: data from [12 and 13]. For explanation see text.

curves). Kauzmann did not specify in [1] his procedure of extrapolating.

The linear extrapolation shows obviously too large deviations from the experimental entropy functions and cannot be useful, in particular for large intervals into the low temperature range (see figure 2b for illustration).

The second extrapolation procedure using the approximations $C_{pl}(T_m)/T$ and $C_{ps}(T_m)/T$ for the molar entropy capacities, yields

$$S_l(T) = S_l(T_m) + \int_{T_m}^T \frac{C_{pl}(T_m)}{T} dT \quad (11)$$

$$= S_l(T_m) - C_{pl}(T_m) \ln\left(\frac{T_m}{T}\right)$$

for the molten state and

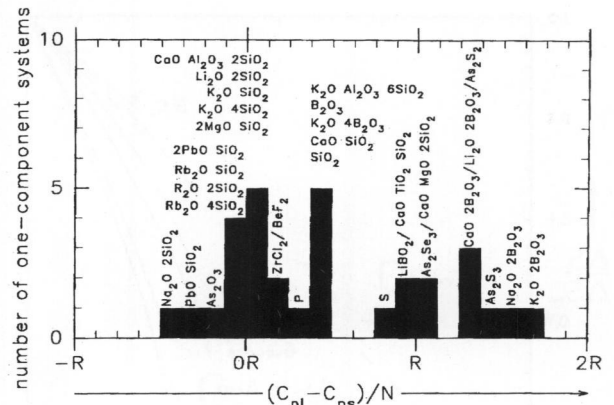


Figure 3. Histogram of the difference $(C_{pl}(T_m) - C_{ps}(T_m))/N$ between the molar specific heat capacities of the molten and crystalline state near the melting temperature, T_m , normalized to the number, N , of atoms per formula unit of one-component systems forming glasses. The unit of the specific heat capacities is the molar gas constant, R , and the interval width is $R/8$. Data from [12 and 13].

$$S_s(T) = S_s(T_m) + \int_{T_m}^T \frac{C_{ps}(T_m)}{T} dT \quad (12)$$

$$= S_s(T_m) - C_{ps}(T_m) \ln\left(\frac{T_m}{T}\right)$$

for the solid (crystalline) state. It seems to fit the experimental entropy curves better for a fairly large interval of temperature.

In contrast to Kauzmann's claim, however, both extrapolations do not tend to negative $\Delta S = S_l - S_s$ necessarily with decreasing temperature: for the linear extrapolation figure 2b is just a counterexample. In the second procedure, the extrapolations via (11) and (12) diverge for $T \rightarrow 0$ K as $S_l(T) \rightarrow (-\infty)$ and $S_s(T) \rightarrow (-\infty)$. But the difference

$$\Delta S(T) = S_l(T) - S_s(T) \quad (13)$$

$$= S_l(T_m) - S_s(T_m) - (C_{pl}(T_m) - C_{ps}(T_m)) \ln\left(\frac{T_m}{T}\right)$$

$$= \Delta S_m - (C_{pl}(T_m) - C_{ps}(T_m)) \ln\left(\frac{T_m}{T}\right)$$

tends to $(-\infty)$ only in the case $C_{pl}(T_m) > C_{ps}(T_m)$, whereas in the case $C_{pl}(T_m) < C_{ps}(T_m)$ the difference of the entropies tends to $(+\infty)$ with the consequence that a Kauzmann temperature, T_K , does not exist. Only if $C_{pl}(T_m) > C_{ps}(T_m)$, one can calculate the T_K by inserting $\Delta S(T_K) = 0$ into (13), which yields

$$T_K = T_m \exp\left(-\frac{\Delta S_m}{C_{pl}(T_m) - C_{ps}(T_m)}\right). \quad (14)$$

Both extrapolations disregard that the specific heat and entropy capacity of solids tend to zero faster than T for $T \rightarrow 0$ K.

One might object that Kauzmann's claim refers to actually undercooled melts forming glasses, only. However, even for glasses it is not generally true that the extrapolated $\Delta S = S_l - S_s$ vanishes or becomes negative with decreasing temperature.

In order to test whether (14) is applicable generally for glass forming melts, the difference of the specific heat capacities ($C_{pl}(T_m) - C_{ps}(T_m)$) of different inorganic one-component systems adjacent to T_m is shown in figure 3 as a histogram. The data are taken from [12 and 13] and the glass forming ability is indicated in [14]. The difference ($C_{pl}(T_m) - C_{ps}(T_m)$) has been normalized to the number, N , of the atoms in the formula unit of the one-component systems. Systems with a negative value of $(C_{pl}(T_m) - C_{ps}(T_m))/N$ cannot show a Kauzmann temperature according to (13). One can clearly see from the data shown in figure 3 that Kauzmann's considerations are not applicable to several inorganic one-component systems, which are nevertheless able to form glasses. In the following, further inadequacies in applying Kauzmann's postulations will be discussed.

From figure 3 one realizes that borates and arsenic sulfides show a large difference $(C_{pl}(T_m) - C_{ps}(T_m))/N$ between the specific heat capacities of the molten and the crystalline state near T_m . Since these compounds show a rather high vapor pressure near T_m , it seems worthwhile reconfirming the data.

3. Comparing the entropy of a melt with that of a solid

Kauzmann's considerations are based on his comparison of the entropy of the melts with that of crystalline solids of the same compound at the same temperature. This is misleading as can be shown by the following argument: the entropy of the melt is larger than that of the crystals in any case in a temperature interval below T_m . Considering the entropy alone crystallization should not be possible as long as $S_{pl}(T) > S_{ps}(T)$ and in particular above the Kauzmann temperature (if there is any), since crystallization is a spontaneous process which occurs according to the second law of thermodynamics necessarily with the production of entropy. Thus, isothermal crystallization should not occur at all if a Kauzmann temperature is absent, since in this case the entropy of the undercooled melt would always be larger than that of the crystalline solid, if Kauzmann's extrapolation was valid. Numerous experiments teach the opposite. Based on this experimental contradiction alone Kauzmann's procedure could be discarded.

