

ENCYCLOPEDIA OF Glass Science, Technology, History, and Culture

VOLUME 1

EDITED BY
PASCAL RICHET

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VOLUME

1

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**Encyclopedia of Glass Science,
Technology, History, and Culture**

Encyclopedia of Glass Science, Technology, History, and Culture

Volume I

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Published simultaneously in Canada.

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Library of Congress Cataloging-in-Publication data applied for

ISBN: 978-1-118-79942-0

Cover Design: Wiley

Cover Images: Courtesy of S. Di Pierro, Saint-Gobain Research Paris; Christian Patzig, Fraunhofer Institute for Microstructure of Materials and Systems, Halle Germany; Dominique de Ligny, Friedrich Alexander Universität Erlangen-Nürnberg; Nicolas Villeneuve, Université de La Réunion

Set in 10/12pt Warnock by SPi Global, Pondicherry, India

10 9 8 7 6 5 4 3 2 1

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Preface



When art meets glassmaking: the visit of the Duchess of Berry (1798–1870) in 1824 to the plate-glass factory of the Royal Manufacture of Saint-Gobain as depicted by Édouard Pingret (1788–1869). The stifling heat, the noise of the furnaces, and the danger for the workers of the molten glass poured from the pot and spread with the steel roller on the large table (Chapter 10.9) have all vanished. Only the theatrical aspect of the scene remains, highlighted by the tall curtain, the duchess's light-colored dress echoing the worker's white smocks, and the children watching the show from the balcony. *Source:* Photo courtesy Saint-Gobain Archives.

The *Encyclopedia* has been designed to satisfy the needs and curiosity of a broad audience interested in the nature, properties, fabrication, and history of glass and looking for consistent, comprehensive, and up-to-date information in a single book. More than 100 chapters involving even more glass experts have been written in a perspective that combines the various aspects of this unique material, be they scientific, technological, industrial, historical, or cultural. Whether coming from academia or industry, the authors have in common a long practice of glass. Their goal is to be informative without being pedantic, to be concrete without being boring, and to give a balanced overview of the field – in a word, to allow a large readership to understand both the amazing properties of the vitreous state and its peculiarities compared with those of other states of matter. Excluding the so-called spin glasses and other kinds of disordered physical systems, the *Encyclopedia* restricts itself to what is now termed *structural* glass.

In all chapters, the authors discuss glass from a materials-science standpoint, but their purpose is not to review in any detail the latest advances of interest to specialists only. Rather, in the form of scholarly introductions, it is to present every topic at a uniform level and in a self-consistent manner. In this way, the main points will be grasped and key information of fundamental or practical use will be made available. The neophyte reader will then be able to consult the specialized literature and, in particular, the select bibliography appended to each chapter.

This approach does not imply that only elementary features are presented, but that concepts are appropriately introduced and any technical information clearly explained so as to avoid the common defect underlined in 1911 by the astronomer Percival Lowell (1855–1916) who emphasized in *Mars and its Canals* that “nothing in any branch of science is so little known as its articulation, — how the skeleton of it is put together, and what may be the mode of attachment of its muscles.” Whereas a very few chapters give a flavor of current technicalities involved in glass research, newly investigated topics are also considered with the goal of ensuring that the *Encyclopedia* remains a useful reference over an extended period of time. Although those views that are at this moment very speculative are generally not discussed at length, they may be stated in the final *Perspectives* of the chapters.

Given the diversity of topics treated, the name of *Encyclopedia* (*Kuklos paideia*, cycle of enlightenments, in Greek) is particularly appropriate. The surprising fact is that such a reference work was not existing at all for glass, in general, even though more than hundreds of thousands of encyclopedias have now been devoted to any topic worth of attention, including glass art in particular. The

Encyclopedia consists of 10 sections preceded by a general introduction and concluded by a postface. It begins with glassmaking and continues with structural, physical, and chemical properties. The stage is then set to turn to issues pertaining to light, to the main inorganic glass families, to organically related glasses, to environmental and other industrial issues, and, finally, to the main facets of the rich glass history. Even in more than 100 chapters, it has not been possible to deal with every important topic relevant to glass. A few more chapters would have been welcomed, but their advantages would not have outweighed the inconvenience of a longer publication time, especially for the *Encyclopedia* contributors.

Each section is preceded by a short introduction summarizing in a few sentences the contents of its chapters for helping readers to decide which ones fit their own interest best. Another purpose of these introductions is to show that, from the first to the last, the chapters are telling a consistent story. Although efforts have been made to avoid overlap, some limited duplication was inevitable to make sure that most contributions could be read independently of the others. Of course, boundaries between chapters or sections are not always clear-cut, so that some arbitrariness has been involved in their delineation. And whereas the scientific and technology contents of the chapters will probably speak for themselves, it might be useful to note that historical aspects are dealt with not only in the last section but also elsewhere each time they can help to open deeper perspectives. As for the *Culture* included in the title of the *Encyclopedia*, it is explicitly treated only in the very last chapter but pervades a great many others, for example, in the history section where beautiful pieces of art are in particular reproduced.

At the end of this endeavor, it is now a pleasure to acknowledge (i) the encouragement initially provided by R. Conradt, N.G. Greaves, J. Livage, J. Lucas, B. Mysen, A. Takada, and Y. Yue when the project took shape; (ii) the warm welcome this project received through G. Geiger and A. Lekhwani when submitted to the American Ceramic Society and John Wiley & Sons; (iii) the invaluable help then brought all the way by Reinhard Conradt and Akira Takada through their constant advice, support, friendship, and careful reviewing work; (iv) the great many graphics and pictures neatly prepared by Joël Dyon to highlight the matter presented in numerous chapters; (v) the efforts of 151 authors working in 23 countries who participated in this ambitious endeavor and went responsively throughout an editorial process aimed at ensuring an overall homogeneity of style and content, and incorporated in their texts the relevant historical and cultural aspects evoked by the *Encyclopedia* title; (vi) the thoughtful comments and apt observations provided

by nearly 200 reviewers whose names are included at the beginning of every chapter to recognize publicly their contributions; (vii) the original pictures or help in different matters generously provided by colleagues, friends, and institutions whose names are mentioned at the relevant places; (viii) the Humboldt Stiftung, the Ludwig-Maximilians-Universität, and Donald Dingwell for the fruitful work done in Munich; (ix) the so many things about glass or high-temperature techniques and processes discussed over the years with T. Atake, J.-L. Bernard, Y. Bottinga, R. Conradt, K.-U. Hess, R. Kerner, B. Mysen, G. Ottonello, J.-P. Petitot, J. Roux, A. Sipp, J.F. Stebbins, A. Takada, C. Téqui, and other colleagues too numerous to be mentioned; (x) the Table of ion data compiled by J.F. Stebbins, the help provided at various stages of this study by É. Fareau, B. Gasparyan, K.-U. Hess, A. Hofmeister, K. Meliksetian, B. Mysen, and M. Wolf as well as thoughtful comments by J.M. Parker and R.F. Tournier on the section introductions; (xi) and finally Michael Leventhal who oversaw the project at Wiley, Stefanie Volk for copy editing and Viniprammia Premkumar for smooth and responsive production of the book.

