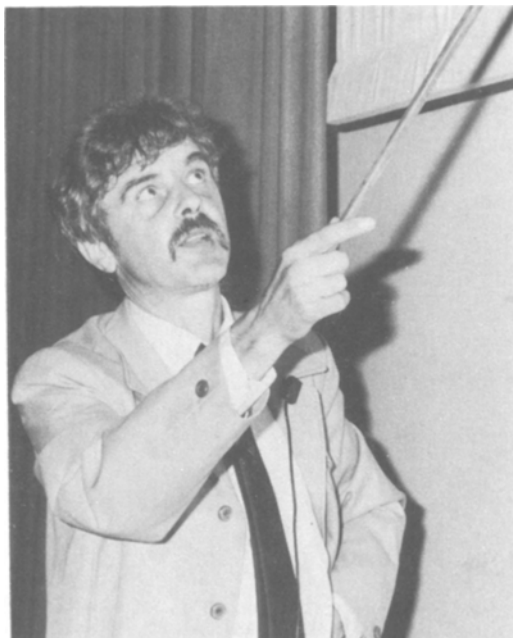


THERMAL TREATMENT AND ANALYSIS INVOLVED IN THE PREPARATION AND INVESTIGATION OF DIFFERENT TYPES OF INORGANIC GLASSES

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The importance of the thermal behaviour of glasses is illustrated. Some procedural characteristics for glass preparation upon quenching are discussed to distinguish the positive effects of increasing cooling rate. The basic thermodynamic quantities, kinetic data and procedural parameters are listed. The glass-transformation interval is treated in detail to demonstrate the temperature-dependences of heat capacity, enthalpy and Gibbs energy for as-quenched and annealed glasses, exemplifying processes of thermally stimulated reordering. Particular attention is paid to DTA measurements, which are of use for the determination of characteristic temperatures and to for the distinction of possible types of processes which occur upon reheating. Most common cases are illustrated by a series of hypothetical ΔH vs. T and ΔT_{DTA} vs. T plots. Different glass formation coefficients based on the onset temperatures are discussed to confirm the general knowledge that their maxima match with concentration regions close to that of invariant melting of the system.

Glass is a material that has been known for several thousand years; it was first prepared by firing sand with soda. The investigation of glasses is mostly performed by chemists with the aid of well-established crystal chemistry [1]. Glass is usually defined as a solid material which lacks the translation periodicity of structural species typical of ordered crystalline substances. However, the absence of characteristic "long-distance" ordered structures does not mean the absence of a particular physical property ordinarily related to a specific atomic network. Among others, glasses can exhibit all types of regular magnetic properties, but can also display the newly discovered spero-, speri-, aspero- and miko-magnetism [2]. This paper emphasizes the thermal analysis [3, 4] of glassy samples as the most essential treatment in general. The activity in glass research gradually developed into three separate, but overlapping areas, according to the materials investigated, as can be documented by the scope of regular meetings:

- The International Congress on Glass (mostly oxides), started in 1933, the latest one, the 14th in New Delhi (India) in 1986:
- The International Conference on Amorphous and Liquid Semiconductors, started in 1966, the latest one, the 12th in Prague (Czechoslovakia) in 1987;
- The International Conference on Rapidly Quenched Metals, started in 1972, the latest one, the 6th, in Montreal (Canada) in 1987.

We can understand that the generally studied field of the thermal behaviour of the glassy state has penetrated into other fields of chemistry and physics, now being a traditional subject treated at SCTAC [3], ICTA [4] and ESTAC conferences.