Furthermore, one must conclude that a spontaneous transition from the undercooled melt to the crystalline state cannot occur at constant temperature (a vertical transition in figure 1). Upon crystallization entropy is necessarily produced and drives the neighborhood of the nucleation centers to higher temperatures. Clearly, the entropy can be removed to lower the temperature. Thus, the entropy difference as a function of the temperature as shown in figure 1 corresponds to different energetic states of the material. In other words, Kauzmann compares two different phases with different entropies and enthalpies (corresponding to the energy as a function of the variables entropy, S , pressure, p , and number of particles, N_A , as defined in (1)), but considers only the entropies of the initial and the final state, whereas the energy of these states has been neglected. A transition from the undercooled melt to the crystalline state is not possible at constant temperature. If such a process is assumed to occur at constant temperature, at least a third

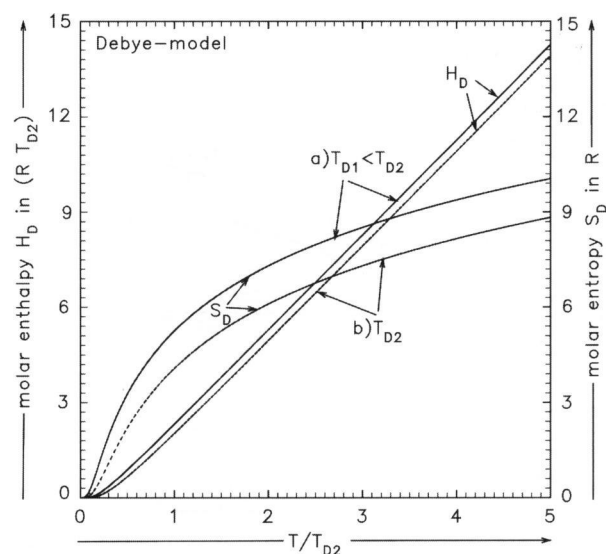


Figure 4. Molar enthalpy (energy), H_D , and entropy, S_D , of two one-component systems as a function of T/T_{D2} according to a Debye model using two different Debye temperatures, (a) T_{D1} and (b) $T_{D2} = 3T_{D1}/2$. The unit of the entropy, S_D , is R and that of the enthalpy, H_D , is $R \cdot T_{D2}$, where R is the universal molar gas constant.

system able to exchange entropy and energy with the undercooled melt and the crystalline solid has to be taken into account. Therefore, it is useless to compare only the entropies of both states or phases at a given temperature. Since the amounts of exchanged entropy and energy have not been specified or considered by Kauzmann, there is no reason being at all confused by a paradox. Neither the entropy nor the energy balance between the undercooled melt and the crystalline state have been established by Kauzmann, which seems to have not yet been realized in the literature until now.

4. Entropy and energy in the crystalline and molten states

Entropy, S , and enthalpy, H , of the undercooled melt and of the crystalline material can be taken into account simultaneously without difficulties by representing S as a function of H of the one-component systems. Since both $S(T)$ and $H(T)$ are known as functions of the parameter "temperature T ", one just needs to eliminate that parameter. $S_D(T)$ and $H_D(T)$ are shown in figure 4 using data from the Debye model, which is discussed in some detail in section 9. For figure 4 two different Debye temperatures, T_{D1} and $T_{D2} = 3T_{D1}/2$, have been used. One might object that this is a special theoretical model, only. However, it is used for illustration purpose, only, and the basic feature, namely the strictly monotonic increase of the entropy and the enthalpy with increasing temperature, is correct. In principle, additional contributions to the specific heat capacities can be taken into account. This would just cause a distortion of the $S(T)$ and $H(T)$ dependences in vertical direction in figure 4. However, the essential monotony must be conserved.

Data of one-component systems consisting of one atom in the formula unit are represented here and in the following theoretical figures for simplicity. If the formula unit consists

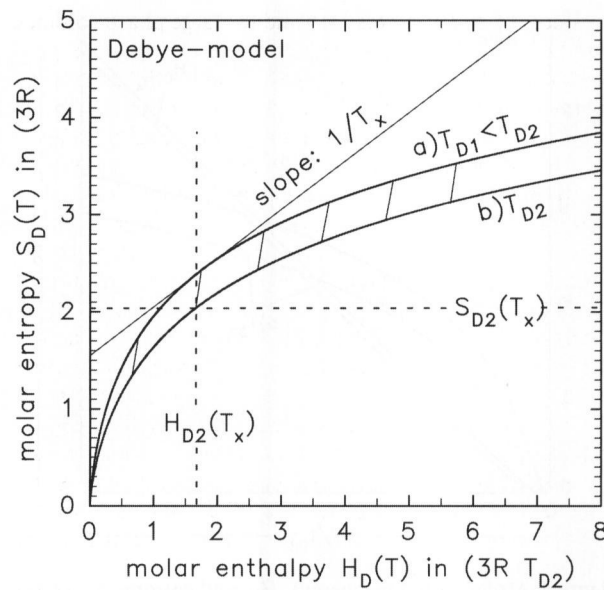


Figure 5. Molar entropy, S_D , as a function of the molar enthalpy, H_D , or $S_D(H_D)$ dependencies of two different single-component systems according to the Debye model. Same data as in figure 4.

of N atoms, the molar entropy and enthalpy as well as their capacities have to be multiplied by N .

Eliminating the parameter T in the respective pair of $S_D(T)$ and $H_D(T)$ dependences of figure 4 one receives the desired $S_D(H_D)$ curves shown in figure 5. Since the following considerations are independent of the special model, the subscript D of the molar entropy, S_D , and enthalpy, H_D , can be omitted.

The basic knowledge about the temperature can also be retained from the $S(H)$ dependence, since at constant pressure and particle number we have from equation (1) $dH = T dS$, which yields

$$\frac{dS}{dH} = \frac{1}{T}. \quad (15)$$

Thus, the inverse temperature is given by the derivative or the slope of the $S(H)$ curves. Therefore, the $S(H)$ curves start at 0K with a vertical slope, which decreases with increasing H and S monotonically to lower values as long as the system exists (with the limit of zero slope at very high temperatures). Some data for the same temperatures of both curves are connected in figure 5 by straight lines. As long as the systems are in the same phase, the $S(H)$ curves must be concave (regarded from the bottom) or $d^2S/dH^2 < 0$. Otherwise the enthalpy and the entropy would increase with decreasing temperature. As a consequence, the structure of the $S(H)$ curves is very simple.

