

Chapter 1

Introduction

Silicate glasses belong with pottery, ceramics and bronze to the oldest materials employed by men. This early widespread application is in some respect due to the broad distribution of glasses in nature. As an example, magmatic rocks can be mentioned, which consist to a large degree of vitreous silicates or completely amorphous natural glasses such as obsidian or amber. It is well-known, that the natural glass obsidian served as a material for the preparation of the first cutting tools of primitive men. In the ancient cultures of Central America, obsidian served as the material for the ritual knives of high priests.

The wide distribution of glasses in nature is not due to chance. The inner part of the earth, characterized by very high values of pressure and temperature, is itself an enormous glass-forming melt. Processes of crystallization and glass-formation connected with the eruption of volcanos and the more or less abrupt cooling processes of parts of this melt determine to a large degree the course of geological processes and the structure and properties of the lithosphere. Natural glasses are widespread not only on earth but also on the moon as it became evident from the investigation of samples of lunar rocks brought to earth by the lunar expeditions (see, e.g., Pye et al. [653]).

The first applications of glasses in primitive societies for a limited number of purposes was followed by a long evolution to the modern glass industries and glass science. From the point of view of the variety of properties of glasses and the spectrum of possible applications the importance of different glasses can hardly be even estimated. The validity of this statement becomes evident if one tries to imagine for a while things surrounding us in everyday life without the components made of vitreous materials. Technical glasses like chemically resistant glass or optical glasses are also well known to everyone. Imagine, for example, a chemical plant, a physical laboratory, a car or a dwelling house without glasses or let us think about the importance of silicate glasses for optical devices, in particular, in microscopy and astronomy.

In addition to the classical oxide and particularly silicate glasses in the last decades new classes of vitreous materials have gained importance, consisting of substances or mixtures of substances for which the possibility of existence in the

vitreous state was thought as being exotic or even impossible. One example in this respect are metallic glasses. Metallic glasses in a period of about 10 years were transferred from a stage of exotic research to the stage of production and world-wide technological application. Similar examples are glassy polymers or vitreous carbon, glass-forming chalcogenide or halide systems. The development of modern methods of information technology e.g. of cable TV is also based on glass, on extremely pure, defect-free vitreous fibres with particular optical properties.

With the increase of the number of substances, which can be obtained in the vitreous state, also the variety of properties and possible applications of glasses has been increased. Beyond the traditional applications in technology and science, glassy materials are also used as substitutes for biological organs or tissues, e.g., as prostheses even in ophthalmology. Glass-forming aqueous solutions with biologically relevant compositions are used as a carrier medium for the freezing-in of biological tissues. Thus, it seems that even life can be frozen in to a glass thus solving the problems of absolute anabiosis within the vitreous state. Porous silicate glass particles are used to supply nutrient solutions to microbial populations and slowly soluble glasses containing exotic oxides are used as an ecologically compatible form of micro-element fertilization.

Besides pure glasses, glass-ceramics like Pyroceram, Vitroceram, Sital – partly crystalline materials formed from devitrifying glasses – are also gaining in importance. In such materials the transformation of the melt into the desired vitro-crystalline structure is initiated by a process of induced crystallization usually caused by the introduction of insoluble dopants (crystallization cores or surfactants) into the melt. As a result heterogeneous materials are formed in which the properties of glasses and crystals are combined. In this way an astonishing variety of new materials with extreme properties and unusual possibilities of application is obtained: classical enamels, glass-ceramics (like Pyroceram) and so called glass ceramic enamels give an example in this respect.

The widespread application and development of different vitreous materials and their production was connected with a thorough study of related scientific and technological aspects, resulting in the publication of a number of monographs, devoted to special classes of vitreous materials or special technological processes like the technology of silicate glasses, glassy polymers, metallic glasses. In these books mainly specific properties of the particular glasses discussed or of the technological processes connected with their production are analyzed.

