

An Introduction to Glass Science and Technology

presents the fundamental topics in glass science and technology including glass formation, crystallisation and phase separation. A detailed discussion of glass structure models with emphasis on the oxygen balance model is also presented. Additional chapters discuss the most important properties of glasses, including physical, optical, electrical, chemical and mechanical properties, and new to this edition, water in glasses and melts. Glass technology is addressed in chapters dealing with the details of glass raw materials, melting and fining, and commercial glass production methods. This expanded second edition also includes new chapters on the compositions and properties of commercial glasses and thermal analysis of glasses and melts. Exercises are included at the end of the chapters.

This introductory text is ideal for undergraduates in materials science, ceramics or inorganic chemistry. It will also be useful to the engineer or scientist seeking basic knowledge of the formation, properties and production of glass.

ISBN 0-85404-639-9



90000



9 780854 046393

Contents

Chapter 1	Introduction	1
1	Definition of a Glass	3
2	The Enthalpy/Temperature Diagram	3
3	Exercises	6
Chapter 2	Principles of Glass Formation	7
1	Introduction	7
2	Structural Theories of Glass Formation	8
3	Kinetic Theories of Glass Formation	11
3.1	Nucleation	11
3.2	Crystal Growth	16
3.3	General Kinetic Treatment of Glass Formation	17
4	Determination of Glass Forming Ability & Glass Stability	21
5	Summary	24
6	Exercises	25
Chapter 3	Glass Melting	26
1	Introduction	26
2	Raw Materials	26
3	Compositional Nomenclature	30
4	Batch Calculations	32
5	Mechanisms of Batch Melting	34
5.1	Release of Gases	35
5.2	Formation of Liquid Phases	35
5.3	Melting Accelerants	37
5.4	Volatilization of Components from Melts	38
6	Fining of Melts	39
6.1	Sources of Bubbles	40
6.2	Removal of Bubbles by Buoyancy Effects	42
6.3	Fining Agents	43
7	Homogenizing of Melts	46

8	Specialized Melting Methods	47
9	Summary	48
10	Exercises	48
Chapter 4	Immiscibility/Phase Separation	51
1	Introduction	51
2	Thermodynamic Basis for Phase Separation	52
3	Mechanisms for Phase Separation	55
4	Immiscibility in Glass Forming Systems	57
5	Determination of Immiscibility Diagrams	62
6	Application of Immiscibility Diagrams	64
6.1	Binary Immiscibility Diagrams	64
6.2	Ternary Immiscibility Diagrams	67
7	Summary	71
8	Exercises	71
Chapter 5	Structures of Glasses	72
1	Introduction	72
2	Fundamental Law of Structural Models	74
3	Elements of Structural Models for Glasses	75
3.1	Coordination of the Network Cations	75
3.2	Bond Angle Distributions	76
3.3	Network Connectivity	76
3.4	Dimensionality	77
3.5	Intermediate Range Order	78
3.6	Morphology	78
3.7	Properties of Specific Ions	79
3.8	Interstitial/Free Volume	79
3.9	Minor Constituents	79
3.10	Comments Regarding Glass Structure Models	80
4	Structural Models for Silicate Glasses	81
4.1	Vitreous Silica	81
4.2	Alkali Silicate Glasses	82
4.3	Alkali/Alkaline Earth Silicate Glasses	89
4.4	Alkali and Alkaline Earth Aluminosilicate Glasses	90
4.5	Rare Earth Alumino/Galliosilicate Glasses	92
4.6	Lead Silicate Glasses	92
4.7	Lead Halosilicate Glasses	93
5	Structural Models for Borate Glasses	93
5.1	Vitreous Boric Oxide	93
5.2	Alkali Borate Glasses	94

5.3	Alkali Aluminoborate Glasses	98
5.4	Alkali Borosilicate Glasses	99
6	Structural Models for Germanate Glasses	100
6.1	Vitreous Germania	100
6.2	Binary Borogermanate and Silicogermanate Glasses	101
6.3	Alkali Germanate Glasses	101
6.4	Alkali Aluminogermanate Glasses	102
6.5	Fluorogermanate Glasses	103
7	Structural Models for Phosphate Glasses	103
8	Structures of Other Inorganic Oxide Glasses	104
9	Halide Glasses	105
9.1	Fluoroberyllates	105
9.2	Glasses Based on ZnCl_2	106
9.3	Fluorozirconate (Fluorohafnate) Glasses	106
10	Chalcogenide Glasses	106
11	Organic Glasses	108
12	Amorphous Metals	108
13	Exercises	109

Chapter 6 Viscosity of Glass Forming Melts 111

1	Introduction	111
2	Viscosity Definitions and Terminology	111
3	Viscoelasticity	115
4	Viscosity Measurement Techniques	117
4.1	Rotation Viscometers	118
4.2	Falling Sphere Viscometers	118
4.3	Fiber Elongation Viscometers	119
4.4	Beam-Bending Viscometers	119
4.5	Other Viscometers	120
5	Temperature Dependence of Viscosity	120
5.1	Fragility of Melts	121
5.2	Free Volume Model for Viscous Flow	123
5.3	Entropy Model for Viscous Flow	123
6	Compositional Dependence of Viscosity	124
6.1	Silicate Melts	124
6.2	Borate Melts	126
6.3	Germanate Melts	128
6.4	Halide Melts	130
6.5	Chalcogenide Melts	130
6.6	Effect of Hydroxyl on Melt Viscosities	131
7	Effect of Thermal History on Viscosity	131

8	Effect of Phase Separation on Viscosity	132
9	Effect of Crystallization on Viscosity	134
10	Summary	135
11	Exercises	136

