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SOME THERMODYNAMIC ASPECTS OF THE GLASSY STATE

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ABSTRACT

The classification, identification and stability of a non-crystalline material as a glass is discussed. General thermodynamic and compositional consideration are presented. Thermal characterization of vitrification processes are specified. A survey is given of the theoretical modelling of thermodynamic descriptions of glass transformation. The thermodynamic functions of undercooled liquids during vitrification are explained.

INTRODUCTION

A traditional definition of glasses involves the natural cooling (about 10^{-2} K s^{-1}) of melts, usually silicates. If other substances are subjected to sufficiently rapid cooling, for example water cooling of chalcogenides (10^2 K s^{-1}), melt spinning of metallic alloys (10^6 K s^{-1}) or even vapour deposition of various organic (alcohol) or inorganic (water) compounds (10^{10} K s^{-1}), glass-like materials are similarly obtained, extending tremendously the amount of data on the formation of glass. Previously such studies mainly have been of academic interest but now find a wider use because of a growing number of practical applications. Such studies were previously often related to the field of the researcher's individual interest but they are now loosing their original character of academic curiosity because of a growing number of practical applications. The different kinds of glassy materials that have been studied extensively include ionic conductor inorganic salts, semiconductor chalcogenides, metallic alloys and various organic polymers. The study of glassy materials focuses on the structural, kinetic and thermodynamic aspects, the latter being the subject of this paper.

CLASSIFICATION, IDENTIFICATION AND STABILITY OF A NON-CRYSTALLINE MATERIAL AS A GLASS

A great variety of non-crystalline solids have recently been prepared by a number of distinct but unconventional methods. The methods employed include

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unusually extreme quenching of melts or vapours and/or electrodepositions, disintegrations, or use of high energies. A disordered distribution of atoms is obtained by freezing melts or as a result of other disordering processes involved in the amorphous material formation. The latter processes usually produce states that are poorly characterized as well as difficult to characterize. That is why non-crystalline solids of an identical composition obtained by various techniques, or by the same technique under different conditions, can differ considerably in their physicochemical properties. A more precise identification thus becomes difficult since certain parameters, like local cooling rate and associated gradients, topological and compositional short-range order, etc., cannot be specified exactly and/or directly. Thus, it is evident that different names are currently used to describe such materials.

Eckstein (ref.1) classifies *non-crystalline solids* as *vitroids* referring to organic and inorganic materials in the *vitreous state*, including *glasses* and *plastics*. According to Roy (ref.2) the concept of non-crystallinity (meaning *structurally disordered*) is considered hierarchially superior to the terms *glassy* and *amorphous*. (The latter is currently more popular to describe the newer types of semiconductor and metallic materials.) Many materials are considered amorphous if they do not exhibit an *experimentally detectable glass transformation point* which, however, can be hidden in the early process of crystallization catalyzed in such cases by excessively active sites or interfaces. A small number of vapour-deposited amorphous materials can even exhibit a pseudo glass transformation (relaxing to the state obtainable by cooling of the corresponding liquid to the same temperature) and then immediately crystallize. The specific class of non-crystalline solids, which we herewith signify by the term *glass*, is understood to be preparable in a more systematic and reproducible fashion compared to others, i.e, by *cooling melts at different quenching rates with the possibility of subsequent heating into the undercooled liquid state without overlapping crystallization* (refs.3,4).

Another problem is the stability definition of a glassy state. According to Suga and Seki (ref.5) the *glassy state is a thermodynamically unstable* one which can be assumed to be an *undercooled metastable state* at a certain instant of continuous cooling by the *glass transformation process* which is considered here as a *general property of all metastable phases*. Therefore, they (ref.5) recommended even further classification of general glasses into *glassy liquids*, *glassy liquid crystals* and *glassy crystals* formed by the *glass transformation of the respective metastable states of liquids* (melts) and *liquid and solid crystalline phases*. The state of a cooled material can be characterized thermodynamically with respect to its corresponding stable phase down to the *glass transformation temperature*, at which a state of internal equilibrium is lost, and even lower with some uncertainty due to the irreversible nature of the glass transformation phenomena. Very thin sections of usually spalt-cooled glasses are sometimes difficult to characterize precisely because of the extreme condition of quenching and the irreversibility associated with their formation. Some of them can even crystallize during reheating before any glass transformation phenomena are observed. However, they are not to be excluded from our somewhat strict classification of glasses, even though, the dividing line between glasses and less respectable amorphous solids is vague, particularly when compositions exhibiting or not exhibiting a glass transformation can overlap.