The curves shown in figure 5 are shifted to start at the zero of the coordinate system. The curve (a) with the lower Debye temperature increases steeper than the other. This can easily be understood by the fact that more lattice vibrations with low energy exist and are excited at the same temperature than in case (b). Similar statements can be made in the case of additional electronic transitions: the more electrons exist in the uppermost energy bands or levels and the smaller the difference to higher levels as compared

to another system, the larger the entropy at the same temperature.

In practice, not all sections of such curves may be accessible experimentally. In the gaseous phase under atmospheric pressure, e. g., the $S(H)$ curve can exist above the boiling temperature, only. Then, they can be used at least piece by piece in those ranges which are experimentally accessible. In the following it is assumed for simplicity that the curves are known.

Both curves in figure 5 are considered to represent different systems until now. On the other hand, both curves may also represent different phases of the same system, such as the crystalline and the molten phase. Then, however, both curves cannot start at the same entropy and enthalpy point at zero temperature; instead they are connected at the melting temperature, T_m , by a straight line determined by the melting enthalpy, $\Delta H_m(T_m)$, and melting entropy, $\Delta S_m(T_m)$. This connecting line is part of a common tangent with the slope $1/T_m$ to both $S(H)$ curves. The result is shown in figure 6. The starting point of curve (b) is now shifted with respect to curve (a) by ΔH_0 to larger enthalpy and by ΔS_0 to larger entropy. These values represent the energy and entropy of the melt with respect to the (stable) crystalline state being undercooled to very low temperatures near $T = 0$ K. They are also called zero-point, residual or configuration entropy and enthalpy. The disordered state obviously has a larger enthalpy and entropy as the ordered crystal for $T \rightarrow 0$ K. This compares to the energy and entropy difference between a disordered and an ordered alloy of the same composition. Since these considerations are independent of the special model, the subscript D of the molar entropy, S_D , and enthalpy, H_D , has been omitted in figure 6.

Heating up a crystalline solid one follows in figure 6 curve (b) from low to higher temperatures. Enthalpy and entropy increase monotonically. If the melting temperature is reached, the entropy and enthalpy will increase by a small amount only to reach a higher temperature if curve (b) is followed further. However, the system can absorb more entropy, if there is a transition to curve (a) without temperature increase. Depending on the amount of entropy the system starts to melt partially and decomposes into two phases represented by curves (a) for the melt and (b) for the solid. The molar ratio between both phases depends on the amount of melting entropy and enthalpy flown into the system. For clarity the melting range has been depicted on a larger scale in figure 7. With increasing entropy flow the system completes its transition to curve (a). Then, it can further absorb entropy and enthalpy in the molten state again accompanied by a temperature increase. (Entropy and enthalpy may be partially used to evaporate and to increase the vapor pressure of the system under constant pressure conditions. Taking this effect into account the corresponding $S(H)$ curves of the molten state (a) may be followed until boiling starts.) In a former paper it has been shown that melting of chemically bonded solids is initiated essentially by electronic transitions from bonding states to antibonding states [15].

Upon cooling the melt will follow in figures 6 and 7 curve (a) from high to lower values until it will depart slightly below the straight interconnection between the melting points on both $S(H)$ curves. Then, the undercooled melt can start to crystallize and the system may decompose

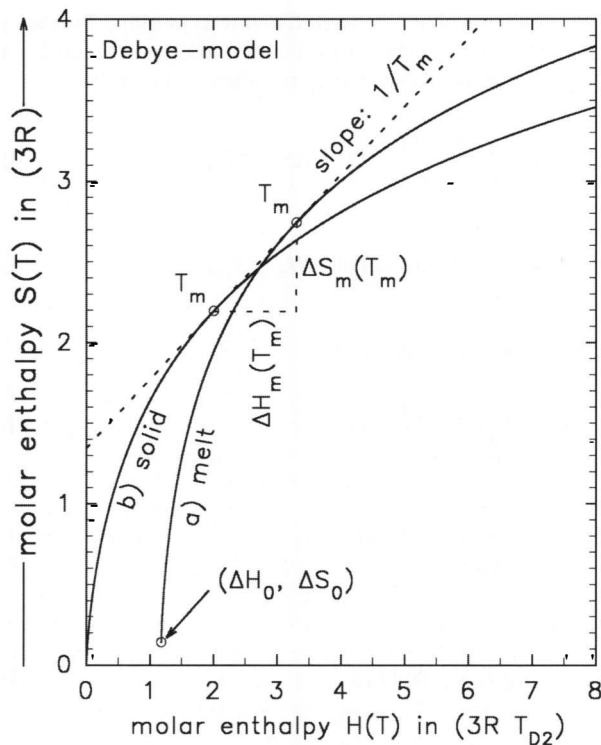


Figure 6. $S(H)$ dependencies of the melt and of the crystalline material considered as homogeneous one-component systems. Both functions are connected via the molar melting enthalpy, ΔH_m , and entropy, ΔS_m , at the melting temperature, T_m ($1/T_m$ is the slope of the common tangent). ΔH_0 and ΔS_0 are the molar enthalpy and entropy of phase (a) with respect to the stable crystalline phase (b) at 0 K.

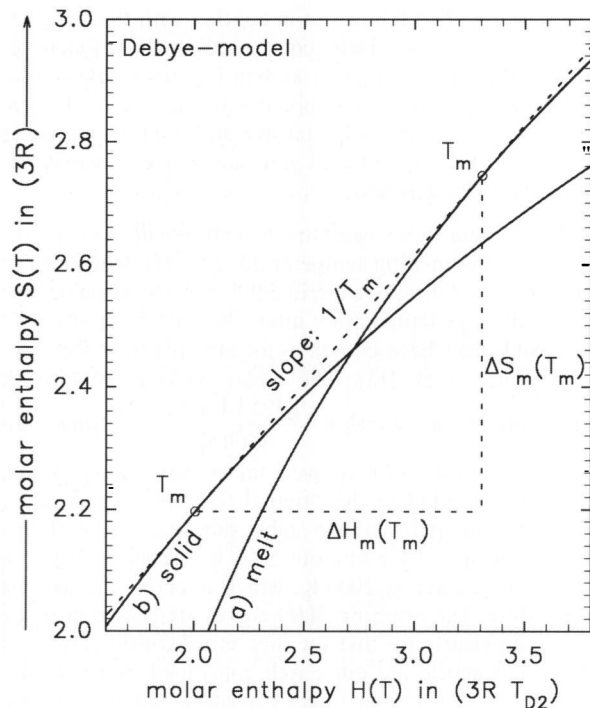


Figure 7. Section of the $S(H)$ dependencies from figure 6 near the melting transition enlarged.

