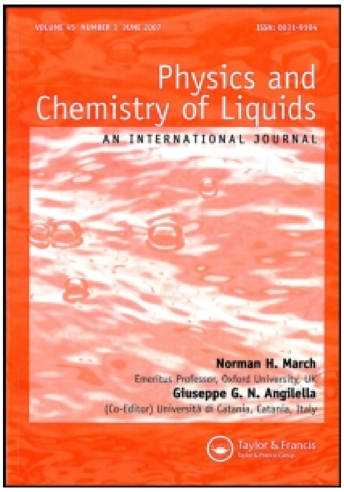

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamics of Supercooled Liquids and their Glass Transition

John Agren[a]
[a] Division of Physical Metallurgy, Royal Institute of Technology, Stockholm, Sweden

To cite this Article Agren, John(1988) 'Thermodynamics of Supercooled Liquids and their Glass Transition', Physics and Chemistry of Liquids, 18: 2, 123 — 139

To link to this Article: DOI: 10.1080/00319108808078586

URL: http://dx.doi.org/10.1080/00319108808078586

Phys. Chem. Liq., 1988, Vol. 18, pp. 123–139
Reprints available directly from the publisher

Printed in the United Kingdom

Thermodynamics of Supercooled Liquids and their Glass Transition

JOHN ÅGREN
Division of Physical Metallurgy, Royal Institute of Technology, S-100 44 Stockholm, Sweden.

(*Received 15 February 1988*)

The thermodynamic properties of supercooled liquids are discussed and a phenomenological model, capable of representing the most important experimental features, is presented. The most characteristic feature is the gradual decrease in entropy, by which the entropy of the liquid approaches that of a crystalline solid on cooling. This behaviour is modeled by means of defects, connected with the individual atoms, which are introduced to an "ideal" amorphous solid on heating. It is suggested that the increase in defect content yields not only an increase in enthalpy but also an extra increase in entropy. A tentative value $\Delta S = R$, the gas constant, per mole of defects is suggested.

The relation between glass-transition temperature and melting point is discussed under the assumption that the glass transition occurs at a certain critical defect content.

Physical interpretations of the new model are discussed. The anomalous behaviour of liquid high-purity SiO_2 is discussed. Finally, liquid Sn and glycerol are analyzed in terms of the model.

Key Words: Defects, entropy, Ehrenfest relations.

1 INTRODUCTION

As a liquid is cooled there is a continuous change in its properties. At first they depend only weakly on temperature, but if crystallisation can be avoided and large undercoolings are obtained the variation becomes very strong. The viscosity, for example, changes by several orders of magnitude within a comparatively narrow temperature range and a glass transition marks the end of this gradual change. At lower temperatures, i.e. in the glassy state, most properties have temperature dependencies similar to those of a crystalline solid. One will thus observe an almost discontinuous change in properties like the heat capacity and the thermal expansion at the glass transition.

At low temperatures, but still above the glass transition, a substantial part of the variation in properties is due to structural changes in the liquid and requires rearrangements on the molecular or atomic level. The term structural relaxation is frequently applied and the rate of the changes is often represented by a relaxation time which is closely related to the atomic mobility. Many authors have suggested that the glass transition is simply a relaxation phenomenon where slow kinetics does not allow the structural relaxation to thermodynamic equilibrium within the experimental time scale. This accounts for the well known observation that an increasing cooling rate, i.e. a shortening of the time scale, displaces the glass transition to a higher temperature.

The structural changes are manifested most clearly in the decrease of the entropy as the liquid is cooled. Kauzmann[1] pointed out that if the decrease would have continued below the glass transition, then the entropy would soon fall below the value of the stable crystalline phase, resulting in a negative value at absolute zero. That result would be impossible and it may thus be concluded that the decrease of entropy

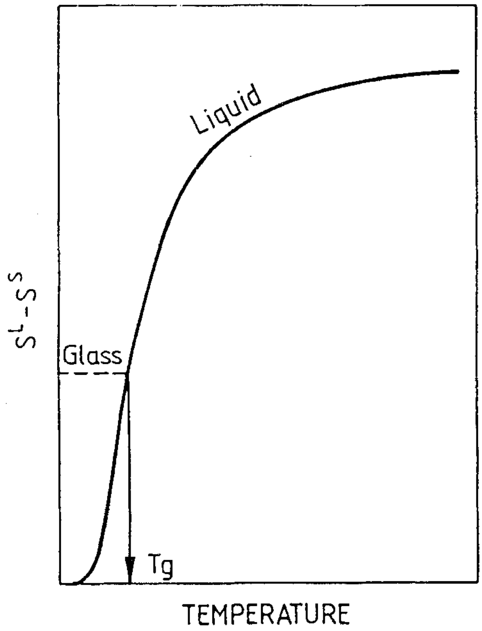

Figure 1 Schematic variation in entropy difference between supercooled liquid and stable crystalline solid.

must stop soon below the glass transition even if the cooling rate was sufficiently low to allow internal equilibrium to be established within the liquid at all temperatures. The equilibrium properties of the liquid would thus look something like the sketch in Figure 1, the idea being that a liquid which has passed through a glass transition and is now in a non-equilibrium glassy state, dashed line, would on long-time annealing relax towards the equilibrium curve.