In recent literature, the glassy state is often called a metastable state which, however, contradicts the common thermodynamic point of view that the metastable state can exist in the stability region of the other neighbouring phase and into which the extrapolation of the Gibbs energy function is possible, i.e., in the vicinity of the first-order transitions, such as melting or crystallization, where a solid can be superheated or, more likely, a melt undercooled, see Fig.1. The glass transformation, however, assumes second-order-like transition, where each phase can exist only on its own stability side because there is a break in the second derivatives of the Gibbs energy (e.g. specific heat C_p) while its first derivative (e.g. entropy S) remains continuous. On the other hand, however, the physical appearance of a glassy solid looks more stable than that of an undercooled melt, the latter being more easily transformable to the nearest state of stable crystals by a slight action to surmount the energy barrier to nucleation. Hence, we come to the discussion of the term solids in terms of vitroids within the framework of rheology. This is because such a solid changes with time and observation time is involved in detecting the extent of change. Reiner (ref.6) introduced the Deborah number* expressing the ratio between the time of material relaxation and that of its observation (DN). Conveniently, we can demonstrate the instability of a glassy state using the textbook case of a variously positioned brick, cf. Fig.1. When a brick is standing on its edge (and/or lying in an unstable position on a very steep slope) its motion is determined by the high viscosity of the surrounding medium (or by a large coefficient of friction of the roughened surface, respectively). It follows that such a form of insta-

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* Prophetess Deborah's famous song after the victory over the Philistines includes the lines "The mountains flowed before the Lord". For illustration we can consider the relaxation time for gases to be in the order of 10^{-12} s, while for glasses within their region of glass transformation it is seconds, DN $\approx$ 1, and approaches 10^{10} s for stable crystals.

bility will also depend on external (procedural) parameters; and in contradiction to the distinct state of metastability, it can be set up in different levels (positions see Fig.1., dashed and dotted lines).

GENERAL THERMODYNAMIC AND COMPOSITIONAL CONSIDERATIONS

Let us thus investigate the behaviour of Gibbs energy in Fig.1. At the melting point the liquid and crystalline phases have an equal Gibbs energy but differ in enthalpy and entropy content. Upon cooling below the melting temperature and entropy of the undercooled liquid decreases more rapidly than that of the stable crystalline phase. Examining these different rates of the entropy loss, we can determine a point where the entire entropy of melting would be diminished, resulting in the entropy of both phases in question becoming identical at the temperature T_0, which Kauzmann (ref.7.) called the pseudo-critical temperature, still above absolute zero. Such a critical trend for the entropy of an undercooled liquid is not always appreciated enough because of the prior intersection by the liquid vitrification where the heat capacity of the liquid changes abruptly to a value close to that of the corresponding crystalline phase, thus preserving a residual entropy characteristic for the glassy state alone. However, an unsolved question remains as to what would happen if the isoentropy temperature of the so-called ideal glass transformation is nevertheless attained by infinitesimally slowing the cooling rate and thereby avoiding irreversible freeze-in from occurring. Although it is more a game of imagination, we have to consider the possible existence of some kind of higher (presumably second) order transition. In this transition the heat capacity of the undercooled liquid changes under the condition of the internal equilibrium to a value similar to that of the congruous stable crystal. The thermodynamic properties of an ideal glass structure thus become very similar to those of the crystalline state (ref.8). The apparent formation of such an equilibrium glassy state can even be suggested as a "fourth state of matter", a promising theme for theoreticians to discuss further, although some mechanical instability arguments imply its occurrence (ref.9).