into melt and solid. However, crystallization may be difficult to initiate immediately near the melting temperature,

T_m , since the $S(H)$ curves are valid for large phase volumes. True homogeneity of the molten phase excludes the presence of a surface. For small phase volumes the crystallization may not occur until the melt is considerably undercooled. Then, the system will follow on curve (a) to lower entropy and enthalpy (and temperatures). If crystallization is initiated at lower temperatures, a transition from curve (a) to (b) will occur locally and an amount of entropy will be produced corresponding to the vertical difference between both curves (a) and (b), which heats up the starting crystal and its environment. A vertical transition in figures 6 and 7 corresponds to conservation of enthalpy in the volume element under consideration, which certainly must be fulfilled, since enthalpy is removed by the comparatively slow process of thermal conduction. Thus, crystallization is necessarily producing entropy, since it occurs spontaneously. The system becomes inhomogeneous and will be decomposed into several homogeneous partial systems, since the crystallization does not occur in each volume element to completion at the same rate.

This qualitative analysis shows that Kauzmann's paradox has no basis since entropy and enthalpy have previously not been considered simultaneously. It is useless to compare alone the entropy of the undercooled melt with that of crystals at the same temperature, since the enthalpies in both states possess different values.

In the case of glass formation, the undercooled melt will stay on curve (a), which continues from high to low temperatures. The consequence is that glass formation does not correspond to a phase transition, since the system remains on the $S(H)$ curve of the melt to lower temperatures avoiding a transition from there to the $S(H)$ curve of the crystalline phase (b), which is thermodynamically stable. The degree of relaxation may be characterized by minor variations of the respective $S(H)$ curve and the values of ΔH_0 and ΔS_0 . For "good" glasses deviations from curve (a) are negligible.

5. Qualitative description of the atomistic changes upon melting and glass formation

The thermodynamic functions and dependencies do not provide information on the atomistic mechanism of melting and glass formation. For chemically bonded solids (i. e. except for solids with dominating van der Waals and H-bridging bonding) melting has been explained on an atomistic level in the following way [15 and 16]: from an analysis of the specific heat capacity, $C_{ps}(T)$, near the melting temperature one can conclude that electronic transitions contribute to $C_{ps}(T)$ in that range of temperature. Hence, an increasing fraction of bonding electrons make transitions from low to high energy levels with increasing temperature. The transitions into higher states are accompanied by a change of the wave functions and of the local charge distributions. As a function of time the charge distribution changes according to the random time series of the different occupied electronic states and drives the core ions to new positions. If the forces are strong enough and the core ions relax to their new positions within the lifetime of the respective excited

electronic states we have a continuously changing arrangement of the core ions or a melt. Near and above the melting temperature the specific heat capacity, the entropy and the enthalpy are increased due to contributions of both the changed lattice vibrations (differing bonding strength) and increasing contributions of electronic transitions (new distribution of electronic levels). The melting entropy, ΔS_m , and enthalpy, ΔH_m , are essentially needed to fill up the larger reservoir of the entropy and enthalpy due to the new and changing arrangement of the constituents including the outer electrons.

The distribution of the electronic energy levels in the molten state differs from that of the crystalline solid. With decreasing temperature the distribution of electrons relaxes to lower electronic states of the disordered arrangement. If the forces of the relaxing electronic distribution are too weak to attract the core ions to new regular positions, the disordered state is maintained and the transformation into a glass takes place. Thus, electronic transitions to higher states with a sufficiently large deviation of the charge distribution freeze out near the glass transformation temperature, T_g , and the disorder can be fixed. This is favoured by a) sufficiently strong directional bonding between neighboring ions, and b) a small temperature interval of recalescence, ΔT_{\min} , relative to the melting temperature, T_m , [17]

$$\frac{\Delta T_{\min}}{T_m} = \frac{\Delta S_m}{2C_{pl} - C_{ps}}, \quad (16)$$

which has to be passed fast enough in order to avoid nucleation and crystallization. The necessary cooling rate to form a glass depends on both conditions a) and b).

In the glass transformation range of inorganic glasses the electronic transitions freeze out exponentially with decreasing temperature. Internal variables necessary for rearrangement of the constituents (such as their position, distribution of the electronic potential) do not exchange freely any longer and are fixed [15 and 16]. If the system remains on curve (a) in figure 6 below T_m , it remains in a metastable state which may depend on the cooling velocity and relaxation during the cooling procedure. Depending on the relaxation and on the rearrangement towards curve (b) in figure 6 the exact $S(H)$ dependence may vary and differing amounts of the entropy, ΔS_0 , and enthalpy, ΔH_0 , of the sample are frozen in. ΔS_0 and ΔH_0 cannot be removed from the sample by conduction. First, they have to be recharged from the configuration onto lattice vibrations (or electronic excitations) in order to be able to be removed from the sample. This is equivalent to crystallization.