The slope of this entropy curve is related to the difference in heat capacity and on exceedingly slow cooling one would thus expect a rather rapid decrease in the heat capacity difference at a temperature somewhat below the glass transition observed for a normal cooling rate. That decrease in heat capacity has been regarded as a manifestation of a thermodynamic glass transition of the liquid.

The purpose of the present report is to present a phenomenological model for representing the properties of supercooled metallic liquids, including their thermodynamic glass transition. However, a brief overview of some important concepts will first be given in the next two sections.

2 STRUCTURAL RELAXATION AND THE GLASS TRANSITION

A general treatment of the properties of supercooled liquids can be tentatively based on the assumption that any liquid property Q depends on the pressure P, the temperature T and some internal variable x that describes the configurational state of the liquid, i.e.

$$Q = Q(P, T, x) \tag{1}$$

In particular, for the Gibbs energy we have

$$G = G(P, T, x) \tag{2}$$

Applying the equilibrium condition for a given P and T,

$$(\partial G/\partial x)_{P,T} = 0 \tag{3}$$

we obtain an expression for the equilibrium value of x,

$$x = x_{\text{eq}}(P, T) \tag{4}$$

As expected, the equilibrium property will thus depend on P and T only.

$$Q_{\text{eq}} = Q(P, T, x_{\text{eq}}(P, T)) = Q_{\text{eq}}(P, T) \tag{5}$$

It thus follows that the variation in the property with P and T will consist of two terms, i.e.

$$\left(\frac{\partial Q_{\text{eq}}}{\partial P}\right)_T = \left(\frac{\partial Q}{\partial P}\right)_{T,x} + \left(\frac{\partial Q}{\partial x}\right)_{P,T}\left(\frac{\partial x}{\partial P}\right)_T \tag{6}$$

and

$$\left(\frac{\partial Q_{\text{eq}}}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_{P,x} + \left(\frac{\partial Q}{\partial x}\right)_{P,T}\left(\frac{\partial x}{\partial T}\right)_P \tag{7}$$

The second term in both equations depends on the structural relaxation because x, i.e. the configurational state, must change in order to maintain the equilibrium as P or T is changed. When the experimental time scale becomes much shorter than the relaxation time this term "freezes in" and only the first term is observed below T_g. It will thus seem as if the property changes almost discontinuously at T_g. The change in heat capacity, for example, can be calculated by identifying Q with the enthalpy H and evaluating ΔC_p at T_g from the last term in Eq. (7). On the other hand, it is important to notice that there will be no change in properties which are related to the first derivatives of the Gibbs energy, i.e. entropy, enthalpy and volume. This is clearly seen by identifying Q with G and observing that above the glass transition the equilibrium condition $(\partial G/\partial x)_{P,T} = 0$ requires that the second term in Eqs (6) and (7) is always zero. The first order derivatives of the Gibbs energy, i.e. S, H and V, thus vary continuously over the glass transition. This is a characteristic feature of a second-order transition and has lead numerous investigators to apply thermodynamics of second-order transitions to the glass transition. This will be discussed in more detail in the next section.

3 INFLUENCE OF PRESSURE ON THE GLASS TRANSITION

For a second-order phase transition the effect of pressure on the transition temperature T_c is given by the so-called Ehrenfest relations, i.e.

$$\frac{dT_c}{dP} = \frac{\Delta\kappa}{\Delta\alpha} \tag{8}$$

$$\frac{dT_c}{dP} = TV\frac{\Delta\alpha}{\Delta C_p} \tag{9}$$

where $\Delta\kappa$, $\Delta\alpha$ and ΔC_p are the differences in compressibility, thermal expansion and heat capacity above and below T_c. Combining the two equations we obtain

$$\frac{\Delta\kappa}{\Delta\alpha} = TV\frac{\Delta\alpha}{\Delta C_p} \tag{10}$$

These relations are applicable, for example, to the onset of long-range magnetic ordering at the Curie temperature in a ferromagnetic material. The validity of the Ehrenfest relations in connection with the glass transition has been investigated for various materials by several authors, see for example Davies and Jones[2] and Goldstein[3].