Chapter 7 Density and Thermal Expansion 138

1	Introduction	138
2	Terminology	138
3	Measurement Techniques	140
3.1	Density	140
3.2	Thermal Expansion Coefficients	141
4	Density and Molar Volume	142
4.1	Compositional Effects	143
4.2	Thermal History Effects	147
4.3	Effect of Phase Separation and Crystallization	150
4.4	Radiation Effects	150
4.5	Pressure Compaction	151
5	Thermal Expansion Behavior	151
5.1	Fundamentals of Thermal Expansion Behavior	152
5.2	Compositional Effects on Thermal Expansion Coefficients of Homogeneous Glasses	154
5.3	Phase Separated Glasses	158
5.4	Thermal History Effects	159
5.5	Effect of Crystallization	160
6	Summary	161
7	Exercises	161

Chapter 8 Transport Properties 163

1	Introduction	163
2	Fundamentals of Diffusion	163
3	Ionic Diffusion	166
4	Ion Exchange	168
5	Ionic Conductivity	169
5.1	Compositional Effects	169
5.2	Activation Energy for Electrical Conductivity	174
5.3	Effect of Phase Separation on Electrical Conductivity	175
5.4	Effect of Thermal History on Electrical Conductivity	176
5.5	Effect of Crystallization on Electrical Conductivity	176
6	Chemical Durability	176
7	Weathering	179

8	Gas Permeation and Diffusion	180
9	Diffusion-Controlled Reactions	184
10	Summary	186
11	Exercises	186

Chapter 9 Mechanical Properties 188

1	Introduction	188
2	Elastic Modulus	188
3	Hardness	190
4	Fracture Strength	191
4.1	Theoretical Strength of Glasses	191
4.2	Practical Strengths of Glasses	191
4.3	Flaw Sources and Removal	192
4.4	Strengthening of Glass	193
4.5	Statistical Nature of Fracture of Glass	195
5	Fatigue of Glasses	196
6	Thermal Shock	197
7	Annealing of Thermal Stresses	199
8	Summary	200
9	Exercises	200

Chapter 10 Optical Properties 202

1	Introduction	202
2	Bulk Optical Properties	202
2.1	Refractive Index	203
2.2	Molar and Ionic Refractivity	205
2.3	Dispersion	207
3	Ultraviolet Absorption	208
4	Visible Absorption	209
4.1	Ligand Field Coloration of Glasses	209
4.2	Amber Glass	211
4.3	Colloidal Metal Colors	211
4.4	Colloidal Semi-Conductor Colors	214
4.5	Radiation-Induced Colors	214
4.6	Solarization	215
5	Infrared Absorption	215
5.1	Infrared Absorption by Bound Hydrogen Species	216
5.2	Infrared Absorption by Dissolved Gases	216
5.3	Infrared Cutoffs or the Multiphonon Edge	217

6	Other Optical Properties of Glasses	218
6.1	Photosensitive and Photochromic Glasses	218
6.2	Opal Glasses	219
6.3	Faraday Rotation	220
7	Summary	220
8	Exercises	221

Chapter 11 Water in Glasses and Melts **222**

1	Introduction	222
2	Effect of Water on the Infrared Spectra	222
2.1	Network Glasses	223
2.2	Other Silicate Glasses	224
2.3	Silane in Glasses	225
2.4	Dissolved Molecular Hydrogen	225
2.5	Isotope Effects	225
3	Formation of Hydroxyl	226
3.1	Reaction with Water	226
3.2	Reaction with Hydrogen	227
4	Diffusion and Solubility of Water in Glasses and Melts	228
4.1	Water Diffusion Measurements in Glasses	228
4.2	Water Diffusion Measurements in Melts	228
4.3	Water Solubility Measurements	229
4.4	Effect of Composition on Water Diffusion and Solubility	230
5	Effect of Water on Properties of Glasses	232
5.1	Glass Transformation Temperature and Viscosity	232
5.2	Density and Refractive Index	234
5.3	Other Properties	235
6	Summary	235
7	Exercises	236

Chapter 12 Thermal Analysis of Glasses **237**

1	Introduction	237
2	Differential Scanning Calorimeters	237
3	Glass Transformation Temperature	239
4	Fictive Temperatures	241
5	Specific Heat Measurements	242
6	Crystallization	244
6.1	Isothermal Crystallization Rates	244
6.2	Dynamic (Non-Isothermal) Crystallization Rates	245
6.3	Pseudo-Nucleation Rate Curves	245
6.4	Independent Determination of Avrami Parameter	246

7	Viscosity	247
8	Summary	248

Chapter 13 Glass Technology 249

1	Introduction	249
2	Classical Forming Methods	249
2.1	Containers	249
2.2	Flat Glass	250
2.3	Glass Fibers	252
2.4	Glass Tubing and Rod	253
2.5	Solid and Hollow Glass Spheres	253
2.6	Lamp Glass	254
3	Specialized Forming Methods	254
3.1	Optical Fibers	254
3.2	Glass-Ceramics	256
3.3	Porous Glass	257
3.4	Dental Products	257
3.5	Sealing and Solder Glasses	258
3.6	Vitreous Silica Products	259
3.7	Sol-Gel Processing	260
4	Summary	260

Chapter 14 Compositions and Properties of Commercial Glasses 262

1	Introduction	262
2	Vitreous Silica	263
3	Soda-Lime-Silica Glasses	264
4	Borosilicate Glasses	266
5	Glass Fibers	267
6	Television Tube Glasses	269
7	Glass-Ceramics	271
8	Other Commercial Glasses	273
9	Summary	274

Bibliography 275

Subject Index 283