Procedural approach to glass formation

Recent studies dealing with glassy materials were focused on structural [1], thermodynamic [2], kinetic [5] and technological [6, 7] aspects of glass formation, as discussed in numerous books [7–17]. In contrast with the classical "chemical" approach [8–12], where glasses have been prepared by the natural cooling of silica-based melts containing additives of non-glass-forming oxides, it is interesting to note that a more recent "physical" approach seeks conditions for the rapid cooling of melts, so as to "freeze-in" the given system under study [11–17]. Thus glasses nowadays involve a greater variety of materials vitrified by widely modified experimental methods [6, 7, 18, 19], where the effective cooling rate spans several orders. Some newly proposed methods of ultra-fast cooling, however, revive traditional techniques employed long ago in the glass industry, e.g. a miniaturized method of pouring melts onto stationary (or horizontally moving)

substrates, or pulling ribbons between two rotating wheels [6, 19]. The similarity between the industrial and laboratory techniques employed to prepare different glasses, regardless of their composition, can be viewed as due to the same nature of the thermally stimulated processes required to form the glassy state in general. It is evident that thermal treatment and the resulting glass formation and crystallization have become joining elements of the materials science of glasses. The degree of individual contributions are roughly illustrated by Table 1, which is of assistance in a consideration of thermally dependent and measurable quantities.

Table 1: Conditioning of vitrification

| Thermodynamic quantities | Kinetic data | Procedural parameters |
|--|--|---|
| <ul style="list-style-type: none"> - melting temperature - positioning of solidus/liquidus line - melt - concentration <li style="padding-left: 20px;">- segregation (non-ideality) <li style="padding-left: 20px;">- wetting angle melt/glass* <ul style="list-style-type: none"> - entropy - enthalpy - Gibbs energy - surface energy - specific heat - thermal conductivity - viscosity - phase separation surroundings <ul style="list-style-type: none"> - temperature - pressure - other force field | <ul style="list-style-type: none"> - melt polymerization due to prolonged tempering - short and long-range diffusion - homogeneous and heterogeneous nucleation - prenucleus sites - crystal growth and its dimensionality - overall (apparent) degree of crystallization - (apparent) rate constant of crystallization and associated activation energies of nucleation, crystal growth and diffusion - dynamics of heat generation and sink - dynamics of external field action | <ul style="list-style-type: none"> - delay of melt transport to the place of controlled quenching - cooling/heating rates - apparatus-induced anisotropy/annealing - sample thickness and surface - contact cooling area and associated heat transfer coefficient - interfacial (front) layer and type of heat exchange - mutual velocities of cooling substrate and melt under quenching - type of force field applied or created during processing - melt hydrodynamics, including gravitational and surface (Marangoni) flows - self-induced crystallization after quenching contact removal |
| (* only approximate values due to ambiguity of unstable state) | <ul style="list-style-type: none"> - short-order and long-order structural relaxation(s) - freeze-in of nuclei as a result of heat treatment - positioning of glass-transformation region | |
| <ul style="list-style-type: none"> - degree of melt undercooling - crystallization temperature on reheating - type of stable/metastable crystalline phase precipitated | | |
| <ul style="list-style-type: none"> - degree(s) of glass/melt disordering - fictive (extrapolated) temperature(s) | | |