Before we discuss the outcome of these investigations it should be emphasized again that the glass transition is a relaxation phenomenon and its pressure dependence should thus be related to the pressure dependence of the kinetic properties of the liquid. Let us assume that the pressure and temperature dependence of the relaxation time is known, i.e. the function $\tau(P, T)$ is known. If the glass transition occurs when the relaxation time τ reaches a critical value τ_c we can calculate T_g for a given pressure P by solving the equation

$$\tau(P, T) = \tau_c \tag{11}$$

The pressure dependence is thus obtained as

$$\frac{dT_c}{dP} = -\frac{(\partial\tau/\partial P)_T}{(\partial\tau/\partial T)_P} \tag{12}$$

If the relaxation time can be expressed as a function of one single internal variable x which has a well defined equilibrium value for each combination of P and T, i.e.

$$x = x_{\text{eq}}(P, T) \tag{13}$$

then we may as well say that the glass transition occurs at a critical x value and rather than Eq. (11) we can write

$$\frac{dT_c}{dP} = -\frac{(\partial x/\partial P)_T}{(\partial x/\partial T)_P} \tag{14}$$

It can be shown that this result leads to the Ehrenfest relations provided that the Gibbs energy depends on only one internal variable. It should also be mentioned that Prigogine and Defay[4] have shown that Eq. (10) must hold if all configurational changes can be characterized by a single internal variable. Their derivation does not make use of any assumption of a second order transition.

The experimental information[3] shows that Eq. (9) is fairly well obeyed for many glass-forming liquids but by no means for all. On the other hand Eq. (8) usually predicts a much stronger pressure effect than observed. Of course, this furthermore implies that the Prigogine–Defay relation, i.e. Eq. (10), is not obeyed. However, it should be emphasized that this information has been taken from non metallic glass-forming substances. So far there seems to be no information available for metallic glasses.

For all the tested cases it is thus evident that the configurational changes, when pressure is applied, cannot be satisfactorily represented by a single internal variable. In this context it is appropriate to mention the work by Roe[5] who presented quite a general mathematical treatment of multiple-variable configurational changes. Earlier Goldstein[3] and Gee[6] had suggested that the experimental fact, that the relation 9 is usually obeyed but 8 is not, implies that the glasses formed at high pressures have approximately the same frozen in configurational enthalpy and entropy as the low-pressure glasses but are denser. The enthalpy and the entropy of a glass would thus be independent of whether its glass transition occured under pressure or not. However, the experimental fact is that the density will be higher if pressure is applied during the glass transition. This immediately leads to two important conclusions. The first one is that the glass transition does not occur at a certain volume but may occur at a certain configurational entropy or enthalpy, i.e. the relaxation time may depend on entropy or enthalpy rather than the volume. The second one is that a glass cannot be characterized satisfactorily by one internal variable only, because it is possible to change the volume without changing the enthalpy and entropy at the same time.

In the present paper we intend to model the Gibbs energy of a liquid as a function of temperature by means of one internal variable. In view of the above discussion it must be emphasized that such a model is not capable of representing the pressure dependence of Gibbs energy. In order to cover the pressure dependence we would need at least one more internal variable which would contribute to the volume to a larger degree than to the enthalpy and entropy. We will not discuss that matter further in the present report, but simply accept that the present approach is intended to model the behaviour of glasses at low pressures.

4 THERMODYNAMIC MODEL

It has been argued, see for example Refs. 7 and 8, that the structure of a liquid metal can be described in terms of defects being introduced into the glassy structure on heating. Under the assumptions that, a) a single kind of defect is considered, b) its enthalpy of formation ΔH_d per mole is constant, c) each defect is connected to a particular atom and d) the defects are distributed at random, then the Gibbs energy would vary with the number of defects according to the following expression, where x is the fraction of atoms having a defect,

$$\Delta G = G - G^\circ = x\Delta H_d + RT\{x \ln x + (1 - x)\ln(1 - x)\} \quad (15)$$

G° is the Gibbs energy of a defect-free system. The equilibrium number of defects is found by looking for the minimum in G. By solving

$$\partial \Delta G/\partial x = 0 \quad (16)$$

we obtain the equilibrium fraction of atoms having a defect

$$x = \frac{e^{-\Delta H_d/RT}}{1 + e^{-\Delta H_d/RT}} \quad (17)$$

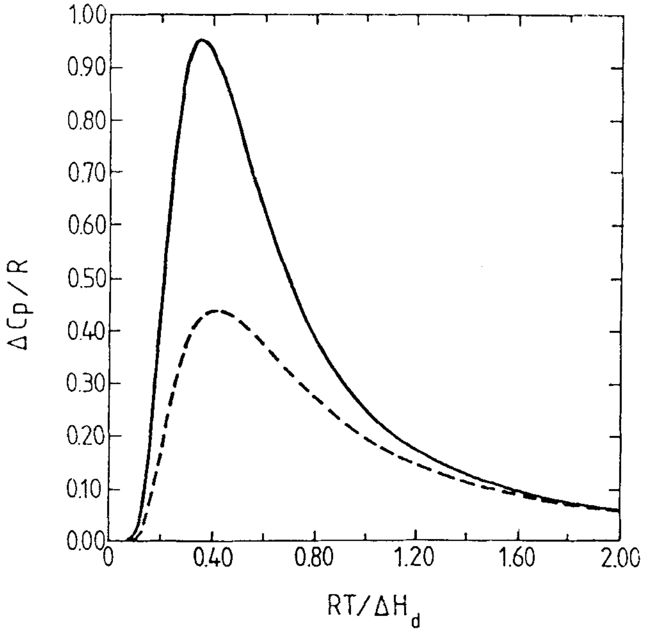

Figure 2 Calculated variation in heat capacity due to defects. Dashed line is calculated assuming that there is no extra entropy connected with the defects. Solid line is calculated assuming an extra entropy of R per mole of defects.