The viscosity of a liquid can be regarded as a reflection of the relation between the thermal energy available at a given temperature and the strength of forces pulling species together and restricting their positions to a given volume within which any molecular rearrangements can occur. The possible rate of these rearrangements rapidly decreases with decreasing volume within which the species are packed. The volume is determined by the strength of the attractive forces and, in turn, this strength is reflected in the values of the characteristic temperatures of the boiling, melting and critical points. According to Angell (ref.10) the basic reason for the "failure" of a liquid to

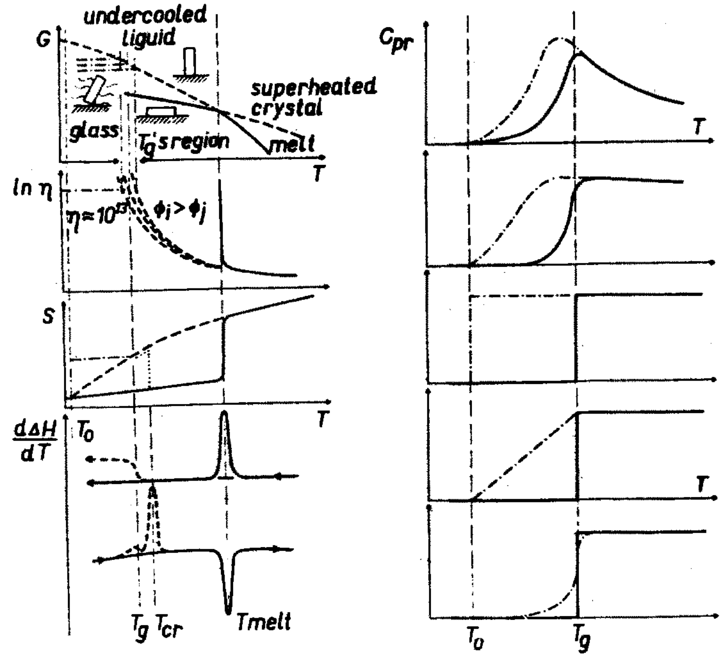

FIG.1. Left panel: A dependence of the system Gibbs energy, G, versus the temperature, T, indicating the characteristic regions of the existence of stable (melt, crystal - full line), metastable (undercooled liquid, superheated crystal - dashed line) and unstable (glass - dashed and dotted line) phases. For comparison, the second plot, the viscosity, shows typical curves representing the action of a system under the different cooling rates with the glass transformation interval, T_g, marked while the yet lower plot shows the behaviour of the system entropy, S, down to the pseudocritical point, T_0. The bottom part corresponds to the derivative of the enthalpy change, ΔH, temperature dependence (related to the associated phase diagram by the lever rule) whose typical shape is similar to that of DSC (and also DTA) curves. The arrows specify the cooling and reheating modes and the temperature T_{cr} indicates the point of metastable crystallization (the dotted line in the S vs T diagram). Right panel: A hypothetical temperature dependence of the reduced heat capacity Δc_{pr} (= $\Delta c_0 / \Delta s$) characteristic for glass formation of metallic alloys and of inorganic oxides and organic polymer (upper two curves) in comparison with the approximations noted in the text: stepwise, linearly deceasing and diffuse-lambda shaped (lower three curves) - suitable for extrapolating the behaviour of a fictive undercooled glass-forming melt.