The *Encyclopedia* is dedicated to them and to all people whose efforts throughout the ages made glass the astonishing, ubiquitous material it has become.

Select Additional Reading

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General Introduction

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Figure 1 Obsidian core found in the sixth to fifth millennia BCE Aknashen Neolithic site in Armenia. As indicated by the *flake scars*, large flakes were detached in a single final strike by an experienced stone knapper. Source: Photo P. Richet.

1 A Historical Random Walk

1.1 The Glass Age

“Among the so many, so varied products, which attest to the industrial genius of mankind, there are very few that have uses as numerous as *glass*, whose properties are so wonderful,” pointed out in 1868 Georges Bontemps (1799–1883), a famous nineteenth-century glassmaker [1], who added: “no matter could replace glass in the most important of its uses.” At the same time, the great popularizer Louis Figuier (1818–1894) stated that it would be too long to list “the services that glass provides to science, the arts, industry, domestic needs, to the individual acts of man in society, to the poor and the rich, to the ignorant and to the learned.” Stressing that “household economics, science, civilization, progress and well-being, we owe almost all this to glass,” Figuier concluded that “born with primitive societies, glass will only disappear with civilization” [2].

Certainly, Bontemps and Figuier could not have guessed that organic polymers known as *plastics* would replace mineral glass in some of its traditional uses. Ironically, however, not only has mineral glass found many more, such as light guide in optical fibers (Chapter 6.4) or scaffold for bone regeneration (Chapter 8.4) to name only two of the latest, but most organic polymers are also glasses in the physical sense of the term. Since its very first origins, the vitreous state has thus opened astonishing ways to create original materials, to satisfy the most diverse needs and even to discover the world at large.

Unlike other well-established materials, glass has gone through more developments in the past 50 years than in two millennia from both industrial and technological standpoints. Whether overwhelming in the glazing of skyscrapers or hidden in telecommunication networks, glass has become still more ubiquitous in the modern environment than at Bontemps and Figuier’s time so that claiming that we are now living in the *Glass Age* is not an overstatement [3, 4]. Whereas original glass compositions have, for instance, been designed for innovative lighting, screen, and display applications (Chapters 6.9 and 6.10), even the traditional products used for glazing and containers are now taking advantage of various new functionalities (Chapters 6.7 and 6.8). But what might be the most fascinating modern feature of glass is the way in which the material can be engineered to satisfy the most opposite requirements. Long celebrated for light transmission (Chapter 6.1), glass can be made opaque to a wide range of electromagnetic radiations from infrared to X-ray wavelengths through addition of appropriately absorbing elements (Chapters 3.13 and 6.2). Chemical inertness is

another major traditional asset of glass, which is in contrast purposely avoided in *water glass* (Chapter 7.5) and bioactive glasses (Chapter 8.4) whose usefulness rests on their intrinsically high chemical reactivity. And whereas extremely low impurity levels are required in optical fibers and other optoelectronic devices (Chapters 6.3–6.6), storage of municipal and nuclear waste relies on the capacity of glass matrices to incorporate large amounts of a great many elements (Chapters 9.10 and 9.11).

Additional examples are not needed here to illustrate further the point as they will be found in numbers in the *Encyclopedia*. It is more appropriate to stress that most of these engineering developments have relied on the improved understanding of the glassy state brought by a better knowledge of its physical, chemical, and structural properties. What a long way has therefore been traveled since man made acquaintance with a strange, dark rock differing from all others by its luster and especially, when split into pieces, by its extremely sharp edges that even flint could not match!

1.2 An Economic Forerunner

Obsidian (Figure 1), a natural glass found in volcanic provinces in various parts of the Earth, has been known from time immemorial. From arrowheads (Figure 2) to blades of any kinds and purposes (Figure 3), its unique properties made it so valuable to hunter-gatherers that it was the very first item to be extensively exchanged over long distances [5]. Well before any man-made object was produced, obsidian thus embodied at an early stage of human evolution the economic notion of competitive advantage, which eventually resulted in its real trade (Chapter 10.1). At the heart of a dynamic corridor between Eurasia and Africa, present-day Armenia played a significant role in this history as a material source for a wide area in the Near East, initially through moving communities that were carrying their tools with them [6]. Armenia is also important because of the new light it has recently shed on the far-reaching issue of the expansion of archaic *Homo sapiens* out of Africa.

According to a claim often made, this expansion followed the important technical change from bifacial to Levallois technique of stone knapping (Figure 3, cf. [7] for their differences). At the Nor Geghi-I site, near Yerevan, both types of tools actually coexist within alluvial sediments sandwiched in between lava flows dated to



Figure 2 The delicate stone knapping of an arrowhead made possible by obsidian in Pre-Colombian present-day Arizona. Source: Photo courtesy Alexandra Navrotsky.

441 000 $\pm$ 6 000 and 197 000 $\pm$ 7 000 years [8]. From a fundamental standpoint, the synchronic use of both techniques by a single human group at this site thus indicates instead that, after human dispersion, the transition occurred independently within geographically distinct areas. From a practical standpoint, the change allowed better tools to be obtained so much faster from a large core (Figure 1) and with little waste. One could in fact conclude from the incredibly high abundance of artifacts buried in a Middle-Paleolithic site such as Barozh 12 [9], next to the Arteni Complex Volcano (Eastern Armenia), that the concept of disposable object was born with obsidian in the Paleolithic!

Man-made glass appeared considerably later, only three and a half millennia ago in the Late Bronze Age in a wide area ranging from the Near East to Egypt and Greece (Chapter 10.2). The vividly colored but expensive material newly produced was originally the preserve of elites who had recognized its aesthetic and practical interest. After 15 centuries of technical improvements and decreases of production costs, it became a basic commodity in the Roman Empire as acknowledged by Petronius (first century CE) in the *Satyricon* where one of his characters uttered: “You will forgive me if I say that personally I prefer glass; glass does not smell. If it were not so breakable I should prefer it to gold; as it is, it is so cheap” [10]. This chemical inertness achieved at reduced cost was of course one of the early assets of glass. As we now know, others were resulting from its lack of long-range atomic order, which makes forming in the most diverse shapes and sizes possible, produces optical isotropy, gives much flexibility in terms of raw materials and coloring elements thanks to the almost limitless extent of its solid solutions, and is at the source of mechanical properties in principle limited only by the strength of interatomic bonds thanks to the lack of weak grain boundaries.