6. Experimental determination of ΔH_0 and ΔS_0

The “residual” or zero-point molar entropy and enthalpy, ΔH_0 and ΔS_0 , are obtained experimentally as follows: in the molten state the enthalpy and the entropy of the glass and of the crystal must coincide as is seen from figure 6. Therefore, one determines the enthalpy and entropy of the crystalline and of the glassy material between $T = 0$ K and the molten state at $T = T_m$ from the integral of the molar specific heat capacities, $C_{p,cr}(T)$ and $C_{p,gl}(T)$, the molar specific entropy capacities, $C_{p,cr}(T)/T$ and $C_{p,gl}(T)/T$, and the molar melting enthalpy and entropy, where the

subscripts “cr” and “gl” refer to the crystalline or glassy state, respectively. The entropy and enthalpy between both temperatures is given for the crystalline material by

$$S_{cr}(T_m) = \int_{0\text{ K}}^{T_m} \frac{C_{p,cr}(T)}{T} dT + \Delta S_{m,cr}(T_m) \quad (17)$$

$$H_{cr}(T_m) = \int_{0\text{ K}}^{T_m} C_{p,cr}(T) dT + \Delta H_{m,cr}(T_m) \quad (18)$$

and for the glassy material by

$$S_{gl}(T_m) \equiv \int_{0\text{ K}}^{T_m} \frac{C_{p,gl}(T)}{T} dT \quad (19)$$

$$H_{gl}(T_m) = \int_{0\text{ K}}^{T_m} C_{p,gl}(T) dT. \quad (20)$$

Then,

$$\Delta S_0 \equiv S_{cr}(T_m) - S_{gl}(T_m) \quad (21)$$

and

$$\Delta H_0 = H_{cr}(T_m) - H_{gl}(T_m) \quad (22)$$

which are the configurational molar entropy and enthalpy frozen in during the glass formation. This is the entropy and enthalpy difference of the glass at $T = 0$ K with respect to the thermodynamically stable crystalline state of the one-component system.

$\Delta S_0 > 0$ at $T = 0$ K is not in conflict with the third law of thermodynamics, which requires $\Delta S_0 = 0$ in the stable state for that temperature. A system is in its stable state if it is in equilibrium with respect to all inner variables, exchanging freely, and if all extensive and intensive variables are finite. In fact, a structural glass is not free to restructurizing, as has been described above in section 5.

Today there is no necessity to extrapolate data of the entropy at the melting temperature to lower temperatures as Kauzmann did, since experimental data are available over sufficiently large temperature intervals. Data for quartz and glassy SiO_2 have been chosen as an example from the work of P. Richet et al. [11]. The molar melting enthalpy of 9.395 kJ/mole and entropy $\frac{9.395 \text{ kJ/mole}}{1700 \text{ K}}$ (melting temperature of quartz: 1700 K) were taken into account, which had been neglected in the original table of their data for quartz. Taking quartz as the stable substance, the enthalpy and the entropy of the vitreous SiO_2 have been adjusted to the data of quartz at 2000 K, which is above the melting temperature. The resulting $S(H)$ curves are shown in figure 8. One can clearly see that the theoretical considerations of the present article are quite well confirmed by the experimental data of [11]. The molar transition enthalpy and entropy for the α - β transition of quartz near 847 K are so small that they cannot be detected in figure 8. However, one must point out that equations (20) and (21) are given as the difference of large numbers, which have to be determined by integration of experimental data. Thus, the accuracy of the data may pose a difficult problem to the procedure.

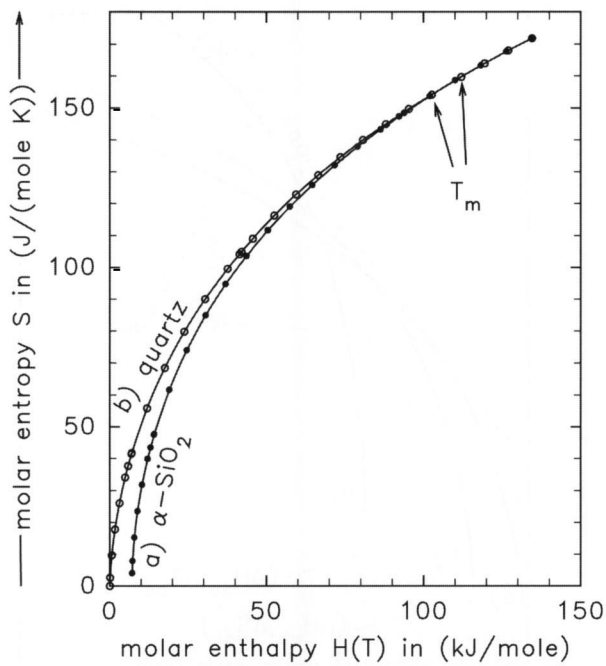


Figure 8. Experimental $S(H)$ curves of quartz and amorphous SiO_2 . The data of the entropy and enthalpy of amorphous SiO_2 have been shifted to match those of quartz at 2000 K. Data from [11].

Nevertheless, there is no doubt from the data shown in figure 8 that the $S(H)$ dependence of the glass is lower than that of the quartz in the complete range of data. In addition, one can observe qualitatively that for the same temperature (indicated by the same value of the derivative $dS(H)/dH = 1/T$ of both $S(H)$ dependences in figure 8), the entropy of the glass is always larger than that of the crystal. The molar configurational entropy and enthalpy are $\Delta S_0 = 4.1 \frac{\text{J}}{\text{mole} \cdot \text{K}}$ and $\Delta H_0 \equiv 7.2 \frac{\text{kJ}}{\text{mole}}$ with respect to quartz.

7. Consequences from the entropy as a function of the energy

The present analysis shows clearly that the crystallization from the undercooled melt (and also condensation of droplets from the undercooled gas phase) is necessarily accompanied by entropy production. This is in contrast to the classical theories of nucleation and crystal growth (and condensation from the gas phase), which do not consider the entropy production at all. These theories cannot provide a convincing and reliable quantitative description of crystallization (and condensation). The same arguments apply also to the so-called kinetic theories of glass formation [10, 18 to 20], since in the estimation of the glass forming capability the nucleation and crystallization is treated in these papers as an isothermal and isentropic process, which clearly requires revision.