crystallize can be attributed to problems in the molecular rearrangements, not so much in the liquid state but predominantly in the crystalline state during ordering - the higher the crystalline symmetry of a phase to be formed the better the glass-forming ability of its mother melt that can be anticipated. The factors determining the probability of a given substance to freeze-in as a glass are then related to the problems of finding a suitable solution in the three-dimensional long-range ordering of the constituent species. The probability of glass formation increases with the formation of liquid mixtures in which the Gibbs energy of the non-crystalline arrangement is decreased while that for the corresponding crystalline phase to precipitate remains unchanged. The more strongly the mixture of components interact, the more rapidly the freezing point of the solvent is depressed and the viscosity increased thus slowing the possible nucleation and the consequent growth of nuclei. The component interaction, however, should not be so strong as to generate a new competing crystallizing phase which would strongly decrease the glass-forming ability of the mother melt. Furthermore, the more stable the crystal is, the higher the resultant melting point which simultaneously produces a less viscous melt and increases the probability of its crystallization.It is well-known that the most easily vitrificable metallic alloys exhibit strong solvent-solute interactions resulting in low eutectic temperatures but in the vicinity of which the existence of any stable binary or ternary compound is not exhibited. On reheating such a glassy composition, a metastable phase is likely to be produced, but this form always decomposes later to a combination of stable components. In this light, the theories describing the stable glass-forming regions in multicomponent systems can be regarded as dealing with the lowering of the Gibbs energy of a given solid phase on dissolution of solutes as a function of solute character (ref.10). The famous Zachariesen rules (refs.11,12), originally derived for oxide systems, may thus be understood as rules for predicting low melting points relative to the forces acting between the species, although many of the new inorganic glasses violate these predictions. Hang et al. (ref.12) recently discussed the prediction of glass formation and devitrification from the point of view of the thermodynamics of regular solutions of complex oxide systems by examining their immiscibility behaviour. A quasichemical model for solutions was also used by Chen (ref.13) who evaluated the alloy formation of transition metal-based glasses based on the binding energies of constituents in relation to changes in glass-formation temperature.

CHARACTERIZATION OF THE VITRIFICATION PROCESS

By measuring a macroscopic property of a liquid during its continuous cooling we can distinguish certain characteristic points and their corresponding temperatures which, however, are related to the procedural parameters of the quenching technique employed (refs.4,15). Positioning of these points can be specified on the basis of thermoanalytical investigations of various physical properties, such as the heat content (by thermometric-DTA and DCC and heat compensation-DSC-measurements), viscosity, elasticity, penetration and thermal expansion (by thermomechanometry and thermodilatometry), electric resistance, coefficient of resistance and dielectricity, thermoelectric power, Hall effect (by thermoelectrometry) and other structural studies (Mössbauer effect, X-ray diffraction, photoemission, etc.). One of the most informative plots of enthalpy change with temperature, resembling common recordings from DTA and/or DSC (ref.4), is presented in Fig.1. A practical way to resolve the freeze-in entropy from the plot of c_p vs ln T was shown by Angell and Rao (ref.16) termed isoentropy glassy state determination.

It is evident that a correlation between the characteristic temperatures and glass-forming ability has been anticipated. A simple relation between T_g and T_{melt} has already been suggested on a theoretical basis by Kauzmann (ref. 7), assuming T_g to have a behaviour similar to T_0. Then a reduced glass transformation temperature T_{gr} was introduced so that $T_{gr} = T_g/T_m$ and values of about 2/3 are attained. Sakka and Mackenzie (ref.17) examined in detail its general validity for a great variety of glasses and found it reasonable. In addition, they reformulated T_{gr} on the basis of the combination of two formulae relating T_{melt} with the thermal expansion coefficient and T_g with the fractional free volume of glass approaching, however, the value of 1/2. The meaning of reduced temperatures in the fast developing field of metallic glasses was extensively dealt with by Davies (ref.18). Angell (refs.19,20) tried to determine the extent of T_{gr} values on the basis of the extrapolated T^0 data evaluated by the Vogel-Tamman-Fulcher equation for viscosity $\mu = \mu^0 \exp k_\mu/(T-T\mu)$. T_μ, which has the unit of temperature, renders the viscosity formally infinite when it equals the temperature of the entire measurements, which suggests a certain rheological limit to the liquidus region from the thermodynamic ($T_\mu = T_0$) and kinetic ($T_\mu = T_g$) points of view (ref.19). This showed, however, that an apparently more appropriate ratio, T^0/T_{melt}, fails to follow the 'two-thirds' and even 'one-half' rules. Hrubý (ref.21) attempted to give a more practical significance to glass-forming tendencies using the easily available ratio given by $K_{gl} = (T_{cr} - T_g) / (T_{melt} - T_{cr})$, see Fig.1, and tested it on various types of chalcogenide glasses. As with T_{gr} the greater the value of K_{gl}, the better the glass-forming ability is approached. In this context, an interesting feature of glass transformation should be emphasised again, viz. T_g is displaced to higher temperatures by an increase in the cooling rate which is also reflected in the experimental variability of T_{gr} and K_{gl} values discussed in more details by Grest and Cohen (ref.22) and Thornburg (ref.23), respectively. The meaning of the crystallization temperature T_{cr} as a material constant is dealt with by Takayma (ref.24).