How was it figured out that glass could completely lose its vivid colors, which first attracted man’s interest, we do not know. The transparency now so closely associated

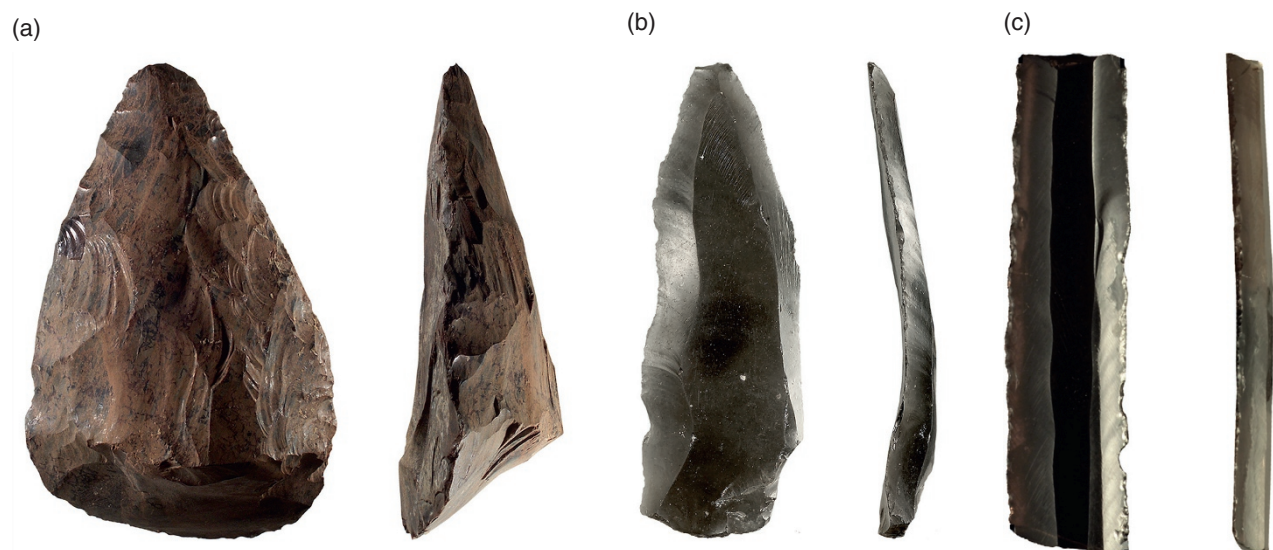


Figure 3 The striking stone-knapping difference between a biface (left) and Levallois point and blade, all made from obsidian (right); length: 20 cm: (a) Acheulean hand axe produced by serial removal of small flakes with a soft hammer (Kuchak-3 open-air site, Aparan Depression, Central Armenia); (b) Levallois Mousterian point, with its plano-convex profile, produced before the reparation of core convexities, and the recurrent method, in which multiple Levallois flakes are detached before reparation (Barozh-12 open-air site, Ararat Depression, Eastern Armenia); (c) Regular flake of the Chalcolithic period produced by pressure flaking from a prismatic core with the aid of a lever (Mastara-1 settlement, Ararat Depression). Source: Photos courtesy Boris Gasparyan.

with glass was first achieved for very special pieces such as cups made in Achaemenid Persia in the fifth century BCE (Chapter 10.0, Figure 1a). But it took several more centuries before transparency became common. The existence of pure, natural carbonates commonly termed natron was the key ingredient to achieve it at a large scale at the beginning of our era [11]. Especially in the Levant, the competitive edge acquired by glassmakers thanks to this substance was such that it led to the establishment of a world market: finished items and glass ingots were traded along well-established commercial routes to be exported as far as East Africa and India [12], the ingots to be shaped locally in small workshops (Chapter 10.3). A first glimpse at globalization?

1.3 A Multifaceted Material

Glass has always aroused much curiosity by its virtue of embodying almost unlimited possibilities for transforming matter. Until the end of the nineteenth century, industrial illustrations of such transformations were the metamorphoses undergone by the large glass pieces that were first blown before being opened and flattened to yield flat panes with the neat fire finish required for transparency (Chapter 10.8). Nowadays, who has never been captivated by the work of a blower, by the action of a delicately controlled fire that gives birth to the most surprising shapes and, in a way, makes the material living for an instant? Even the proverbial brittleness of glass is part of this powerful imaginative world: its fracture indeed seems as unpredictable as it is dramatic, as illustrated by a tempered drinking glass suddenly exploding after several bounces when falling onto the ground.

To this kind of amazement also contributed early the miracles wrought by glass ever since it first restored sight to visually impaired people in the thirteenth century (Chapter 10.10). It is thus no wonder that Leonardo da Vinci (1452–1519) devoted efforts to design a device for machining eyeglasses. Shortly after, the transparent glazing of windows opened houses on the outside world at about the same time as the telescope and the microscope led to the discovery of the universe from the infinitely large to the infinitely small (Chapter 10.10). Grinding of optical lenses was then extensively practiced by Galileo Galilei (1564–1642) himself and considered a trade worth earning a living by the eminent philosopher Baruch Spinoza (1632–1677). That glassmaking had something special is actually indicated by the fact that, in France, it was long the only trade that the nobility could practice as *gentlemen glassmakers* without losing its special status.

To acknowledge all what civilization was owing to this material, the polymath and glassmaker Mikhail Vasilyevich Lomonosov (1711–1765) wrote in Russia a long poem entitled *Letter on the use of Glass*. “A whole year would hardly suffice me to reach the end of worthy praise for Glass” [13], Lomonosov thus claimed when mentioning not only the telescope, the microscope, or the barometer, but also the thrilling electrical researches of his time based on the accumulation of charges on the glass disks of electrostatic machines (Chapter 10.10). Such was the interest raised by the *vitreous* (positive) and *resinous* (negative) electricities “that people of all genders and ranks were then begging for the favor of being subjected to electric shock, to the point that the noble and courageous Professor Georg Matthias Bose (1710–1761) said with philosophical heroism: *I would not regret dying of an electric shock, since the account of my death would provide the subject of an article in the Memoirs of the Royal Academy of Sciences of Paris*” [14]. Could this admirable *philosophical heroism* have been elicited by a material other than glass?

At the same period, glass became the source of another kind of emotions when the famous Benjamin Franklin (1706–1790) was inspired by “the sweet tone that is drawn from a drinking glass, by passing a wet finger around the rim” [15] to design in 1761 the *glass armonica* whereby it was a set of overlapping wet glass cones of different sizes that was rotating to emit a *sweet, ethereal, or pathetic* tone through the friction of fingers. The instrument met with rapid success such that, beginning with Wolfgang Amadeus Mozart (1756–1791) [16], quite a few great composers wrote short pieces for it. The fashion for glass was such that a German living in Paris named Beyer presented in 1785 to the Académie des Sciences his *forte-piano* with glass plates, acted upon by wool-covered hammers, which Franklin christened *glass-cord* [17]. And it was a flute made from lead-crystal glass that the Parisian instrument maker Claude Laurent (d. 1848) patented in 1806 and produced in white, cobalt-blue, and uranium-green hues; in spite of its weight, its musical qualities and reduced temperature-induced pitch changes ensured its popularity for several decades [18].

This select series of anecdotes probably makes it unnecessary to emphasize again the importance of glass in daily and social life stressed above by Bontemps and Figuier. It might in contrast be useful to mention that the antique tradition or ornamental glass was revived at the same period by Georges Frédéric Strass (1701–1773), who became the French King’s jeweler, when he invented *strass*, or *rhinestone*, a high-lead crystal glass bearing various metal oxides that is still made today to imitate precious stones.

1.4 The Silica Paradoxes

1.4.1 Biogenic Silica vs. Flint

Historically, glass owes its importance to silicates. But what substances could have replaced silicate glasses in their diversity of uses on a silicon-free planet? The question would be moot if carbon – the next of kin of silicon in the Periodic Table – and, therefore, life and human beings would have also been lacking. More seriously, however, reflecting on the origin of the silica sources used in glassmaking is not a futile exercise.

