Contents

Foreword *V*

Preface *XVII*

Contributors *XIX*

1 Introduction *1*
Jürn W. P. Schmelzer and Ivan S. Gutzow

2 Basic Properties and the Nature of Glasses: an Overview *9*
Ivan S. Gutzow and Jürn W. P. Schmelzer
2.1 Glasses: First Attempts at a Classification *9*
2.2 Basic Thermodynamics *14*
2.2.1 The Fundamental Laws of Classical Thermodynamics and Consequences *14*
2.2.2 Thermodynamic Evolution Criteria, Stability Conditions and the Thermodynamic Description of Nonequilibrium States *22*
2.2.3 Phases and Phase Transitions: Gibbs's Phase Rule, Ehrenfest's Classification, and the Landau Theory *26*
2.3 Crystallization, Glass Transition and Devitrification of Glass-Forming Melts: an Overview of Experimental Results *36*
2.4 The Viscosity of Glass-Forming Melts *46*
2.4.1 Temperature Dependence of the Viscosity *46*
2.4.2 Significance of Viscosity in the Glass Transition *54*
2.4.3 Molecular Properties Connected with the Viscosity *57*
2.5 Thermodynamic Properties of Glass-Forming Melts and Glasses: Overview on Experimental Results *59*
2.5.1 Heat Capacity *59*
2.5.2 Temperature Dependence of the Thermodynamic Functions: Simon's Approximation *65*
2.5.3 Further Methods of Determination of Caloric Properties of Glass-Forming Melts and Glasses *74*
2.5.4 Change of Mechanical, Optical and Electrical Properties in the Glass Transition Range *76*

2.6 Thermodynamic Nature of the Glassy State *82*
2.7 Concluding Remarks *88*

3 Generic Theory of Vitrification of Glass-Forming Melts *91*
Jürn W. P. Schmelzer and Ivan S. Gutzow
3.1 Introduction *91*
3.2 Basic Ideas and Equations of the Thermodynamics of Irreversible Processes and Application to Vitrification and Devitrification Processes *95*
3.2.1 Basic Assumptions *95*
3.2.2 General Thermodynamic Dependencies *96*
3.2.3 Application to Vitrification and Devitrification Processes *100*
3.3 Properties of Glass-Forming Melts: Basic Model Assumptions *103*
3.3.1 Kinetics of Relaxation *103*
3.3.2 Thermodynamic Properties: Generalized Equation of State *105*
3.4 Kinetics of Nonisothermal Relaxation as a Model of the Glass Transition: Change of the Thermodynamic Functions in Cyclic Cooling-Heating Processes *107*
3.4.1 Description of the Cyclic Processes under Consideration *107*
3.4.2 Temperature Dependence of the Structural Order Parameter in Cyclic Cooling and Heating Processes *108*
3.4.3 Definition of the Glass Transition Temperature via the Structural Order Parameter: the Bartenev–Ritland Equation *110*
3.4.4 Structural Order Parameter and Entropy Production *113*
3.4.5 Temperature Dependence of Thermodynamic Potentials at Vitrification *115*
3.4.5.1 Configurational Contributions to Thermodynamic Functions *115*
3.4.5.2 Some Comments on the Value of the Configurational Entropy at Low Temperatures and on the Kauzmann Paradox *121*
3.4.6 Cyclic Heating-Cooling Processes: General Results *123*
3.5 The Prigogine–Defay Ratio *125*
3.5.1 Introduction *125*
3.5.2 Derivation *127*
3.5.2.1 General Results *127*
3.5.2.2 Quantitative Estimates *133*
3.5.2.3 An Alternative Approach: Jumps of the Thermodynamic Coefficients in Vitrification *135*
3.5.3 Comparison with Experimental Data *137*
3.5.3.1 The Prigogine–Defay Ratio *137*
3.5.3.2 Change of Young's Modulus in Vitrification *140*
3.5.4 Discussion *142*
3.6 Fictive (Internal) Pressure and Fictive Temperature as Structural Order Parameters *143*
3.6.1 Brief Overview *143*

3.6.2 Model-Independent Definition of Fictive (Internal) Pressure and Fictive Temperature *146*
3.7 On the Behavior of the Viscosity and Relaxation Time at Glass Transition *149*
3.8 On the Intensity of Thermal Fluctuations in Cooling and Heating of Glass-Forming Systems *152*
3.8.1 Introduction *152*
3.8.2 Glasses as Systems with Frozen-in Thermodynamic Fluctuations: Mueller and Porai-Koshits *153*
3.8.3 Final Remarks *158*
3.9 Results and Discussion *158*