Many modelistic approaches to understand the various features of vitrification have been described in the literature (ref.25). Free volume theory has laid emphasis on the concomitant decrease in volume and fluidity of glass-forming melts in the undercooled region. A recent extension of this model was made by Cohen and Grest (refs.22,27) in conjunction with the percolation concept to impute a first-order character in the glass transformation at $T < T_g$. Considering a real glass as microheterogeneous, glass transformation can be associated with the melting of clusters, recognizing thus the presence of an intermediate range of structures between the crystalline and non-crystalline states. Possible limitations of these models were discussed by Rao et al. (refs.3,25,27). Some other approaches can be briefly mentioned. Goldstein (ref.28) has suggested that the configurational state of an undercooled liquid can be described by an energy hypersurface of position and momentum coordinates and that T_g occurs when the system of particles gets trapped upon cooling into one of the many potential minima which are present on such a hypersurface. Jäckle (ref.29) has presented glass transformation as a transition from ergodic to non-ergodic behaviour and discussed the meaning of the residual entropy of a glass. Ngai (ref.30) advanced a unified model of low-frequency dissipation based on the dispersion approach. Edwards (ref.31) argued that the concepts in the theory of viscoelasticity offer a good basis for describing the polymeric types of glasses. The degrees of freedom can be separated by their relaxation times into those that relax faster than the quenching operation and those that are slower. Harris (ref.32) showed that a simple model of glass transformation can be described by the statistical mechanics of a set of non-interacting particles each of them being able to assume either of the two energy levels considered. Recognizing a parallel between metallic, chalcogenide glasses and native solid electrolytes Phillips (ref.33) related glass formation to directionless units and proposed possible disproportionation on a molecular scale as a dominant barrier to crystallization. Glass transformation itself is assumed to be a result of increasing cluster size where its surface/volume ration involved means that the cluster interior is ordered while the surface layer remains disordered.

THERMODYNAMICS OF THE GLASS TRANSFORMATION

Fundamental theoretical studies were made by DiMarzio and Gibbs (ref.34) and Adam and Gibbs (ref.35) showing that the sluggish relaxation is underscored by the existence of an equilibrium glassy state. Experimental glasses are perceived through their kinetic properties and one should be able to arrive at a consistent description of the glassy state from the phenomenological viewpoint.

The glass transformation bears some resemblance to the second-order phase transition, the latter, however, obeying Ehrenfest's relations $dP/dT = \Delta c_p/TV\Delta\alpha = \Delta\alpha/\Delta\mathcal{K}$, where P, V, α and $\mathcal{K}$ are the pressure, volume, volume expansion and compressibility, respectively. Due to the kinetic origin of glass transformation, this relationship is not fulfilled during most experiments and the degree of its irreversibility is described by the Prigogine and Defay factor π (refs.32-41).

$$\pi = T_g V_g \quad \Delta\alpha^2 / \Delta c_p \Delta\mathcal{K} \geq 1 \qquad (1)$$

Some atttempts to generalize such a description were made using internal variables ξ , and corresponding affinities A having the role of the generalized forces and fluxes. The concept of internal parameters was best described in the frequently cited study by Davies and Jones (ref.36). The essential difficulties arise, however, when we attempt to associate ξ with physically identificable quantities. Breuer and Rehage (ref.37) suggested that eq.(1) is valid only if $\partial\xi/\partial T = 0$ so that, for example,

$$\frac{dP}{dT} = \frac{\Delta c_p}{TV\Delta\alpha} - \frac{1}{\Delta\alpha}\left(\frac{\partial S}{\partial\xi}\right)_{T,P}\left(\frac{\partial\xi}{\partial T}\right)_g \qquad (2)$$