It is not widely known that 15 billion tons of *biogenic* silica glass are yearly produced in seawater by diatoms, sponges, and some other living organisms. Such a biological production has major effects on the Earth's global ecosystem and has now become a *biomimetic* source of inspiration for designing wholly new materials (Chapter 8.1). Interestingly, biogenic silica also had noteworthy implications for glassmaking because of its recycling into the opal or microcrystalline quartz of *flint*. Flint, or *chert* as it is called in geology, is commonly found as abundant nodules horizontally embedded in limestone (Figure 4). Its deposition thus requires carbonate

dissolution followed by silica precipitation and, thus, percolating waters undersaturated with respect to calcium carbonates but oversaturated with respect to silica. Without going into the details of the process and of its control by pH and geological context [19, 20], it will suffice here to state that biogenic silica accumulating at the bottom of the sea is the source of the dissolved silica that reprecipitates as flint. And it happens that flint was the raw material used in England from the seventeenth century to remedy the lack of sand pure enough for making optical glass and luxury ware (Chapter 10.10).

In passing, one can also note that silica has been biogenically produced relatively late in evolution compared with calcite and aragonite, the main CaCO_3 polymorphs, but then met with immense success especially with diatoms. A major reason was the advantages of an amorphous compared with a crystalline substance in terms of optical or mechanical properties for the materials protecting the living organisms (Chapter 8.1); amorphous calcium carbonates do exist, but they serve instead as intermediate reaction steps, which are short lived and thus end up crystallizing [21], which is not surprising as molten CaCO_3 is

Figure 4 The abundant beds of black flint present in a 80-m high limestone cliff of the English Channel at the Pointe du Chicard in Yport (Normandy). Same beds of the Upper Cretaceous used in the past for making *flint* glass in England on the other side of the Channel. Height visible on the picture: 10 m. Source: Photo P. Richet.



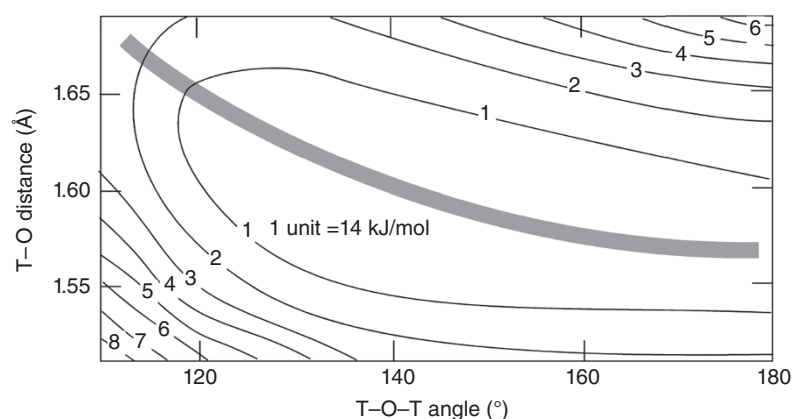


Figure 5 The strong contrast between the potential energy changes induced by variations of Si-O distances and S-O-Si angles indicated by the calculated surfaces of constant energy of $\text{H}_6\text{Si}_2\text{O}_7$ clusters. Source: After [23].

not itself a good glass-forming liquid. Interestingly, formation of biogenic silica would have first been a way to evacuate toxic Si at too high concentrations from cells. By a twist of evolutionary history, it would have become a protecting device so efficient for organisms [22] that it has since then played a major role in the global ecosystem, causing, for instance, the Si concentrations to be so low in seawater.

1.4.2 A Quantum-Chemical Factory: The Production of Silica Sand

Although glassmaking would have been possible without sand, it is unlikely that flint would have led to the invention of glass as it requires thorough grinding to become a reactive raw material. Regardless of grinding costs, it is also doubtful that flint would have been a silica resource widespread and convenient enough for an expanding glass industry. The fundamental importance of silica sand thus remains undisputed. Geologically, sand is produced via the weathering of granite and related SiO_2 -rich igneous rocks. The most abundant rock of the Earth's crust, granite is made up of quartz and alkali $[(\text{Na},\text{K})\text{AlSi}_3\text{O}_8]$ and plagioclase $[(\text{Na}_x, \text{Ca}_{1-x})\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_8]$ feldspars. Whereas feldspars progressively transform into clay under the action of meteoric waters, quartz resists and accumulates as sand either on the spot or downstream.

The very presence of quartz at the Earth's surface appears to be a clear geochemical anomaly, however, which thus deserves some explanation. With typical 75 wt % SiO_2 , the melts from which granite crystallizes represent the end products of *magma differentiation* (Chapter 7.2). Owing to their very high viscosities, they rarely rise up to the Earth's surface to erupt as obsidian flows but crystallize slowly instead at some depth to yield large-grained rocks. These melts are the last produced after partial crystallization of primary magmas, which form themselves deep in the Earth's mantle by partial melting of SiO_2 -poor, MgO -rich rocks (~45 wt % for both oxides, along with ~7 % FeO , 2 % Al_2O_3 , 1 % CaO , and a few % at most alkali oxides). Because oxygen bonds more

strongly with silicon than with the other elements (Table A.1), one might think that SiO_2 -rich minerals should be the most refractory. As a result, the SiO_2 content of primary magmas should be lower than that of their source rock and decrease further through partial crystallization on their way up to the Earth's surface. Such a trend is opposite to the SiO_2 increase observed. It is in contrast consistent with the fact that cristobalite, the high-temperature polymorph of SiO_2 at room pressure, is less refractory than lime (CaO), periclase (MgO), and even forsterite (Mg_2SiO_4) whose melting temperatures are about 600, 800, and 175° higher than the 2000 K of cristobalite, respectively.

The paradox lies in the fact that bond strengths are usually considered within the framework of ionic forces, which are by definition nondirectional. Now, directionality is an inherent feature of Si-O bonding in view of its markedly covalent character. Because electron delocalization through polymerization and creation of Si-O-Si linkages is not large enough to constrain geometrically the arrangements of the SiO_4 tetrahedra, the same energy variations are, for instance, caused in $\text{H}_6\text{Si}_2\text{O}_7$ clusters by a small 0.02 Å change of the Si-O bond length and by a large 20° modification of the O-Si-O inter-tetrahedral angles (Figure 5). Bending of these linkages is thus so easy that configurational rearrangements take place without involving much energy [24]. The fact is most simply illustrated by the transitions of α -quartz and α -cristobalite to their dynamically disordered β -forms near 573 and 250 °C, respectively. Hence, fusion of these minerals does not require the breaking of bonds involved in ionic crystals. The SiO_2 enrichment and resulting quartz crystallization induced by magma differentiation are thus mainly driven by the sp^3 hybridization of silicon orbitals, which causes largely polymerized crystals to melt at temperatures much lower than would be expected from the Si-O and Al-O bond strengths [24]. In other words, the existence of silica sand originates in a quantum-chemical effect, without which glassmaking would not have existed.

2 Some Basic Concepts of Glass Science

2.1 From Metastability to Relaxation

The silica issue illustrates how answers to apparently simple problems can require in-depth analyses for which theoretical concepts presented in various chapters of the *Encyclopedia* should prove useful. To help readers whose knowledge of the glassy state is minimal, however, the rest of this introduction will be devoted to a brief presentation of some basic concepts pertaining to glass and nonequilibrium systems, which will thus not need to be commented upon in specific chapters.