The contributions to the entropy and heat capacity due to the defects are obtained as

$$\Delta S = \partial \Delta G/\partial T = -R\{x \ln x + (1-x)\ln(1-x)\} \tag{18}$$

$$\Delta C_p = -T\partial^2 \Delta G/\partial T^2 = R\left(\frac{\Delta H_d}{RT}\right)^2 \frac{e^{-\Delta H_d/RT}}{(1+e^{-\Delta H_d/RT})^2} \tag{19}$$

These expressions or similar ones have been derived many times[7,8]. It must be emphasized that in this type of model the entropy contribution due to the defects only depends on their amount and that contribution would also exist in a non-equilibrium liquid, i.e. a glass where a certain x value is fixed by freezing. However, the contribution to the heat capacity from the defects comes entirely from the variation of x with temperature and for a glass with a constant x we would have $\Delta C_P = 0$.

The dashed line in Figure 2, shows how Eq. (19) predicts C_P to vary with temperature. It is evident that it rises too slowly to its maximum to be suitable for modeling the transformation from a glass to a liquid.

The model can be modified by assuming that the formation of a defect is not only connected with an increase in enthalpy but also an extra increase in entropy. An attempt to model such an effect may be based upon the arbitrary assumption that a state, where each atom has a defect, would have an extra entropy R relative to the state free of defects. Formally this modification of the model can be accomplished as follows

$$G - G^\circ = x(\Delta H_d - RT) + RT\{x \ln x + (1-x)\ln(1-x)\} \tag{20}$$

$$x = \frac{e^{1-\Delta H_d/RT}}{1+e^{1-\Delta H_d/RT}} \tag{21}$$

$$\Delta S = xR - R\{x \ln x + (1-x)\ln(1-x)\} \tag{22}$$

$$\Delta C_P = R\left(\frac{\Delta H_d}{RT}\right)^2 \frac{e^{1-\Delta H_d/RT}}{(1+e^{1-\Delta H_d/RT})^2} \tag{23}$$

We will now discuss some implications of the present model. Although the glass-transition temperature T_g actually depends on the cooling rate we shall make the simplifying assumption that it occurs whenever a certain defect concentration is reached. If the relaxation time is a function of the defect concentration x only, we may equally well say that the glass transition occurs when the relaxation time reaches a critical value.

Figure 3 shows how the changes in entropy and Gibbs energy, due to the postulated defects, vary with temperature. We shall now discuss the

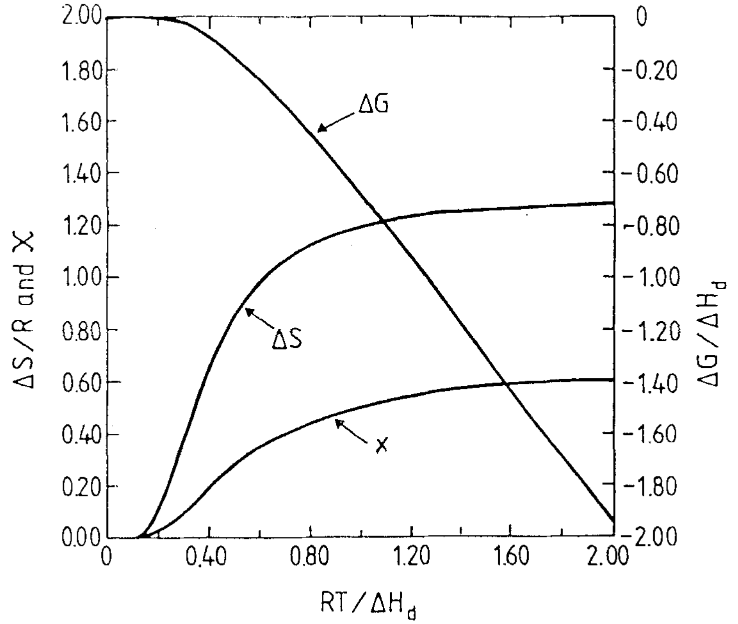

Figure 3 Calculated variation with temperature of Gibbs energy, entropy due to the defects and the defect content *x*.

implications of a model calculation based on the assumption that the glass transition occurs when 15% of the atoms have a defect. From Eq. (21) we can then obtain the corresponding temperature, normalized to ΔH_d, as $RT/\Delta H_d = 0.37$. By accepting the popular rule of thumb that the glass transition scales with the melting point T_m of a stable crystalline phase according to $T_g \approx T_m/3$ we then immediately have $RT_m \approx \Delta H_d$, i.e. the melting point is located at $RT/\Delta H_d \approx 1$. The entropy curve gives a value $\Delta S = 1.2R$ at that temperature and that would be the melting entropy if the crystalline and perfectly glassy states have the same entropy. That seems to be a reasonable value in comparison with Richard's rule which gives a value of about R.