The present representation can be extended to all kinds of first order phase transitions: there must be at least two $S(H)$ curves of two phases of the same one-component system which are connected by a common tangent and the difference of the coordinates of the points of contact is de-

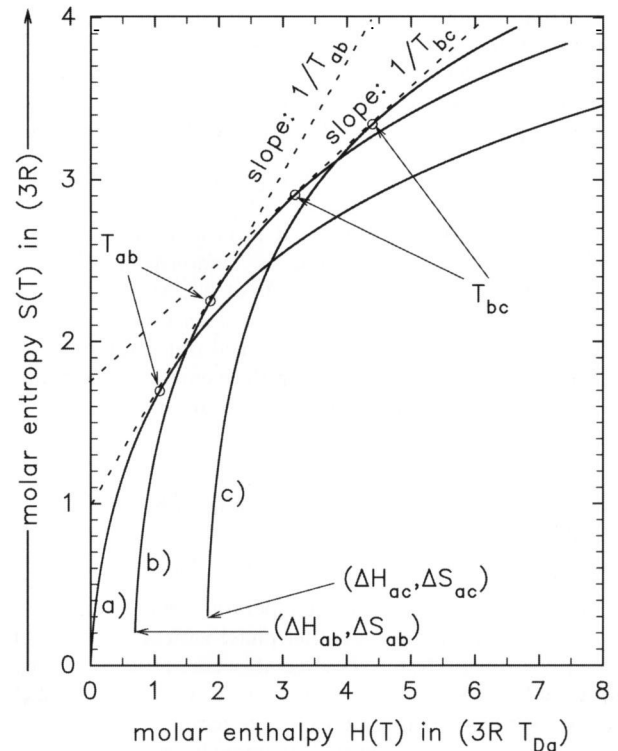


Figure 9. $S(H)$ curves representing different homogeneous phases of a one-component system, in which two phase transitions of first order actually can take place one after the other, if they are not hindered by kinetics. If curve (c) represents a gaseous phase and the other curves represent solid phases or the melt, curve (c) must be shifted by a much larger amount vertically and horizontally, since the boiling entropy and enthalpy is in general much larger (an order of magnitude or more) than the entropy and enthalpy of other phase transitions of first order.

finied by the entropy and the enthalpy of the corresponding phase transition. This implies that the entropy of the high temperature phase must be larger than that of the low temperature phase. Structural phase transitions of first order may be accompanied by a decrease in the phonon frequencies (softening of the restoring forces). This allows a larger amount of entropy to be stored in the lattice vibrations. Also, the symmetry of the structure may be increased, which corresponds to an increase in degeneracy. In fact, structural phase transitions from low to high temperatures are generally accompanied by an increase in symmetry of the arrangement of the constituents. In reverse, reducing the temperature, the entropy and enthalpy may be reduced by breaking the symmetry. There are numerous examples known in crystallography. An additional example is provided by the Jahn-Teller effect.

Several phase transitions of first order may occur in sequence with increasing temperature. Necessary is that two neighboring $S(H)$ curves possess a common tangent with positive slope and the slope is decreasing for subsequent transitions as shown in figure 9. The difference of the coordinates of the points of contact is given by the enthalpy and entropy of the phase transition as shown in figure 6.

The enthalpy and entropy differences, ΔH_0 and ΔS_0 , at 0 K with respect to the ideal standard state of the previous phase (or to the stable state) cannot be determined from the

transition enthalpies $\Delta H_{\alpha\beta}(T_{\alpha\beta})$ and entropies $\Delta S_{\alpha\beta}(T_{\alpha\beta})$, since the full $S(H)$ curves have to be considered. It can be larger or smaller than $\Delta H_{\alpha\beta}(T_{\alpha\beta})$ and $\Delta S_{\alpha\beta}(T_{\alpha\beta})$, which give only a rough estimate of the order of magnitude. Instead the procedure described in section 6 has to be applied.

Even in the case of a given phase minor enthalpy and entropy differences may be observed between two representatives, if the concentration of defects in both systems is different. A practical example is demonstrated by the Wigner effect, when in components of nuclear reactors defects are created due to the nuclear fission products. These defects are accumulated until they heal out spontaneously and set their enthalpy free and produce entropy, which may cause uncontrolled increase of temperature.

The enthalpy and entropy can be increased to a minor degree also by increasing the surface of the system, such as to produce porous materials or foams or powders. Thus, the possibility of $\Delta H_0 \neq 0$ and $\Delta S_0 \neq 0$ with respect to the standard or stable state is rather the rule than the exception.

It may occur that a high temperature phase cannot be reached if a transition to another phase with an even higher $S(H)$ curve is preferred, because it occurs at a lower temperature. This is demonstrated by curves (a), (b) and (c) in figure 10. Then, heating up from low temperatures a phase transition occurs from curve (a) immediately to curve (c) and the phase represented by curve (b) is hidden, since it would be reached from (a) at a higher temperature than phase (c). Curve (b) cannot be reached from curve (c) upon heating either but temporarily by under cooling the system on curve (c) to lower values of the entropy (at lower temperatures), from which a transition can take place to curve (b) under production of entropy. From (b) it transforms to phase (a) spontaneously, if such a transition is not hindered by kinetics. Thus, upon cooling more phases may be detected than during heating (compare with Ostwald's rule of steps.)

If the $S(H)$ curve representing the melt is hidden, i. e. its entropy values are not sufficiently large at high temperatures as compared to the $S(H)$ curve of the subsequent gaseous state, the system transforms directly from the solid phase into a gas without preceding melting. At constant pressure of one atmosphere, the $S(H)$ curve of the gaseous state starts at T_{ac} in figure 10 to sublime with a pressure of one atmosphere. Then, curve (c) is not defined for temperatures below T_{ac} , since the atmospheric pressure cannot be maintained below that temperature. At T_{ac} however, it has a common tangent with the previous solid phase. Otherwise, the vapor would have a temperature different from the solid phase.

These considerations are obviously not restricted to a transition from a solid to a gaseous phase but apply also to a transition from a liquid to a gaseous phase. If curve (b) in figure 9 corresponds to the molten phase and (c) to the gaseous phase, T_{bc} represents the boiling temperature, T_{boil} , and curve (c) for a vapor pressure of one atmosphere does not exist below T_{bc} .