4 Generic Approach to the Viscosity and the Relaxation Behavior of Glass-Forming Melts *165*
Jürn W. P. Schmelzer
4.1 Introduction *165*
4.2 Pressure Dependence of the Viscosity *166*
4.2.1 Application of Free Volume Concepts *166*
4.2.2 A First Exception: Water *169*
4.2.3 Structural Changes of Liquids and Their Effect on the Pressure Dependence of the Viscosity *171*
4.2.4 Discussion *173*
4.3 Relaxation Laws and Structural Order Parameter Approach *174*
4.3.1 Basic Equations: Aim of the Analysis *174*
4.3.2 Analysis *175*
4.3.3 Discussion *177*

5 Thermodynamics of Amorphous Solids, Glasses, and Disordered Crystals *179*
Ivan S. Gutzow, Boris P. Petroff, Snejana V. Todorova, and Jürn W. P. Schmelzer
5.1 Introduction *179*
5.2 Experimental Evidence on Specific Heats and Change of Caloric Properties in Glasses and in Disordered Solids: Simon's Approximations *182*
5.3 Consequences of Simon's Classical Approximation: the $\Delta G(T)$ Course *194*
5.4 Change of Kinetic Properties at T_g and the Course of the Vitrification Kinetics *195*
5.5 The Frenkel–Kobeko Postulate in Terms of the Generic Phenomenological Approach and the Derivation of Kinetic and Thermodynamic Invariants *198*
5.6 Glass Transitions in Liquid Crystals and Frozen-in Orientational Modes in Crystals *208*
5.7 Spectroscopic Determination of Zero-Point Entropies in Molecular Disordered Crystals *212*

5.8 Entropy of Mixing in Disordered Crystals, in Spin Glasses and in Simple Oxide Glasses *213*
5.9 Generalized Experimental Evidence on the Caloric Properties of Typical Glass-Forming Systems *215*
5.10 General Conclusions *219*

6 Principles and Methods of Collection of Glass Property Data and Analysis of Data Reliability *223*
Oleg V. Mazurin
6.1 Introduction *223*
6.2 Principles of Data Collection and Presentation *225*
6.2.1 Main Principles of Data Collection *225*
6.2.2 Reasons to Use the Stated Principles of Data Collection *228*
6.2.3 Problems in Collecting the Largest Possible Amounts of Glass Property Data *230*
6.2.4 Main Principles of Data Presentation *231*
6.3 Analysis of Existing Data *232*
6.3.1 About the Reliability of Experimental Data *232*
6.3.2 Analysis of Data on Properties of Binary Systems *233*
6.3.2.1 General Features of the Analysis *233*
6.3.2.2 Some Factors Leading to Gross Errors *237*
6.3.2.3 Some Specific Examples of the Statistical Analysis of Experimental Data *239*
6.3.2.4 What is to Do if the Number of Sources Is Too Small? *243*
6.4 About the Reliability of the Authors of Publications *246*
6.4.1 The Moral Aspect of the Problem *246*
6.4.2 An Example of Systematically Unreliable Experimental Data *247*
6.4.3 Concluding Remarks *251*
6.5 General Conclusion *253*

7 Methods of Prediction of Glass Properties from Chemical Compositions *255*
Alexander I. Priven
7.1 Introduction: 120 Years in Search of a Silver Bullet *255*
7.2 Principle of Additivity of Glass Properties *257*
7.2.1 Simple Additive Formulae *257*
7.2.2 Additivity and Linearity *258*
7.2.3 Deviations from Linearity *259*
7.3 First Attempts of Simulation of Nonlinear Effects *260*
7.3.1 Winkelmann and Schott: Different Partial Coefficients for Different Composition Areas *260*
7.3.2 Gehlhoff and Thomas: Simulation of Small Effects *260*
7.3.3 Gilard and Dubrul: Polynomial Models *262*
7.4 Structural and Chemical Approaches *264*
7.4.1 Nonlinear Effects and Glass Structure *264*
7.4.2 Specifics of the Structural Approach to Glass Property Prediction *266*