At the assumed melting point of $RT/\Delta H_d = 1$ we can read the value $\Delta G = -0.7\Delta H_d$. We may thus conclude that a melting temperature $3T_g$ will occur if the difference in enthalpy at the absolute zero between the perfectly glassy state and crystalline state is $0.7\Delta H_d$. The melting point will be higher than $3T_g$ if the enthalpy difference at absolute zero is larger. It will be lower than $3T_g$ if the enthalpy difference is lower. Of course, these conclusions hold only if there are no other factors contributing to the Gibbs energy difference and if the formation of one mole of defects gives an extra entropy increase of R. Admittedly, the model defined by Eq. (20) has not yet been put on a clear physical basis. In the next section R in the term RT will be related to the so-called communal entropy.

5 COMPARISON BETWEEN GLASS TRANSITION IN METALS AND OTHER LIQUIDS AND THE PHYSICAL NATURE OF POSTULATED DEFECTS

5.1 General Characteristics

The increase of heat capacity with increased supercooling is a characteristic feature of liquid metals. In the present report it has been modeled by introducing a single kind of defect. An examination of other glass-forming liquids reveals that this is by no means a universal behaviour. On the contrary, it may even be an exception observed only for metals. An organic liquid like glycerol has a comparatively constant ΔC_p below T_m and at T_g it decreases more or less discontinuously to a very low value[9]. The behaviour of polymers[10] and inorganic glasses like B_2O_3[11] and silicate glasses[12] seems similar, although very pure SiO_2 glasses have a peculiar behaviour which will be discussed later.

5.2 Physical Nature of Defects

For many metals the difference in heat capacity between liquid and solid is small at the melting point, although the high melting transition metals seem to show a much more complex behaviour, see Hultgren's compilation[13]. Anyway, the heat capacity of the liquid metal at the melting point is always above $3R$. A value slightly above $3R$ is expected classically if each atom has three vibrational degrees of freedom. We may thus conclude that the majority of the atoms in a metallic liquid are vibrating around their equilibrium positions. This corresponds to the so-called cage picture, proposed by Cohen and Turnbull[14] and recently observed in molecular dynamics simulations[15], where each atom is allowed to vibrate within a small cage formed by its nearest neighbors. So far we have not discussed the physical nature of the defects introduced in Section 4. In that section we suggested that the defects should be connected not only with an increase in enthalpy but also an extra increase in entropy which we chose rather arbitrarily equal to the gas constant R. The contribution to the heat capacity was derived from the configurational changes only, i.e. from the changing number of defects. At the melting point of a metal the change is small and the configurational contribution to the heat capacity will be small.

This is manifested in the fact that the liquid and crystalline metals have roughly the same heat capacity in the temperature range around the melting point. By the same token glassy and crystalline metals have approximately the same heat capacity because the configurational changes of the glass are frozen in.

It has been suggested[16] that the entropy of fusion of metals is caused mainly by the transition from localized to non-localized atoms. When all atoms are in the completely non-localized state they share the free volume and there will be an extra entropy, the so-called communal entropy[17] which is exactly R, compared to when each atom is confined to move within its own cell. The communal entropy concept seems natural when treating dilute gases but its meaning is somewhat more difficult to visualize in a dense liquid, especially when we know that most of the atoms are vibrating in a metallic liquid. Anyhow, the concept has some merits and we can regard it as a justification for associating the entropy R with the postulated defects. *We can then interpret the configurational changes on cooling as a gradual transition from non-localized to localized atoms.*

It is evident that a liquid with complex molecular constituents in addition to loss of communal entropy can exhibit a similar loss of other types of degrees of freedom. For example, Prigogine and Defay[4] have suggested that the configurational changes of glycerol on cooling are caused by the gradual loss in rotational degrees of freedom. We can make a crude test of this hypothesis by introducing a second kind of defect in our model. According to Guggenheim[18] an additional rotational degree of freedom will contribute with

$$\Delta G_r = RT \ln\left(\frac{s\theta_r^{3/2}}{\pi^{3/2} T^{3/2}}\right) \tag{24}$$

to the Gibbs energy per mole of molecules, θ_r is a characteristic temperature and s a symmetry number. The contribution to the heat capacity is $(3/2)R$. Assuming three rotational degrees of freedom per molecule we can model this by adding to Eq. (20) the following expression

$$3y(\Delta U_r + \Delta G_r) + 3RT\{y \ln y + (1-y)\ln(1-y)\} \tag{25}$$

where y is the fraction of glycerol molecules that can rotate, and ΔU_r is the energy required at absolute zero in order to allow for the rotation. The two parameters ΔU_r and $s\theta_r^{3/2}$ can now be adjusted in order to fit the experimental information on ΔC_p and ΔS_f. It must be emphasized that this is not intended as a rigorous thermodynamic model for glycerol but only as a crude way of testing the suggestion by Prigogine