8. Discussion

The present representation of the melting transition by $S(H)$ curves allows taking into account correctly both en-

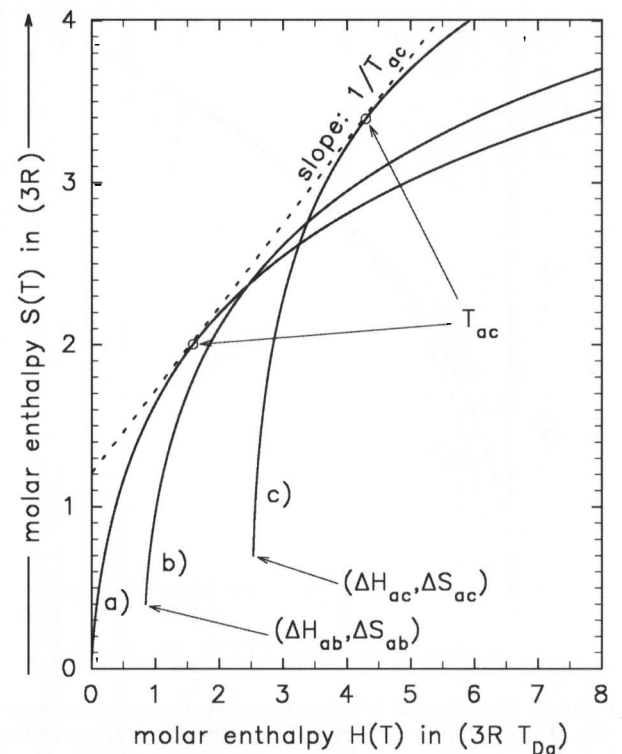


Figure 10. $S(H)$ curves representing three different homogeneous phases of a one-component system with the phase (b) being hidden if the system is heated from low temperatures. If curve (a) represents a solid, (b) a liquid and (c) a gas at the usual pressure, the solid sublimates. Phase (b) can be accepted during cooling from high temperatures at least temporarily, if a sufficient undercooling on curve (c) is possible and if the transition to phase (b) is not hindered.

trophy and enthalpy of the crystals, the molten phase and the melting transition. The considerations and results are unambiguously extended to other phase transitions of first order without difficulty. Heating up the system under consideration a transition from one $S(H)$ curve to a suitable other $S(H)$ curve takes place, if both $S(H)$ curves have a tangent with positive slope in common. The slope of the tangent corresponds to the reciprocal of the temperature at which the phase transition of first order occurs. The mechanism inducing the phase transition needs not to be known exactly. In fact, from theoretical considerations it is generally specified just as a transition occurring between suitable $S(H)$ curves characteristic of the system under consideration. The mechanism or which subsystem is able to store additional entropy and enthalpy must be analyzed carefully in order to determine the cause of the instability of the phases. It seems that phase transitions are caused by lattice vibrations and, in particular, by the electronic systems and electronic transitions [15].

Cooling from high temperature, such as from a melt, to lower temperatures may avoid crystallization and a glass is formed if the cooling rate is fast enough (for necessary conditions see [17]). Thus, glass formation corresponds to a continuation of the $S(H)$ curve of the melt to low temperatures. If the glass is kept at higher temperatures for a sufficiently long time, crystallization occurs reversing the melting transition at lower temperatures. This phase transition occurs obviously at lower temperatures under entropy pro-

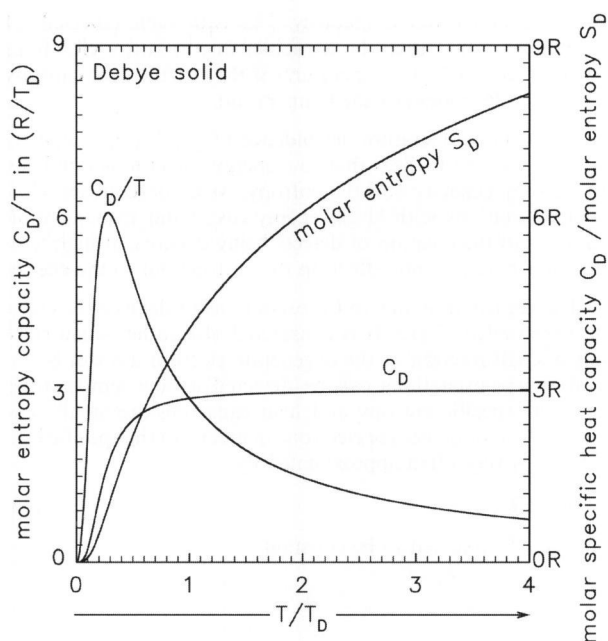


Figure 11. Molar specific heat capacity, C_D , entropy capacity, C_D/T , and entropy, S_D , according to a Debye model as a function of T/T_D . The units are R for C_D and S_D and R/T_D for C_D/T .

duction on an atomic scale (the same is true also for condensation from the gaseous phase). Thus, the well-known classical theories on nucleation and crystal growth from the melt (or droplet growth from the gaseous phase) require revision.

In the representation shown above, Kauzmann's paradox (worrying about the entropy of an undercooled melt being smaller than that of the corresponding crystal) does not cause a problem. The reason is that both entropy and enthalpy are considered simultaneously neglecting the additional deficits in Kauzmann's earlier consideration, which have eventually been objected to already. The confusion could have been avoided easily if Kauzmann had interpolated the entropy between the melting temperature and 0 K instead of extrapolating. Assuming both for a crystal and a glass $S(0\text{ K}) = 0$ as an approximation, the interpolation from the melting temperature yields for the entropy in the molten state

$$S_l(T_m) \frac{T}{T_m}$$

which is for the same temperature always larger than the entropy in the crystalline state

$$S_s(T_m) \frac{T}{T_m}$$

since $S_l(T_m) - S_s(T_m) = \Delta S_m > 0$. Then, right from the beginning Kauzmann's paradox is nil. Thus, for short the paradox in Kauzmann's paradox is that there is no paradox.

If the S and H axis in the respective figures are interchanged, one arrives at an equivalent representation by $H(S)$ curves, which obviously is the inverse to the present representation. Then, the enthalpy is considered as a func-

tion of the entropy. Since the slope of the $H(S)$ curves corresponds directly to the temperature, T , the $H(S)$ curves start with a horizontal tangent for $S = 0$ at 0 K and the slope must increase monotonically until it reaches a vertical tangent. All the results from the preceding sections remain mutatis mutandis also valid in this representation.