The aim of the present book is different. The specific properties of various vitreous materials are not studied in detail but the attempt is made to point out the main fundamental properties and features which are common to all glasses independent of the substrate they are formed from and the way they are produced. Hereby particular attention is directed to the specification of the thermodynamic nature of any glass independent of its composition or any other specific properties. Special glasses or technologies connected with their production will be discussed only as far as it is desirable as an illustration of general statements or conclusions.

The present monograph is structured as follows. In Chap. 2 we first give a phenomenological description of processes which can be observed during the cooling of

glass-forming melts. Properties of the melts and the glasses are described together with the way of evolution of historically important ideas and suggestions concerning the nature of the vitreous state and the mechanism of glass formation. The basic definitions, derivations and equations, required for the theoretical interpretation of the experimental results, are introduced and discussed briefly to allow even non-specialists in glass science to follow in detail the conclusions derived later. The experimental results summarized in this chapter give the basis for a test and verification of theoretical developments outlined in the subsequent parts.

A detailed analysis of the experimental results and their theoretical interpretation, given in Chap. 2, leads to the conclusion, that glasses from a thermodynamic point of view are frozen-in non-equilibrium systems. The thermodynamic description of such states and their specific thermodynamic properties is outlined in Chap. 3. This discussion is based on the general postulates of the thermodynamics of irreversible processes and, in particular, on the method of description of non-equilibrium states, developed by De Donder. The thermodynamic analysis is followed in Chap. 4 by an outline of basic ideas concerning the structure of different glasses.

Chapter 5 is devoted to statistical-mechanical model calculations of properties of glass-forming melts which allow one an interpretation of experimental observations, for example, in the framework of the free-volume theory of liquids. In Chaps. 6–10, criteria are developed to answer the question under which conditions a given substance can be brought into the vitreous state. Of major importance in this respect are problems of the kinetics of nucleation (Chaps. 6 and 7) and crystal growth (Chaps. 8 and 9) and factors determining the overall course of phase transformations in glass-forming systems (Chap. 10). These processes may be affected considerably by a primary liquid phase separation as outlined in detail in Chap. 11.

The crystallization of glass-forming melts, its initiation and control or inhibition, respectively, determines to a large degree the possibility to transform a melt into a glass or to synthesize a glass-ceramic material with a predetermined structure, degree of crystallization and desired properties. On the other hand, crystallization processes and phase transformations in glass-forming melts have served as model systems for the development and verification of different concepts concerning the kinetics of phase transformation processes also in other fields of science and technology. By both reasons the derivation of criteria of glass formation is started with a thorough discussion of the kinetics of nucleation and growth processes.

The criteria for glass formation derived in Chap. 10 show that there is no principal division between different substances with respect to the ability to be transformed into the vitreous state. For some substances the conditions for glass formation can be realized easily in laboratory, for other materials sophisticated methods, e.g., ultra-rapid cooling, vapor quenching or plasma sputtering have to be applied. For a third group of substances the criteria obtained indicate that even the most elaborated of the existing vitrification techniques developed till now with cooling rates reaching about ten millions degrees per second are not sufficient to produce a glass. There is, however, no principal limitation that with more powerful methods these substances could be also vitrified in future. From such a point of view it follows as a general consequence that the vitreous state is a possible form of existence of, in principle,

all pure substances or mixtures. In this respect, glass science is no more the description of a limited number of materials but a general theory for a state, possible for practically all substances.

The transformation of more and more materials into the frozen-in non-equilibrium state of a glass is connected also with a substantial change in the meaning of the word glass. Originally under glasses only amorphous (in the sense of non-structured) frozen-in non-equilibrium systems were understood. At present every frozen-in non-equilibrium state (non-amorphous systems included) is denoted sometimes as a glass, e.g., frozen-in crystals, crystalline materials with frozen-in magnetic disorder (spin glasses) etc.