In preamble, it would be useful to define precisely what a glass is before discussing any of its properties. In accordance with its intrinsically disordered nature, however, glass might be pleasantly defined as a material that is difficult to define in an unambiguous or fully consistent manner. In Chapter 10.11, a glass is nonetheless defined as a macroscopically homogeneous amorphous solid whose properties (physical, chemical, or structural) vary with its preparation conditions. Usual definitions differ depending on whether the emphasis is put on the disordered atomic structure of the material or on the existence of a *glass transition* separating a solid material at lower temperature from a supercooled liquid at higher temperatures. Because glass structures depend on the type of system considered, they are described in widely different ways for oxides, metals, or organic polymers so that they do not lend themselves to a brief, general presentation.

Although a glass transition cannot always be observed, its phenomenology and its implications on glass properties are in contrast common not only to all glass-forming liquids, but also to partially disordered systems such as *plastic crystals*. In view of their dual practical and theoretical importance, the main features of the glass transition will thus be summarized here in a qualitative way. Without making any reference to recent advances in the field, the purpose is simply to describe the phenomenology of vitrification and its effects on physical properties, to introduce some of the groundbreaking concepts that have been proposed to account for them, and to highlight some simplifying features thanks to which intrinsically complex glass problems become more tractable.

A main source of difficulty is that the *time* parameter must be considered because of the kinetic nature of the glass transition. In the backdrop is the way in which the Gibbs free energy of a glass-forming liquid would be minimized under given experimental conditions and, thus, the kinetics at which physical properties *relax* after changes in intensive thermodynamic variables (Chapter 3.7). The largest and most rapid decrease of the Gibbs free energy would of course be ensured by crystallization. To bypass it, it has been known from time immemorial that a melt must be cooled rapidly enough.

Other things being equal, vitrification is favored by large freezing-point depressions near eutectic compositions, which result in increased viscosities and reduced thermodynamic driving forces for crystallization.

With very few exceptions (e.g. [25]), however, supercooled liquids do crystallize more or less rapidly upon prolonged annealing. Perhaps also influenced by the early twentieth-century conception that glasses were supercooled liquids (Chapter 10.11), a commonly held assumption is that any glass would eventually crystallize. This assumption is in fact plainly contradicted by the 4.6-billion year old glasses found in meteorites (Chapter 7.1). What has ensured their long-term preservation has been the extremely dry conditions of extraterrestrial space, which have prevented them from weathering. Since their SiO₂-poor compositions would make them prime candidates for ready devitrification, the almost infinite metastability enjoyed by these glasses is especially significant. The crystallization issue will thus be left aside in the following.

2.2 Relaxation: Phenomenological Aspects

Atomic mobility is the hallmark of the molten state as illustrated by the ready flow of a liquid adjusting to the shape of its container. Contrary to crystals where atomic positions are fixed and strongly constrained by long-range symmetry, liquids are characterized by dynamic disorder, i.e. by unceasing atomic rearrangements. This structural incompatibility between a crystal and a liquid makes any progressive transformation of one phase into the other impossible. In contrast, the vitrification of liquids is clearly a continuous process during which disordered structures become frozen in as revealed by progressively increasing viscosities, which eventually becomes so high that the materials have mechanically become a solid.

At high temperatures, the liquid is in internal thermodynamic equilibrium because its properties are time independent and uniquely determined by two intensive variables, usually taken to be pressure and temperature. At high viscosities, however, this simplicity no longer holds true as seen if one exerts a stress on the liquid at constant temperature or change the temperature at constant stress (Figure 6a). For a window glass [26], a constant, equilibrium shear viscosity is, for example, reached more rapidly in the former case than in the latter but this difference does not need to be commented upon here because pressure and temperature changes are of a different nature. Of greater importance is that Boltzmann superposition principle (Chapter 10.11) applies because, if both perturbations are simultaneously exerted, the response of the system is the sum of the two individual responses (Figure 6a).

In practice, temperature changes matter most. When high viscosities are measured at successively lower temperatures and then at higher temperatures (Figure 6b), two conclusions follow: (i) the time needed to reach the

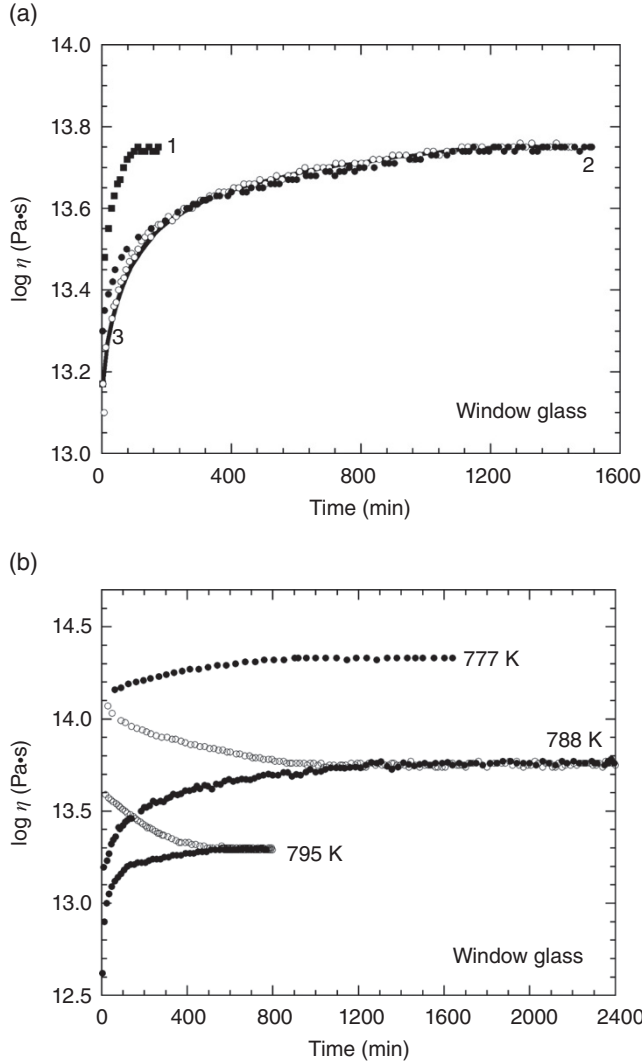


Figure 6 Viscosity relaxation of window glass (Source: Data from [26]). (a) Time dependence of the viscosity at 788 K after: (1) application of a 110 MPa stress; (2) a temperature change from 819 to 788 K with this stress; (3) exerting simultaneously these stress and temperature changes. (b) Attainment of the equilibrium viscosity; sample equilibrated at 795 K, then quickly brought for equilibration at 788 K and at 777 K (open symbols) before following the same procedure for reversing the equilibrium values first measured at 788 and 795 K (open symbols).

constant equilibrium values increases tremendously with decreasing temperatures; (ii) the approach to equilibrium is slower when the sample was previously equilibrated at a lower than at a higher temperature. Hence, the rate at which these changes occur depends not only on temperature but also on the thermal history of the sample, i.e. on the instantaneous structure as well. Because thermodynamic equilibrium is reached when the structure has adjusted to the new intensive parameters, the process is termed *structural relaxation*.