Similarly, Staverman (ref.38) attempted to define π on the basis of the partial derivatives according to the internal parameters in question. DiMarzio (ref.39) examined the above derivation and resolved that it leads to the equilibrium conditions $-dP/dT = \partial S/\partial\xi_i / \partial V/\partial\xi_i = \partial S/\partial\xi_j / \partial V/\partial\xi_j$ for all pairs of the order parameters i and j. Because π is always greater than one, he (ref.39) concluded that such a concept is not fully appropriate. Gupta and Moynihan (ref.40) proved the validity of the π ratio for the systems with multiple order parameters showing that eq.(2) must hold for each member of the set of order parameters not including the assumption (ref.34,39) that $\partial^2 G/\partial\xi_i\partial\xi_j = 0$ for $i \neq j$. Therefore, the systems for which only one order parameter is required to specify the state are trivial special cases because the order parameter, as the extensive thermodynamic variable, can be arbitrarily subdivided into subsets. If a single order parameter is sufficient to characterize the given glass, the rate of a selected property change $\dot{Z}_i$, given by $dZ_i/dt = (\partial Z_i/\partial\xi)_{T,P} \times (\partial\xi/\partial t)$, is proportional to another one $\dot{Z}_j$. If the rates of different property relaxation, however, are not proportional to each other, this means that more ξ are to be involved (ref.41). The practical aspects of the pressure effect on T_g was dealt with in refs. 42 and 43.

Following from the dissipation inequality, Christistensen (ref.44) provides a thermodynamic admissibility criterion for the glass transition temperature which is characterized as the base temperature at which, for a constrained sample with no volume change, the stress response to changes in temperature is instantaneous, with no explicit evidence of a memory effect (creep response). In this connection it is notable that the derivation mentioned above reveals a transitional behaviour when internal variables have a certain relationship.

When a glass is held at a temperature below T_g its structure changes slowly with time towards a certain equilibrium state characterizable by a fictitious temperature lying on the intersection of extrapolated states of glass and undercooled liquid, respectively. The temperature difference between the fictitious and the actual temperatures thus gives a measure of the departure of the material from equilibrium which, however, is true only when a single order parameter is involved. When the description requires multiple order parameters we need instead an adequate number of fictitious temperatures to achieve an equally detailed picture of its actual state. The problem and usefulness of the concept of fictitious temperatures was well developed by Moynihan et al. (refs.45-47). It should be noted, however, that the very important and extensively studied field of processes dynamics (refs.48-51) is not dealt with as it extends from kinetic theories on nucleation growth processes (refs.18-52) which is a special discipline of thermodynamics. Here, it is worth mentioning the illustrative use of hypothetical diagrams, either that of the enthalpy change versus temperature (ref.53), (cf.Fig.1), or that of the Gibbs energy versus the concentration (refs.48,49) making possible the characterization of the type of accessible processes that occur in the given system.

THERMODYNAMIC FUNCTIONS OF UNDERCOOLED LIQUIDS DURING VITRIFICATION

Most thermodynamic studies deal with the behaviour of heat capacity during vitrification, e.g., Ramachandrarao et al. (ref.54) correlated the discontinuous change in thermal expansion and heat capacity with each other using expressions for the ideal entropy of mixing in substitutional solutions of the components of different size. Similarly, Hillert (ref.50) assumed that the abnormal heat capacity of the non-crystalline phase above T_g is due to localized defects and describes its configurational entropy by the model of interstitial solutions. A very illustrative approach was developed by Gutzow (refs.55-57) who assumed that the difference between thermal capacities of liquid c_p^{liq} , and crystalline, c_p^{cr}, phases is approximately constant, c_0, and that there exists a limiting temperature, T_0, at which this difference vanishes. Using differences in the molar entropies, s, enthalpies, h, and chemical potentials, μ, well-known from classical thermodynamics, we can write (ref.55)

$$\Delta s^{liq,cr} = \Delta s_{melt} - \int_{T}^{T_{melt}} \Delta c_p^{liq,cr} \, dT/T \tag{3}$$

$$\Delta h^{liq,cr} = \Delta h_{melt} - \int_{T}^{T_{melt}} \Delta c_p^{liq,cr} \, dT \tag{4}$$

$$\Delta \mu^{liq,cr} = - \int_{T}^{T_{melt}} \Delta s^{liq,cr} \, dT \tag{5}$$

Introducing dimensionless quantities

$T_r = T/T_{melt}$, $T_{or} = T_o/T_{melt}$ and $T_{gr} = T_g/T_{melt}$ we obtain