9. Appendix

9.1 Debye model of the molar specific heat capacity and energy (enthalpy) as a function of temperature

The molar specific heat capacity due to lattice vibrations at constant volume is calculated according to the Debye model as a function of the temperature, T , by (see textbooks on thermodynamics, [21 to 27] e. g.)

$$C_D(T/T_D) = 9R \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{\left(\frac{T_D}{T} \right)^4 \exp\left(\frac{T_D}{T} \right) d\left(\frac{T_D}{T} \right)}{\left(\exp\left(\frac{T_D}{T} \right) - 1 \right)^2} \quad (23)$$

with the Debye temperature

$$T_D \equiv \frac{h \nu_D}{k_B} \quad (24)$$

Herein, R is the universal molar gas constant, h is Planck's constant, k_B is Boltzmann's constant and ν_D is the maximum frequency of a parabolic spectral frequency density of the lattice vibrations. Usually the spectral density is obtained by suitable averaging over the longitudinal and transversal vibrations, to give a single Debye temperature (equation (24)). Then, equation (23) is a universal function of T/T_D . $C_D(T/T_D)$ is shown in figure 11 (right-hand scale). One can clearly see the transition from the well-known power law

$$C_D(T/T_D) = \frac{12\pi^4 R}{5} \left(\frac{T}{T_D} \right)^3 \quad (25)$$

at low temperatures, $T < T_D/10$, to the classical limit of the molar specific heat capacity due to the lattice vibrations

$$C_D(T/T_D) = 3R \quad (26)$$

for $T > T_D$.

Under constant pressure a Debye solid does not expand. Therefore, equation (23) applies both to constant pressure and constant volume conditions, i. e. $C_D = C_V = C_p$ in this case. The energy under constant pressure, corresponding to the enthalpy, can be calculated as a function of the temperature just by integrating equation (23) over the temperature in agreement with equation (8):

$$H_D(T) = \int_{0\text{ K}}^T C_D(T) dT \quad (27)$$

Here, the enthalpy is normalized as being zero at $T = 0\text{ K}$. With this normalization H_D is shown in figure 4 for two different Debye temperatures T_{D1} and T_{D2} together with the corresponding entropy S_D as a function of T/T_D . For $T/T_D > 1$ the enthalpy (and the inner energy E_D in the case of constant volume) increases approximately proportional to the temperature.

9.2 Entropy capacity and entropy of a Debye solid as a function of the temperature

From the molar specific heat capacity one easily calculates the molar specific entropy capacity,

$$dS_D/dT = C_D(T/T_D)/T, \quad (28)$$

which corresponds to the specific entropy capacity both at constant volume and pressure. It is also displayed in figure 11 (left-hand scale) as a function of T/T_D . If the ordinate is divided in units of R/T_D and the abscissa in units of T/T_D , it is a universal function. At low temperatures, $T < T_D/10$, the specific molar entropy capacity is proportional to T^2 using $C_D(T/T_D)$ from equation (25)

$$\frac{C_D(T/T_D)}{T} = \frac{12\pi^4 R}{5 T_D} \left(\frac{T}{T_D}\right)^2, \quad (29)$$

whereas for $T > T_D$ it decreases with the temperature as

$$\frac{C_D(T/T_D)}{T} = \frac{3R}{T}, \quad (30)$$

since $C_D = 3R$ according to equation (26) in that range. Between both ranges one can clearly see a maximum of which the height has been determined approximately as $2.033 \times 3R/T_D$ for $T/T_D = 0.28$.

The molar entropy due to lattice vibrations is given by the integral

$$S_D(T) = \int_0^T \frac{C_D(T)}{T} dT. \quad (31)$$

Equation (31) with equation (23) can be integrated numerically. $S_D(T)$ is also shown in figure 11, where the right-hand scale applies. Qualitatively it is easily discussed: at low temperatures, $T < T_D/10$, one integrates equation (29). Then, the molar entropy increases as

$$S_D(T) = \frac{4\pi^4 R}{5} \left(\frac{T}{T_D}\right)^3. \quad (32)$$

For $T = T_D$ it reaches a universal value of $S_D(T_D) = 1.36 \times 3R \approx 4R$ approximately, which is independent of T_D , whereas by integrating equation (30) the specific molar entropy increases logarithmically at temperatures $T > T_D$. Then, for $T > T_D$ one can approximate $S_D(T)$ by

$$S_D(T/T_D) = S_D(T_D) + 3R \times \ln(T/T_D). \quad (33)$$

At low temperatures the molar entropy capacity increases as T^2 and the molar entropy as T^3 with the temperature, T , since the spectral phonon density increases as ν^2 (ν : frequency of the phonons) and more and more phonon states with different energy are accessible by increasing thermal excitation. At sufficiently large temperatures all phonons with different energies of the solid can be excited and the respective average numbers of phonons at all given frequencies increase proportional to T , which causes a logarithmic dependence of the entropy.

The Debye entropy both at constant volume and pressure, $S_D(T/T_D)$, due to the lattice vibrations is a unique function of the temperature in relative units T/T_D . The smaller T_D the larger is the entropy at a given temperature. Thus, solids are in corresponding states of the entropy, if their temperatures relative to their T_D are the same. Assuming that melting of solids occurs for the same entropic state, one would expect that the melting temperatures T_m correlate with T_D . Such a correlation, however, is not observed [15]. Thus, melting is not driven by the entropy in the lattice vibrations or by the energy stored in the vibrations alone.

The present considerations apply to the lattice vibrations of solids as an important capacity to store energy and entropy. However, energy and entropy may also be stored in a solid due to electronic transitions, magnetic excitations, creation of defects and phase transitions. Such additional effects can be clearly observed if their contribution is large enough compared to the respective capacities of the lattice vibrations or if they

can be separated unambiguously. This is possible especially at low temperatures, when the capacities due to lattice vibrations are small and at high temperatures if the specific heat capacity is nearly independent of the temperature.

From the temperature dependence of the entropy capacity $C_D(T/T_D)/T$ one realizes that low energy excitations dominate the entropy capacity and the entropy. As a consequence, electronic excitations with larger energy (like band to band transitions) and the creation of defects being effective at high temperatures have a minor effect on the entropy but to the energy.

The contribution due to the excitations of the electrons near the Fermi edge of metals is considered also rather small since only a small fraction of the degenerate electron gas can be excited. These excitations can be detected at low temperatures when the specific entropy and heat capacities are small. The contribution of quasi-free electrons in metals to the specific heat capacity is very often approximated by

$$C_{el} = \gamma \cdot T \quad (34)$$

wherein γ is assumed to be constant.

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