To characterize the rate at which the shear viscosity (η) or any other property Y approaches a new equilibrium value, Y_e , one defines the relaxation time, τ_Y , as

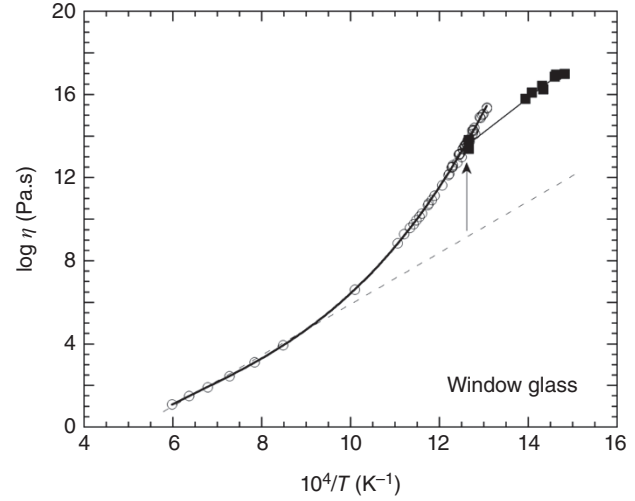


Figure 7 Viscosity of window glass; solid line VFT fit to the data; dashed line: Arrhenius fit made to the high-temperature measurements; arrow: onset of departure from the equilibrium viscosity; solid squares and line: isostructural viscosities. Source: Data from [26, 27].

$$\tau_Y = -(Y_t - Y_e) / (\partial Y / \partial t), \quad (1)$$

where Y_t is the value actually measured at time t . If τ_Y were constant, the relaxation would be exponential:

$$(Y_t - Y_e) = (Y_0 - Y_e) \exp(-t/\tau_Y), \quad (2)$$

where Y_0 is the initial Y value, so that after a time τ_Y , the variation of Y would be a fraction $1/e$ of the initial departure from the equilibrium value. Regardless of the actual non-exponential nature of relaxation, measurements, for example, made on window glass at 777 K point to relaxation times much higher than one hour (Figure 6b). A measurement performed in only a few minutes would thus refer to a fixed configuration, i.e. to a glass. Depending on the timescale of the experiment, one observes that the nature of response is thus either liquid- or solid-like.

The glass *transition range* is that temperature interval where, depending on the timescale of the experiment performed, time-dependent observations are made. It signals the change from the liquid state, where a great many different atomic configurations are unceasingly explored, to another state where atoms become trapped in fixed positions and properties become again time independent. In statistical-mechanical jargon, this change is said to represent the loss of *ergodicity* and, thus, of internal thermodynamic equilibrium.

Experimentally, the loss of equilibrium can be readily followed by viscometry. Over an interval as wide as 10 – $10^{15.5}$ Pa·s, the viscosity of a glass-forming melt can be reproduced empirically with the Vogel–Fulcher–Tammann (VFT) equation (Chapters 4.1 and 10.11):

$$\log \eta = A + B/(T - T_1), \quad (3)$$

where A , B , and T_1 are constants (Figure 7). If only high-temperature measurements are considered, then a simpler Arrhenius equation is generally adequate, viz.

$$\log \eta = \log \eta_0 + \Delta H_\eta / RT, \quad (4)$$

where η_0 is a pre-exponential term and ΔH_η the activation enthalpy for viscous flow. Consistent with the aforementioned effects of thermal history (Figure 6b), the increasing departure of the viscosities from an Arrhenius fit made to the high-temperature data (Figure 7) indicates that, independently of any thermal-energy decrease, the structural rearrangements induced by lower temperatures progressively hinders viscous flow. The effect is still more apparent when measurements are made rapidly such that structural relaxation does not take place. Under these conditions, the *isoconfigurational* viscosity is indeed lower than the viscosity of the equilibrium supercooled liquid at the same temperature (Figure 7).

2.3 The Glass Transition

2.3.1 Standard Glass-Transition Temperature

For the experimental timescales of the order of a few minutes typical of measurements of macroscopic properties, one observes that, regardless of chemical composition, time-dependent results begin to be observed when the viscosity becomes higher than about 10^{12} Pa. For convenience and comparison purposes, one defines the *standard* glass-transition temperature, T_g , as the temperature at which the viscosity of the liquid reaches this value of 10^{12} Pa.s.

2.3.2 Volume Effects

The enhanced thermal expansion coefficient observed upon heating of a glass rod in dilatometry experiments is one of the most familiar manifestations of the glass transition (Figure 8a). The marked increase over an interval of about 50 K is rapidly followed by sample collapse because the viscosity rapidly decreases so much that the sample begins to flow under its own weight before structural relaxation is complete. As a result, the volume thermal expansion coefficient [$\alpha = 1/V (\partial V / \partial T)_P = 3/l (\partial l / \partial T)_P$] may be rigorously determined from the slope of the dilatometry curve for the glass, but not for the supercooled liquid.

In dilatometry experiments, one usually defines the glass-transition temperature as the intersection of the tangents to the lower- and higher-temperature curves. This temperature generally differs somewhat from the standard T_g simply because the glass transition depends on the particular experimental conditions of the experiment. With respect to enthalpimetry, dilatometry has the advantage of yielding absolute values of the property of interest, namely, the volume (and density). The influence of thermal history on density can thus be readily determined (which is why it was observed as early as in 1845, cf. Chapter 10.11). In contrast, the thermal expansion coefficient of glasses generally does not markedly

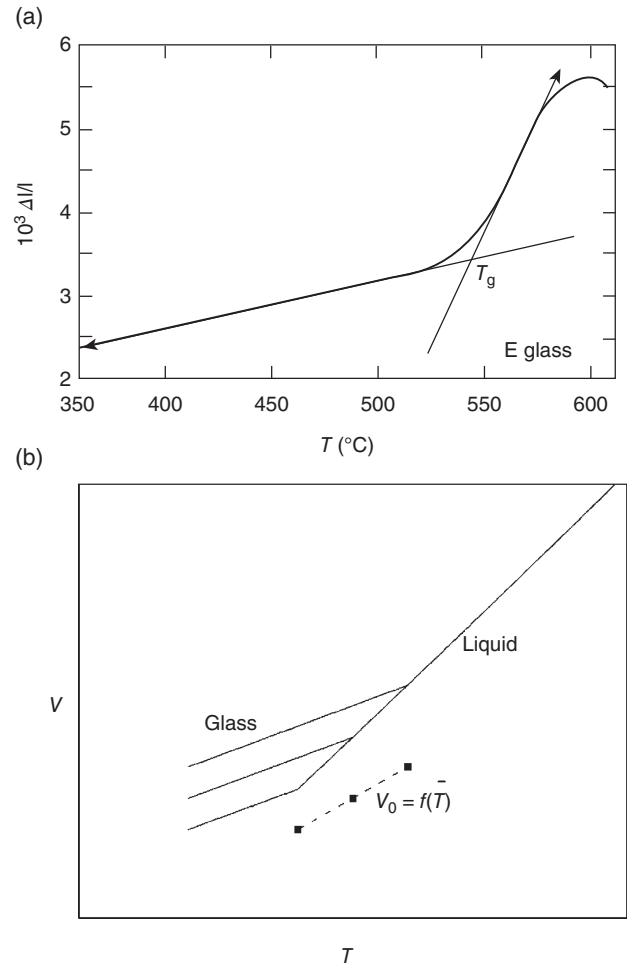


Figure 8 Volume effects of the glass transition. (a) Linear thermal expansion coefficient of E glass (Chapter 1.6) heated at 10 K/min; l = sample length (Source: Data from [28]). (b). Dependence of the volume of a glass on its fictive temperature.