The thermal treatment involved in the process of quenching [19] is of predominant importance as some methods which permit the desired glass formation are either under- or over-estimated. If the limit of the bulk material is assumed to be a layer of at least 100 nm which has an intimate surface/interface cooling contact, the maximum cooling rate is estimated to be as high as 10^9 deg/s. This can be achieved only by surface laser glazing, or possibly approached by the flash heating of very thin metallic ribbons. The direct scanning of such high temperature changes is almost impossible and we have to rely on secondary evidence (a lamellar spacing etc.). In practice, however, we usually deal with much lower heating/cooling rates, applied to more voluminous materials with different surface/volume properties, in combination with our experimental possibilities. For example, if a melt of oxides at about 1200° is simply poured between two metallic plates to obtain a 1–3 mm thick glassy layer; a cooling rate of 10^2 – 10^3 deg/s is obtained. A comparable cooling rate can also be attained on liquid cooling; if a drop about 3 mm in diameter is immersed in a suitable liquid (low-temperature fused metals, oils or various salt solutions; but certainly not liquid nitrogen due to the strong insulation of the evaporated gaseous envelope). To increase the cooling rate by one order, the sample thickness must be decreased far below 1 mm, or a filament about 0.5 mm in diameter must be drawn directly out of the melt (and preferably cooled by a stream of inert gas). Centrifugation of a melt into tiny drops (less than 0.5 mm in diameter) spattered against surrounding metallic walls increases the cooling rate by one order again. Direct measurement of the resulting temperature changes is gradually less and less possible. On the other hand, we can easily measure temperature changes to follow the quenching processes of chalcogenide melts sealed in a quartz tube of 5 mm inner diameter by placing a thermocouple in the melt [18]. Surprisingly, we find little changes in the effective cooling rates on immersion into different cooling liquids from an original 900° . The cooling rate decreases from $5 \cdot 10^2$ deg/s down to $3 \cdot 10^2$, $2 \cdot 10^2$ or merely 10^2 deg/s for a 10% aqueous solution of KOH, a mixture of water with ice, liquid nitrogen, and self-cooling in air. It is evident that it is more crucial to increase the cooling rate by extension of the contact with the cooling surface (illustrated by the first case of silica melt processing) than by the change of the heat sink properties of the cooling medium (illustrated by the second case). Attempts to detect real rates of cooling, however, may, help towards an evaluation of more precise individual methods, and may thus become part of the greater family of as yet non-traditional thermoanalytical methods.

Glass-transformation region

The question of "what is glass" can be correctly approached only by assuming an appropriate picture of the glass-transformation region [21]. Thermal evidence of the "vitreous solid-to-liquid" transformation has been discussed for many years. The change from the configurationally frozen state of constrained instability to that of internal metastability is manifested thermally by an abrupt rise in heat capacity C_p within a narrow temperature interval around the temperature of glass transformation, T_g . However, this characteristic temperature is missing for a certain class of "amorphous" materials prepared by a disordering process [20] different from the method of continuous cooling of melts. In most cases it is impossible to subsequently heat such an amorphous material to form the undercooled liquid state without interfering crystallization the earlier onset of which is probably catalyzed by the increased activity of the material. For ordinary, as-quenched glass, the experimental relaxation time of a given frozen structure represented by T_g is said to be proportional to the shear stress relaxation time [21], related to a shear viscosity ($\approx 10^{13}$ P). Glass transformation resembles a second-order transition, but for kinetic reasons it only partly obeys the first Ehrenfest relations [3, 21]. The discrepancy arises from the temperature positioning and transformation broadening due to the relaxation time set up by the cooling rate applied. Corrections relating to the use of certain "disordering" parameters (fixed for each T_g) did not find wide applicability, owing to the difficulty of their association with real, physically identifiable parameters. Probably the best solution is the introduction of the concept of fictive temperatures defined upon the enthalpy relation [22, 23] as the temperature at which the non-equilibrium glass and quasi-equilibrium melt coexist with each other. If a glass is annealed at a temperature below T_g , a relaxation process towards a more "equilibrated" glassy state is often observed [19] for all types of oxide [24], chalcogenide [25, 26] and metallic [27–29] glasses. One characteristic of such a process is the very slow kinetics, which is dependent upon the previous thermal history of the material. Figure 1 demonstrates a hypothetical representation of possible shifts associated with thermal treatments where calorimetric measurements become a powerful tool in investigating the thermal behaviour around and below T_g [19, 25, 29]. During the reheating of annealed glass, the enthalpy curve (Fig. 1b) tends to meet earlier that of an undercooled melt and/or to cross this line to form an endotherm; the extents of the two effects (together with the lowering of the horizontal position, similarly to that caused by slower cooling during the original