7.4.3 First Trials of Application of Structural and Chemical Ideas to the Analysis of Glass Property Data *267*
7.4.4 Evaluation of the Contribution of Boron Oxide to Glass Properties *267*
7.4.4.1 Model by Huggins and Sun *268*
7.4.4.2 Models by Appen and Demkina *268*
7.4.5 Use of Other Structural Characteristics in Appen's and Demkina's Models *271*
7.4.6 Recalculation of the Chemical Compositions of Glasses *272*
7.4.7 Use of Atomic Characteristics in Glass and Melt Property Prediction Models *278*
7.4.8 Ab Initio and Other Direct Methods of Simulation of Glass Structure and Properties *279*
7.4.9 Conclusion *280*
7.5 Simulation of Viscosity of Oxide Glass-Forming Melts in the Twentieth Century *280*
7.5.1 Simulation of Viscosity as a Function of Chemical Composition and Temperature *280*
7.5.2 Approaches to Simulation of Concentration Dependencies of Viscosity Characteristics *282*
7.5.2.1 Linear Approach *282*
7.5.2.2 Approach of Mazurin: Summarizing of Effects *283*
7.5.2.3 Approach of Lakatos: Redefinition of Variables *284*
7.5.2.4 Polynomial Models *284*
7.5.3 Conclusion *285*
7.6 Simulation of Concentration Dependencies of Glass and Melt Properties at the Beginning of the Twenty-First Century *286*
7.6.1 Global Glass Property Databases as a Catalyst for Development of Glass Property Models *286*
7.6.2 Linear and Polynomial Models *286*
7.6.3 Calculation of Liquidus Temperature: Neural Network Simulation *289*
7.6.4 Approach of the Author *291*
7.6.4.1 Background *291*
7.6.4.2 Model *292*
7.6.4.3 Comparison with Previous Models *294*
7.6.4.4 Conclusion *296*
7.6.5 Fluegel: a Global Model as a Combination of Local Models *296*
7.6.6 Integrated Approach: Evaluation of the Most Probable Property Values and Their Errors by Using all Available Models and Large Arrays of Data *297*
7.7 Simulation of Concentration Dependencies of Glass Properties in Nonoxide Systems *299*
7.8 Summary: Which Models Were Successful in the Past? *301*
7.9 Instead of a Conclusion: How to Catch a Bluebird *306*

8 Glasses as Accumulators of Free Energy and Other Unusual Applications of Glasses *311*
Ivan S. Gutzow and Snejana V. Todorova
8.1 Introduction *311*
8.2 Ways to Describe the Glass Transition, the Properties of Glasses and of Defect Crystals: a Recapitulation *313*
8.3 Simon's Approximation, the Thermodynamic Structural Factor, the Kinetic Fragility of Liquids and the Thermodynamic Properties of Defect Crystals *318*
8.4 The Energy, Accumulated in Glasses and Defect Crystals: Simple Geometric Estimates of Frozen-in Entropy and Enthalpy *324*
8.4.1 Enthalpy Accumulated at the Glass Transitions *324*
8.4.2 Free Energy Accumulated at the Glass Transition and in Defect Crystals *327*
8.5 Three Direct Ways to Liberate the Energy, Frozen-in in Glasses: Crystallization, Dissolution and Chemical Reactions *331*
8.5.1 Solubility of Glasses and Its Significance in Crystal Synthesis and in the Thermodynamics of Vitreous States *332*
8.5.2 The Increased Reactivity of Glasses and the Kinetics of Chemical Reactions Involving Vitreous Solids *339*
8.6 The Fourth Possibility to Release the Energy of Glass: the Glass/Crystal Galvanic Cell *340*
8.7 Thermoelectric Driving Force at Metallic Glass/Crystal Contacts: the Seebeck and the Peltier Effects *344*
8.8 Unusual Methods of Formation of Glasses in Nature and Their Technical Significance *348*
8.8.1 Introductory Remarks *348*
8.8.2 Agriglasses, Glasses as Nuclear Waste Forms and Possible Medical Applications of Dissolving Organic Glasses *350*
8.8.3 Glasses as Amorphous Battery Electrodes, as Battery Electrolytes and as Battery Membranes *352*
8.8.4 Photoeffects in Amorphous Solids and the Conductivity of Glasses *353*
8.9 Some Conclusions and a Discussion of Results and Possibilities *354*

9 Glasses and the Third Law of Thermodynamics *357*
Ivan S. Gutzow and Jürn W. P. Schmelzer
9.1 Introduction *357*
9.2 A Brief Historical Recollection *360*
9.3 The Classical Thermodynamic Approach *363*
9.4 Nonequilibrium States and Classical Thermodynamic Treatment *366*
9.5 Zero-Point Entropy of Glasses and Defect Crystals: Calculations and Structural Dependence *368*
9.6 Thermodynamic and Kinetic Invariants of the Glass Transition *369*
9.7 Experimental Verification of the Existence of Frozen-in Entropies *371*

9.8 Principle of Thermodynamic Correspondence and Zero-Point Entropy Calculations *376*
9.9 A Recapitulation: the Third Principle of Thermodynamics in Nonequilibrium States *377*

10 On the Etymology of the Word "Glass" in European Languages and Some Final Remarks *379*
Ivan S. Gutzow
10.1 Introductory Remarks *379*
10.2 "Sirsu", "Shvistras", "Hyalos","Vitrum", "Glaes", "Staklo", "Cam" *380*
10.3 "Vitreous", "Glassy" and "Glasartig", "Vitro-crystalline" *382*
10.4 Glasses in Byzantium, in Western Europe, in Venice, in the Balkans and Several Other Issues *384*
10.5 Concluding Remarks *385*

References *387*

Index *407*