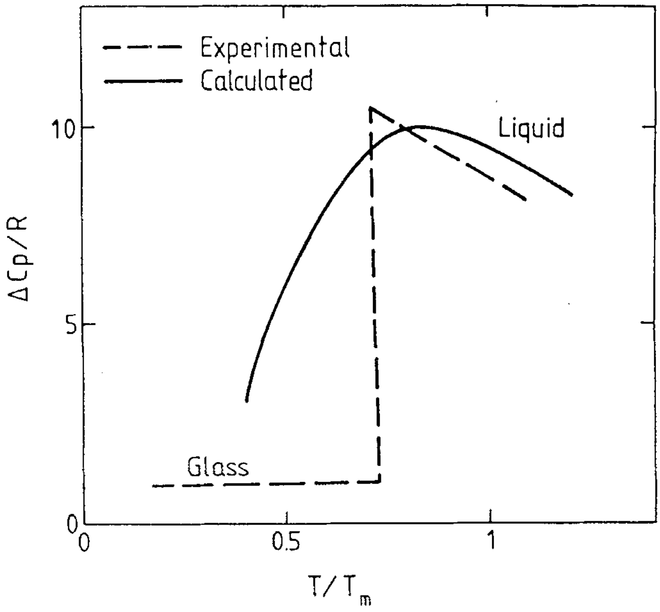

Figure 4 Variation with temperature of difference in heat capacity between liquid and solid glycerol. Solid line is calculated from present model. Dashed line is experimental data, Ref. 4.

and Defay. The evaluation, which is discussed in the next section, shows that the model yields a reasonable result and a comparison between calculated and experimental ΔC_p is given in Figure 4.

5.3 Anomalous Behaviour of High-Purity SiO_2

High-purity liquid SiO_2 has a thermodynamic behaviour which is quite different from normal liquid silicate glasses and other glass-forming liquids. This is shown in Figure 5, depicting the difference in heat capacity ΔC_p between the vitreous phase and cristobalite[19]. As can be seen there is a continuous increase in ΔC_p with temperature. The glass transition can be varied within several hundred kelvins by varying the cooling rate. In practice the temperature where the viscosity is 10^{13} poise is referred to as the glass point and for pure SiO_2 that value occurs at 1190°C[20].

The anomalous behaviour of ΔC_p for SiO_2 is also revealed in the very low entropy of fusion for cristobalite, namely $0.5R$[19]. It is thus quite evident that SiO_2 on melting forms a liquid which has not as high entropy as one would normally expect. This is possible if the melting

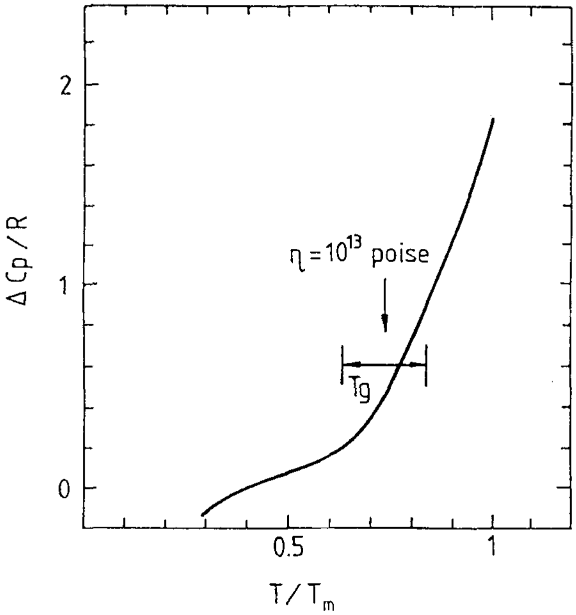

Figure 5 Variation with temperature of difference in heat capacity between liquid and solid SiO_2 (cristobalite). From Pankratz[19].

occurs close to the thermodynamic glass transition. According to section 1 this will happen if the difference in enthalpy between the amorphous and crystalline phases is small at absolute zero. It is thus suggested that ΔC_p of SiO_2 would increase strongly with temperature above the melting point and pass through a maximum at some temperature and then decrease or at least level out. The thermodynamic behaviour of SiO_2 would then be similar to that of other glass-forming liquids, e.g. glycerol, and the main difference would be that SiO_2 has a very low melting point compared to its glass transition. Unfortunately, we have not been able to find any information regarding the high-temperature behaviour of pure SiO_2.