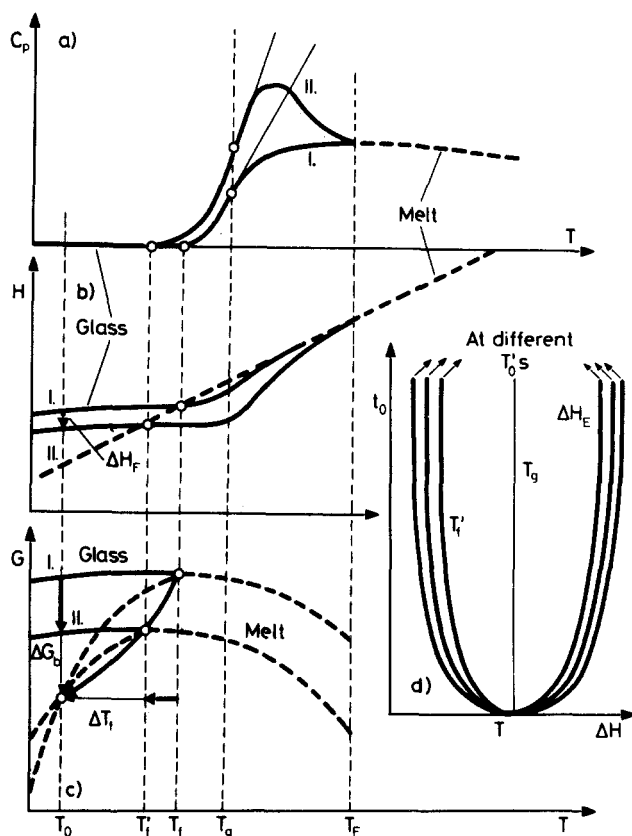


Fig. 1 Theoretical thermal characteristics of the glass-transition region (resembling the experimental case of $\text{Ge}_{20}\text{Te}_{80}$ [25] with the marked specific temperatures (dashed vertical lines) T_0 , T_f , T_f' , T_g and T_F of glass (annealing), of the intersection of the extrapolated states of annealed (') and asquenched glass with that of the undercooled melt, of the point of inflection in the C_p vs. T curve and of the undercooled melt (before quenching), respectively.

(a) A typical temperature-dependence of the measured thermal capacity C_p for as-quenched (I) and annealed (II) glass.

(b) Enthalpy plot showing the deviation of the glassy state (solid horizontal lines I and II) from the undercooled melt (dashed).

(c) Gibbs energy plot exhibiting two parabolas ($\Delta G(T) \cong -(T-T_f)^2 / 2T_f$ [22, 25] associated with each maximum), describing the undercooled liquid state dashed at T_f and T_f' (horizontal solid lines for glass). The bold full curve ($\Delta G(T_f) \cong (T_f - T_0)^2$ [25], crossing all three circles) means that T_f approaches T_0 on annealing; however, the relaxation towards lower $G(T_f(t_0))$ (vertical arrows) is much faster than towards T_f (horizontal arrows).

(d) Isothermal evolution of endothermal heats ΔH_E (right), fictive T_f (left) and glass-transition T_g (middle) temperatures for the glassy samples annealed for time t_0 at a prefixed temperature T_0 .

freeze-in) are a measure of certain "reordering". Experimental evidence (Fig. 1d) reveals the time *vs.* temperature dependence of these phenomena and the process of equilibration deserve special attention in terms of the established thermodynamic parameter [25, 30] (cf. Fig. 1c).

Experimentally measurable temperatures

DTA and/or DSC are the most convenient methods to measure the macroscopic behaviour of a glass, distinguishing certain characteristic points [31] and their corresponding temperatures. Besides the easy positioning of peaks, which yields data on crystallization and melting, the stepwise changes associated with glass transformation are more sensitive for detection (bearing in mind their dependence on the sample history), even tending sometimes to develop into shapes of endothermic peaks (cf. the preceding section). Glass transformation can even separate into two regions if two glassy structures coexist, or it can be preceded by an inexpressive pseudoendotherm attributed to local and/or cooperative structural relaxation [19] below T_g . The analysis of sequences of thermal effects in order to distinguish multiple crystallization [31] is usually complicated by the formation of metastable phases [32–34] and still remains a fascinating field of thermal analysis with the aid of phase diagrams and $T-T-T$ diagrams [31], to be complemented, however, by independent morphology observations. A series of possible cases are sketched in Fig. 2, showing the thermal dependence of enthalpy changes and their corresponding derivatives analogous to DTA traces (marked in terms of the experimentally detected deviation, ΔT , from the base line). This well demonstrates how a kinetically favoured precipitation can play a decisive role [33]. Such an easy collection of characteristic points during glass reheating allows examination for a correlation between the onset temperatures and glass-formation capabilities conventionally studied in the form of compositional dependences of reduced quantities [34–37] (see Fig. 3). Such plots, however, show the usually overlooked fact that the desired region of best glass formation, coinciding with the extreme values, corresponds to a narrow compositional interval; in other words, it confirms the general knowledge that the best glass formation is anticipated in the vicinity of a eutectic point, i.e. around the minimum temperature of invariant melting of the system.