depend on thermal history. At least above room temperature. The volumes of glasses produced at different cooling rates will then plot as a series of parallel lines (Figure 8b). To characterize the state of the glass, it suffices to know the temperature at which equilibrium was lost, which is directly given by the intersection of the glass and supercooled volumes (Figure 8b). This parameter is called the *fictive temperature* ($\bar{T}$), which thus represents the temperature at which the configuration of the glass would be that of the equilibrium liquid (Chapter 10.11). Knowing $\bar{T}$, it is then straightforward to determine the glass volume as a function of the fictive temperature, for example, at room temperature (Figure 8b).

2.3.3 Frequency Dependence

For exploring further the kinetics of the glass transition, one can vary the experimental timescale not only through

changes of the heating rate for a given technique, but through changes of the technique itself. In view of their relative simplicity, acoustic measurements of the adiabatic compressibility are especially interesting in this respect. For an isotropic solid, this compressibility is related to the velocities of compressional (v_p) and transverse (v_s) acoustic waves by:

$$\beta_S = 1/[\rho(v_p^2 - 4/3v_s^2)], \quad (5)$$

where ρ is the density. In a liquid of low viscosity, the attenuation of compressional waves is so rapid that one can usually consider that these waves do not propagate at all, in which case the compressibility reduces to

$$\beta_S = 1/\rho v_p^2. \quad (6)$$

Acoustic measurements are typically made with transducers working at MHz frequencies. Under these conditions, the response of the material to the compression exerted adiabatically by the acoustic waves is probed at timescales of the order of 10^{-6} seconds. To be induced by an acoustic wave, configurational changes must thus take place at timescales at least 10^6 – 10^7 shorter than those of dilatometry or calorimetry experiments. Their onset is thus correlatively observed at much higher temperatures. For a sodium silicate (Figure 9a), they are revealed above 700°C by a temperature interval where

v_p decreases markedly and becomes frequency-dependent. With respect to dilatometry or calorimetry experiments, the glass transition shifts from about 500 to 900°C , with a difference of about 50° between the measurements made at 1 and 5.6 MHz. At higher temperatures, equilibrium values of the compressibility are finally measured near 1100°C when the ultrasonic velocity becomes independent of frequency.

Experiments can be made at even shorter timescales when hypersonic sound velocities are measured by Brillouin inelastic scattering of photons by phonons (Chapter 2.2). At the timescales of the order of 10^{-10} seconds of these interactions, the glass transition shifts to higher still temperatures. For calcium aluminosilicates (Figure 9b), relaxed compressional velocities are typically observed only above 2200°C [30] where they begin to match the values determined by ultrasonic methods (Figure 9b). The first effect noticed when the temperature is increased is a slight kink (at around 750°C in Figure 9b), which disappears if the velocities are plotted against the volume of the sample instead of its temperature. This kink thus signals the increase in thermal expansion at the volume glass transition, whereas structural relaxation at the extremely short timescale of Brillouin scattering experiments becomes significant only at much higher temperatures. Interestingly, the shear sound velocities can then be measured for the supercooled liquid

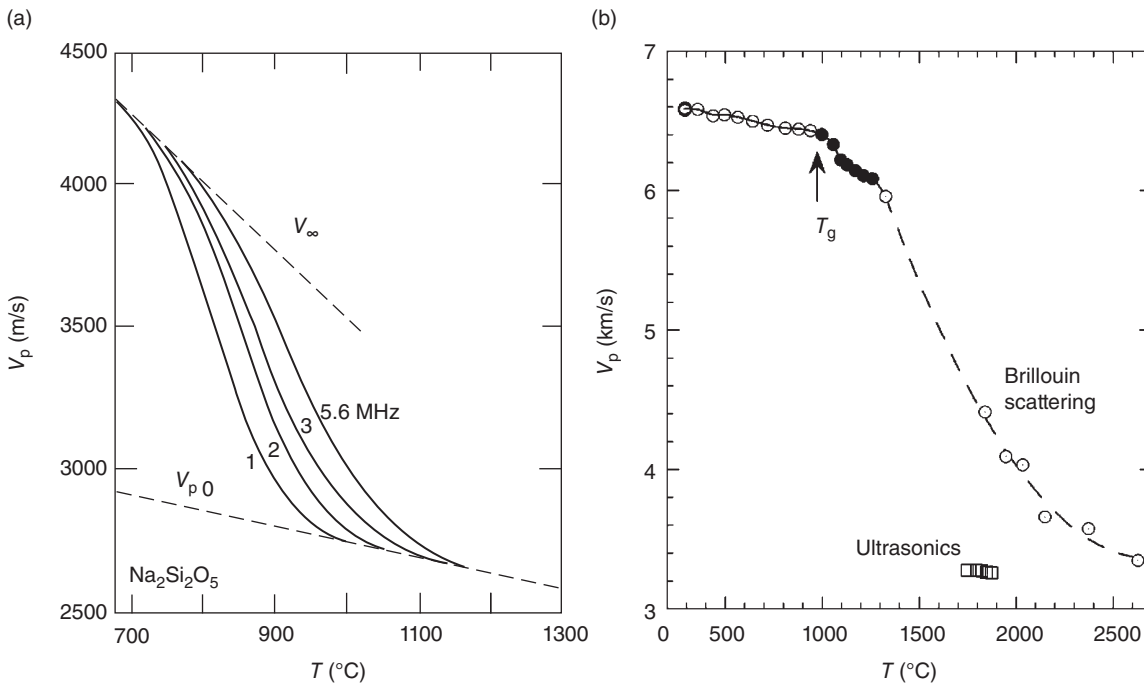


Figure 9 Frequency dependence of the glass transition range. (a) Compressional acoustic-wave velocities of sodium disilicate measured at the frequencies (MHz) indicated (Source: Data from [29]); larger width of the glass transition range than in dilatometry because of the actual distribution of relaxation times. (b) Compressional hypersonic sound velocities measured for $36 \text{ SiO}_2 \cdot 16 \text{ Al}_2\text{O}_3 \cdot 48 \text{ CaO}$ melt (mol %) by Brillouin scattering and ultrasonic methods. Source: Data from [30, 31].