6 APPLICATION OF THERMODYNAMIC MODEL TO EXPERIMENTAL DATA

6.1 Pure Sn

In order to test the ability of the model to represent thermodynamic data it will now be applied to a liquid metal, pure Sn. One reason for choosing Sn for the comparison is that the heat capacity for liquid Sn has been measured for rather large undercoolings[21]. These data together with data from Hultgren's compilation[13] were analyzed by means of the computer program for optimization of thermodynamic model parameters developed by Jansson[22] and the parameter ΔH_d was evaluated. It was soon found that in order to fit the experimental data satisfactorily a more complicated temperature dependence than a constant entropy had to be introduced in the Gibbs energy for forming one mole of defects. By allowing for a general temperature dependence of the kind represented by the series expansion

$$\Delta G_d = a - RT + cT \ln T + dT^2 \ldots \tag{26}$$

we obtain instead of Eq. (20)

$$G - G^\circ = x\Delta G_d + RT\{x \ln x + (1 - x) \ln(1 - x)\} \tag{27}$$

$$x = \frac{e^{-\Delta G_d/RT}}{1 + e^{-\Delta G_d/RT}} \tag{28}$$

This correction is not unexpected and without trying to give it a physical interpretation we can conclude that it makes the communal entropy less important.

The ideal amorphous phase was approximated as having the same entropy and heat capacity as β Sn, i.e.

$$G^\circ_{\mathrm{Sn}} = G^\beta_{\mathrm{Sn}} + A \tag{29}$$

where A is a constant which can be identified with the enthalpy of formation of the ideal glass from β at absolute zero.

The result of the evaluation is shown in Figure 6. As a comparison a curve calculated from a recent assessment by Jönsson and Ågren[23] is included. The parameters needed to calculate the various thermodynamic quantities are given in the appendix.

6.2 Glycerol

In order to test if the behaviour of a more complex molecular liquid could be understood by introducing an additional type of defect glycerol was chosen. The extra type of defect, was associated with the occurrence of rotations of the molecules. Three rotational degrees of freedom per molecule were assumed and the following expression was used for the Gibbs energy per mole of molecules relative to an ideal amorphous solid.

$$\begin{aligned} G - G^\circ = {} & x(\Delta H_d - RT) + RT\{x \ln x + (1 - x) \ln(1 - x)\} \\ & + 3y(a + bT - (3/2)RT \ln T) + 3RT\{y \ln y \\ & + (1 - y) \ln(1 - y)\} \end{aligned} \tag{30}$$

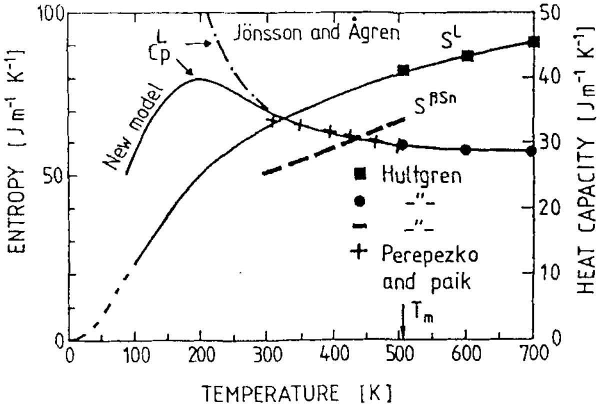

Figure 6 Heat capacity, and entropy of liquid Sn, and entropy of solid Sn according to different sources.

As previously, x is the fraction of molecules having the first kind of defect and y is the fraction of atoms having the second type. It should be mentioned that it has been assumed that all the three rotational degrees of freedom are equivalent. The equilibrium values of x and y are obtained by solving

$$\partial \Delta G / \partial x = 0 \tag{31}$$

$$\partial \Delta G / \partial y = 0 \tag{32}$$

ΔH_d, a and b are adjustable parameters to be evaluated from the experimental data taken from Prigogine and Defay[4] and from Owen[24]. The result is shown in Figure 4 and has already been discussed. The parameters are given in the appendix.

7 SUMMARY

It has been shown that the most characteristic thermodynamic features of supercooled liquids and their glass transition can be interpreted by means of a simple model. The gradual decrease in entropy on cooling, by which the entropy of the liquid approaches that of a crystalline solid, has been modeled by means of defects, connected with the individual atoms. The defects are introduced to an "ideal" amorphous solid on heating.

It has further been suggested that the increase in defect content yields an extra increase in entropy. At first a tentative value $\Delta S = R$, the gas constant, per mole of defects was suggested. It was then found that a more general series expansion is needed in order to fit experimental information available for real substances.