Fig. 2 Hypothetical enthalpy (H) plots (lower) and corresponding DTA curves (ΔT) for some characteristic cases that may be met during investigation of a glass upon reheating. Temperatures specific for individual changes indicated on the ΔT vs. T plots are marked by verticals.

(1) The formation of a "stable" glass which does not tend to crystallize upon reheating (solid line), in comparison with an invariant solidification (dotted) of melt during normal congruous melting/freezing.

(2) Glass readily crystallizing, where the crystallization peak arises just after the glass transformation.

(3) Glass which is difficult to crystallize, where the crystallization peak emerges just in front of the peak of melting, possibly showing a certain degree of mutual interference.

(4) Heat-treated metal-metalloid glassy alloy [19, 29] exhibiting two small low-temperature peaks, reflecting the occurrence of two more or less separated structural relaxations of local and medium-range rearrangements and consequent long-range regrouping.

(5) Amorphous material which does not exhibit an experimentally detectable glass transformation, which is possibly hidden in the early starting process of crystallization (probably catalyzed by excessively active sites and (or) interfaces). The crystallization peak, however, displays the change of C_p characteristic of T_g [20].

(6) Two consecutive glass-transformation regions, characteristic of admixtures in an oxide matrix [32], caused by the liquid-liquid type phase separation occurring even in the metastable melt or secondary induced in glass upon prolonged annealing. The resulting separation usually helps towards the further distinction of the consequent crystallization processes, c. f. (7).

(7) Most typical case of two-stage crystallization, associated either with the first separation of the closest metastable crystalline phase, later transforming to a stable phase, as initiated by the for-

mation of another non-crystalline phase of the first melt, or with the formation of two gradually precipitating stable phases.

(8) Possible formation of a metastable phase below the existence of a kinetically less favourable stable phase due to external effects (impurities, heterogeneous seeds, etc.) [33]. It may exhibit different courses (dotted) in accordance with the thermal treatment of the system (e.g. polymerization due to prolonged tempering of chalcogenide [36] or silicate melts).

(9) The positioning of metastable phase lines (dashed) may be different, and even sloped, crossing the stable line at different angles, thereby creating various degrees of metastability of the system. Merely thermal data are often unsatisfactory to distinguish what kind of process is involved without complementary data on the morphology of the system [15, 16].

(10) Example of variant melting in the two-phase region (solid line) with possibly interference by variant metastable melting (dotted). It is worth noting that a repeated cycle of consecutive heat treatment at each temperature of glass transformation, crystallization and melting, respectively, can lead to an improved glass-forming ability; for example, certain chalcogenide systems may avoid crystallization originally characteristic of as-quenched samples.