$$\Delta c_{pr} = \Delta c_p^{liq,cr} / \Delta s_{melt} \tag{6}$$

$$\Delta s_r = 1 - \int_{T_r}^{T} \Delta c_{pr} \, dT_r/T_r \tag{7}$$

$$\Delta h_r = \Delta h^{liq,cr} / (\Delta s_{melt} T_{melt}) = 1 - \int_{T_r}^{T} \Delta c_{pr} \, dT_r \tag{8}$$

$$\Delta \mu_r = \Delta \mu^{liq,cr} / (\Delta s_{melt} T_{melt}) = \int_{T}^{T_r} \Delta s_r \, dT_r \tag{9}$$

The desired numerical values can be calculated from certain assumptions. We can predict the behaviour of Δc_{pr} as shown in Fig.1, according to the three gradual approaches: stepwise (Gutzow, ref.55), linearly decaying and diffuse (Hillert, ref.50) and lambda shaped (refs.3,4) as known from the theory of broadened phase transitions. In addition we can employ known experimental evidence for the estimation of T_{gr} as discussed above (1/2 and 2/3). The entropy difference frozen-in due to the glass formation is for a typical glass-forming melt about 1/3 ($=\Delta s_r \approx \Delta s_g / \Delta s_{melt}$) but can deviate for those glasses that are difficult to prepare (1/4 through 1/2). For the simplest case of a step-wise change we can calculate exploratory data by the introduction of T_{gr} and Δs_r into the equations listed in Table 1 - using the condition of $s_r = 0$ at $T_r = T_{or}$. The temperature dependence of the thermodynamic potential difference read from the above equations (ref.57):

$$\Delta \mu_r = \int_{T_r}^{T_{gr}} \Delta s_r \, dT_r + \int_{T_{gr}}^{1} (1 + c_o \ln T_r) \, dT_t = \Delta s_r (T_{gr} - T_r)$$

$$+ (1 - c_o)(1 - T_{gr}) - c_o T_{gr} \ln T_{gr} = a - b \, T_r$$

Extension of this model by the introduction of decreasing values of Δc_{pr} does not change the limiting values in the Table. It just helps for a better fit with reality.

TABLE 1

equations			$T_{gr} = \frac{2}{3}$	$T_{gr} = \frac{1}{2}$			
T_{or}	$T_r = T_{or}$	$T_{or} =$ $(\Delta s_r = 0)$	$(2/3)^{3/2} = 0.54$	$(1/2)^{3/2} = 0.35$	$(1/2)^{4/3} = 0.4$	$(1/2)^{5/3} = 0.315$	$(1/2)^2 = 0.25$
Δc_{pr}	1	c_o	$\frac{2}{3\ln(3/2)}$	$\frac{2}{3\ln 2}$	$\frac{3}{4\ln 2}$	$\frac{3}{5\ln 2}$	$\frac{1}{2\ln 2}$
	0	0	$= 1.645$	$= 0.96$	$= 1.08$	$= 0.87$	$= 0.72$
Δs_r	1	$s(T_r)$	1/3	1/3	1/4	2/5	1/2
	0	0					
Δh_r	1	$\Delta h(T_r)$	$=0.452$	$=0.178$	$=0.46$	$=0.565$	$=0.64$
	0	h_o	$=0.243$	$=0.35$	$=0.35$	$=0.4$	$=0.46$
$\Delta\mu_r$	1	$\Delta\mu(T_r)$	$=0.28-0.33\,T_r$	$=0.53-0.33\,T_r$	$=0.43-0.25\,T_r$	$=0.61-0.4\,T_r$	$=0.735-0.5\,T_r$
	0	μ_o	$=0.1$	$=0.42$	$=0.35$	$=0.49$	$=0.61$

where $\Delta s(T_r) = 1 + c_o \ln T_r$, $\Delta h(T_r) = 1 - c_o\ 1 - T_r$ and

$$\Delta\mu(T_r) = (1 - c_o)(1 - T_r) - c_o T_r \ln T_r$$

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