We have not discussed the properties of the hypothetical ideal amorphous phase, but simply assumed that it has an entropy and a heat capacity similar to that of a crystalline phase. It was further suggested that the anomalous behaviour of liquid high-purity SiO_2 is caused by the fact that the difference in enthalpy between crystalline and ideal amorphous phase at absolute zero relative to the enthalpy of formation of the defects is unusually small yielding an unusually low melting point compared to the glass transition.

Physical interpretations of the new model have been discussed and one type of defect is connected with the so-called communal entropy for the case of simple metals. For more complex molecular liquids additional types of defects have been suggested.

Acknowledgements

The author wishes to express his gratitude to Professor Mats Hillert for many stimulating discussions and his continuous encouragement during the course of this work. The author also would like to thank Mr. Armando Fernandez Guillermet for many valuable suggestions and for his continuous interest in the subject.

This is a part of a project sponsored by the Swedish Board for Technical Development.

References

1. W. Kauzmann. *Chem. Rev.*, **43** 219 (1948).
2. R. O. Davies and G. O. Jones. *Advances in Physics*, **2**, 370 (1953).
3. M. Goldstein. *J. Chem. Phys.*, **39**, 3369 (1963).
4. I. Prigogine and R. Defay. *Chemical Thermodynamics* (Longmans Green, London, 1954), 297.
5. R.-J. Roe. *J. Appl. Phys.*, **48**, 4085 (1977).
6. G. Gee. *Contemp. Phys.*, **11**, 313 (1970).
7. P. Ramachandrarao, B. Cantor and R. W. Cahn. *J. Mater. Sci.*, **12**, 2488 (1977)
8. M. Hillert, in *Rapidly Solidified Amorphous and Crystalline Alloys*, eds. B. H. Kear, B. C. Giessen and M. Cohen, (Elsevier, 1982).
9. Ref. 4, p. 295.
10. J. M. O'Reilly and F. E. Karasz, in *Transitions and Relaxations in Polymers*, Ed. R. F. Boyer, J. Polymer Sci., part C, no. 14 (1966), p. 49.
11. F. D. Richardson. *Physical Chemistry of Melts in Metallurgy* vol. 1 (Academic Press, London, 1974) 113.
12. C. R. Bacon: Am. J. Sci., **277**, 109 (1977).
13. R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley and D. D. Wagman. Selected values of the thermodynamic properties of the elements, ASM 1973, p. 473.
14. M. H. Cohen and D. Turnbull. *J. Chem. Phys.*, **31** 1164 (1959).
15. F. Yonezawa and M. Kimura. *J. Non-Cryst. Solids*, **61** and **62**, 761 (1984).
16. R. Fowler and E. A. Guggenheim. *Statistical Thermodynamics*, (Cambridge, 1952).
17. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird. *Molecular theory of liquids and gases*, (John Wiley & Sons Inc., New York, 1954), p. 274.
18. E. A. Guggenheim. Thermodynamics (Elsevier Science Publishers, B.V., 1967).

19. L. B. Pankratz. Thermodynamic Properties of Elements and Oxides, US Department of Interior, Bureau of Mines, Bulletin 672, 1982.
20. G. Hetherington, K. H. Jack and J. C. Kennedy. *Physics and Chemistry of Glasses*, **5**, 130 (1964).
21. J. H. Perepezko and J. S. Paik. *J. Non-Cryst. Solids*, **61** and **62**, 113 (1984).
22. B. Jansson. Thesis 1984, Div. Phys. Metall., Royal Inst. Techn. S-100 44 Stockholm, Sweden.
23. B. Jönsson and J. Ågren. *Metall. Trans. A.*, **17A**, 607 (1986).
24. A. E. Owen, in *Amorphous Solids and the Liquid State*, Eds. N. H. March, R. A. Street and M. Tosi (Plenum Press, New York) 395.

Appendix Optimized parameters (Jmol^{-1})

Crystalline β Sn

$$G^{\beta}_{\mathrm{Sn}} - H^{\beta\mathrm{Sn}}_{298} = -7241.9 + 98.808T - 21.592T \ln T - 0.0090471T^2$$

(from Ref. 22)

Liquid Sn

$$G_{\mathrm{Sn}} - G^{\circ}_{\mathrm{Sn}} = x\Delta G_d + RT\{x \ln x + (1 - x)\ln(1 - x)\}$$

where

$$G^{\circ}_{\mathrm{Sn}} - G^{\beta}_{\mathrm{Sn}} = 4225$$

$$\Delta G_d = 5162 - RT - 1.4548T \ln T + 4.3434\ 10^{-3}T^2 + 1.463097\ 10^{-6}T^3$$

Liquid glycerol

$$G - G^{\circ} = x(\Delta H_d - RT) + RT\{x \ln x + (1 - x)\ln(1 - x)\} + 3y(a + bT - (3/2)RT \ln T) + 3RT\{y \ln y + (1 - y)\ln(1 - y)\}$$

where

$$\Delta H_d = 5025$$

$$a = 3179$$

$$b = 57.57$$