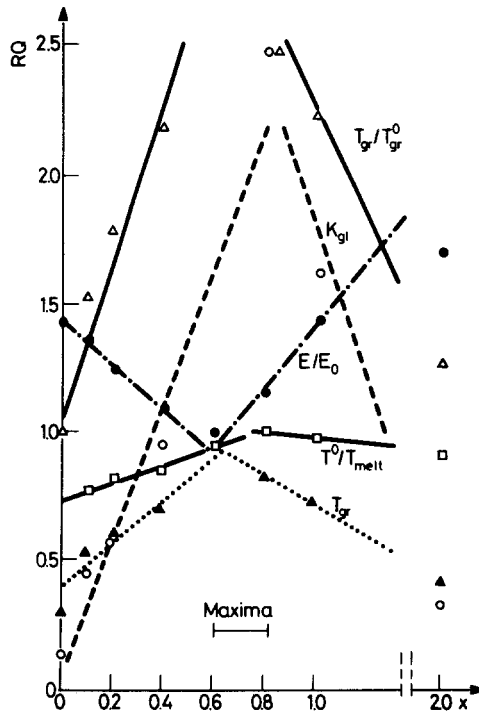


Fig. 3 Compositional dependence of different coefficients (in reduced representation) associated with glass-forming ability (derived for the system As_2Te_3 with added $X = Ge$ [36, 37].

- ▲ $T_{gr} = T_g/T_{melt}$ is the reduced glass-transformation temperature [35];
- $K_{gl} = (T_{cr} - T_g)/(T_{melt} - T_{cr})$ is Hruby's [36] glass-forming capability coefficient;
- △ T_{gr}/T_{gr}^0 , □ T_{melt}/T_{melt}^0 are other standardized quantities [34];
- E/E^0 is the activation energy ratio for crystallization [34, 37] (superscript 0 refers to the standard value chosen for normalization).

Perspectives

Computer simulation seems to permit a better understanding of activation energies associated with glass formation interpreted in terms of structural rearrangements based on the theoretical free volume model, as recently shown by a Spanish group [38–40] for thermodilatometry and DSC curves.

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Zusammenfassung — Es wird die Bedeutung des thermischen Verhaltens von Glas verdeutlicht. Einige technologische Kenngrößen der Glasherstellung beim Abschrecken sowie grundlegende thermodynamische Größen, kinetische Daten und technologische Parameter, wurden beschrieben, um bei steigender Abkühlgeschwindigkeit positive Einflüsse erkennen zu können. Zur Unterstreichung thermisch stimulierter Umordnungsprozesse und zur Verdeutlichung der Temperaturabhängigkeit von Wärmekapazität, Enthalpie und freier Enthalpie von abgeschrecktem und kühlgeglühtem Glas wird das Intervall der Glasumformung ausführlich behandelt. Erhöhte Aufmerksamkeit wurde DTA-Messungen geschenkt, um charakteristische Temperaturwerte festzustellen und um eventuelle Typen der Prozesse, die beim Nachhitzen ablaufen, zu erkennen. Die häufigsten Fälle werden durch hypothetische $\Delta H-T$ und $\Delta T_{DTA}-T$ Diagramme illustriert. Verschiedene Glasformationskoeffizienten für die Anfangstemperatur wurden diskutiert, um den allgemeinen Fakt zu bekräftigen, daß deren Maximum mit den Konzentrationsbereichen nonvariant schmelzender Systeme übereinstimmt.

РЕЗЮМЕ — Показана важность знания термического поведения новых стеклообразных материалов. Обсуждены некоторые методологические характеристики получения стекол при резком охлаждении, с тем чтобы различить положительные эффекты увеличения скорости охлаждения. В связи с этим приведены основные термодинамические величины, кинетические данные и методические параметры. Детально обработан интервал стеклообразования с тем, чтобы показать температурные зависимости, энтальпии и энергии Гиббса для охлажденных и оттоженных образцов стекол, являющихся примером процессов термически стимулированного переупорядочения. Особое внимание было уделено ДТА измерениям, позволяющим определять характеристичные температуры и различать возможные типы процессов, происходящих при повторном нагреве. Наиболее общие случаи представлены большим числом гипотетических графиков в координатах $\Delta H - T$ и $\Delta T_{DTA} - T$. Исходя из начальных температур, обсуждены коэффициенты образования стекол с целью подтверждения того факта, что их максимум сочетается с концентрационными областями, близкими к таковым при инвариантном плавлении этой системы.