Glass-forming melts represent a unique material also with respect to their rheological properties. In particular, in the vicinity of the transformation region from the melt to a glass glass-forming systems cannot be considered usually as classical Newtonian liquids. The specific rheological properties of glass-forming melts are of significance for most of the technological processes in glass production and also for processes of crystallization and cluster growth. This is the reason why these properties are considered in detail in Chap. 12.

As it is seen from the given overview of the contents the present book is directed to an analysis of the fundamental problems of glass science which are of importance for the understanding of the properties of glasses, in general. In this discussion of the basic ideas concerning the vitreous state the historic course of their evolution is also briefly mentioned. Hereby not a chronologically exact or comprehensive description is attempted but a characterization of the inner logic of this evolution, the interconnection of different ideas. This approach implies that in addition to the most fruitful concepts and ideas, which, as it turned out later, were real milestones in the evolution of glass science, also proposals are analyzed, which already at the time of their formulation or by the subsequent developments were shown to be incorrect or even misleading, at least, as far as it is known today. To the opinion of the authors only by such an approach can a correct picture of the evolution of science as a struggle between different or even contradicting ideas be given. On the other hand, the detailed analysis of differing proposals and the proof that some of them are not correct is of an undoubted heuristic value. Such an approach can also prevent any overenthusiasm with respect to insufficiently substantiated new hypotheses or to old already refuted ideas presented in a modern form. This was one of the leading ideas in writing the first edition of the present book. It is also followed in this second edition.

A discussion of the vitreous state and of the history of glass science would be incomplete without a short characterization of the contributions of, at least, some of the men, whose names are closely connected with the development of the modern theory of glasses. G. Tammann, O. Schott, E. Berger, I. F. Ponomaryev, A. Winter-Klein, D. Turnbull, A. A. Lebedev, E. A. Porai-Koshits and many others became well-known in science mainly by their investigations of basic properties of glasses, of the nature of the vitreous state, of the interconnections between crystallization and glass formation, of the structure of glasses. Important insights into the understanding of glass structure are due also to such outstanding

representatives of structural chemistry, in general, like V. M. Goldschmidt, G. Hägg, L. Pauling and J. Bernal. V. M. Goldschmidt was the first to develop geometrical or crystal-chemical criteria for glass formation, which allowed one the prediction of a whole new class of glass-forming systems. Based on Goldschmidt's ideas W. H. Zachariasen formulated his beautiful model of glass structure while J. Bernal, also using a geometric approach, indicated in the early 1960s the possible existence of metallic alloy glasses.

The scientific importance of problems connected with the characterization and the properties of the vitreous state as a specific physical state also becomes evident from the fact that some of the most outstanding physicists and chemists of the past century, people like W. Nernst, A. Einstein, F. Simon, L. Pauling, I. Prigogine, Ya. I. Frenkel, L. Anderson, N. Mott were involved in the study of glasses. Thus, A. Einstein in a famous article, devoted to the basic principles of statistical physics, as early as in 1914, mentioned the possibility that glasses have to be considered not as equilibrium but as non-equilibrium systems. This hypothesis was verified many years later by F. Simon, who started his investigations trying to reconcile the behavior of glasses with the Third law of thermodynamics, formulated by W. Nernst. These investigations led to a reformulation of the Third law and gave a stimulus for the extension of thermodynamics to non-equilibrium states.

G. Tammann in addition to his own pioneering work on glass properties and the process of vitrification was also the first scientist to try to summarize the basic results obtained at his time in his remarkable book "Der Glaszustand", published first in 1933. The present monograph represents an attempt to take up Tammann's approach and to summarize the basic principles and ideas of glass science, including the new developments, in one volume. Hereby we tried to follow – we hope, successfully – the advice given by Albert Einstein: *"Everything should be done as simple as possible but not simpler"*.

The Vitreous State

Thermodynamics, Structure, Rheology, and
Crystallization

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