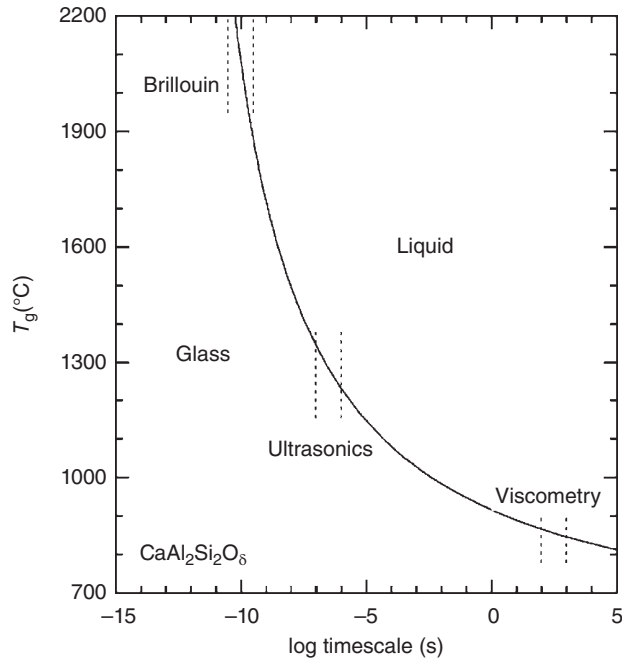


Figure 10 Time dependence of the boundary between the glass and liquid phases of $\text{CaAl}_2\text{Si}_2\text{O}_8$. Source: Data from [32].

well above the standard glass-transition temperature as long as its viscosity is not too low [32]. The material is not really a “glass” because its configuration changes rapidly with temperature, but a “glass-like” material whose solid-like part of its acoustic properties may be probed. Finally, another noteworthy feature of the glass transition range is its markedly increasing width apparent from Figures 8b to 9a and b, which originates in the fact that a distribution of relaxation times, and not a single time, must be considered. Complete relaxation is thus controlled by the slowest mechanisms whose retarding effects are the greatest for the shortest experimental timescales.

In conclusion, the question as to whether a given substance is a liquid or a glass cannot be answered if the observational timescale is not specified. One must consider instead that the transition between the two kinds of phases is represented by a curve in the timescale–temperature plane (Figure 10). The picture is actually still more complex because the glass transition also depends on pressure. With the exception of some open 3-D network structures, T_g generally increases with pressure because an increasing compaction makes configurational rearrangements more difficult. At constant timescale, the glass transition is thus represented by another curve in the pressure–temperature plane (Figure 11). And the description is still more complex if the effects of composition are also considered. If all factors are dealt with together, the glass transition then becomes a

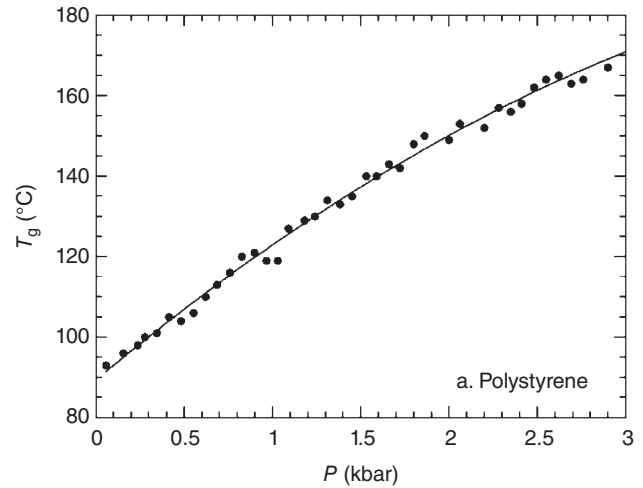


Figure 11 Pressure dependence of the glass transition of atactic polystyrene. Source: Zero-frequency Brillouin scattering data from [33].

hypersurface in the pressure–temperature–composition–timescale space.

2.3.4 An Irreversible Transition

The glass transition was first signaled by anomalous increases of the heat capacity, and its kinetic nature by the dependence of these anomalies on the thermal histories of the samples investigated (Chapter 10.11). Such effects are clearly apparent in early C_p measurements made on B_2O_3 (Figure 12a) where three different temperature intervals are distinguished [34]. Above about 270 °C, the liquid phase is in internal thermodynamic equilibrium because its heat capacity is uniquely defined by temperature (and pressure). In the 270–100 °C interval, internal equilibrium is lost as C_p is no longer defined by temperature only. The measurements made upon heating and cooling differ and C_p differences of up to 20% are found between samples initially cooled rapidly and slowly. Also noteworthy is the fact that the observed C_p hysteresis prevents a reversible thermodynamic pathway from being followed. It points instead to the creation of entropy through cycling in this interval and, therefore, demonstrates the irreversibility of the glass–liquid transformation.

Below 100 °C, C_p depends again only on temperature. If integrated from 270 to 100 °C, however, the C_p and C_p/T differences between the rapidly and slowly cooled samples represent enthalpy and entropy differences, respectively. These are constant below 100 °C as the glass C_p does not depend sensitively on thermal history. They can be readily calculated for any two glasses, like a volume difference, if their fictive temperatures are known (Chapter 3.6). An important conclusion then follows: the existence of an entropy difference at 0 K between

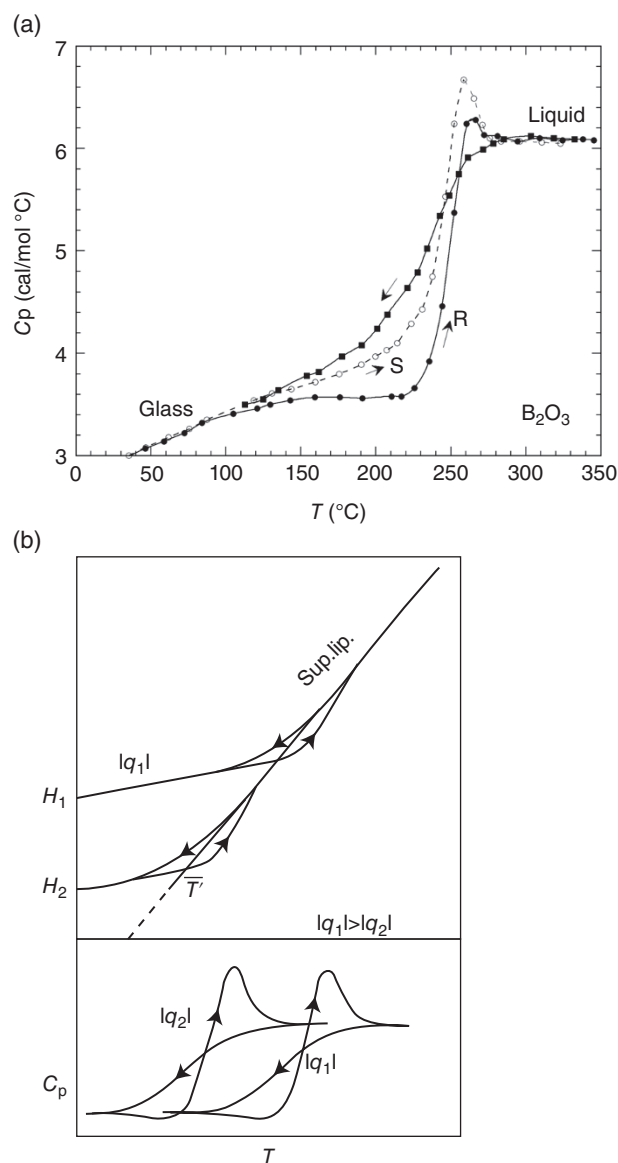


Figure 12 Irreversibility of the glass transition: heat capacity hysteresis measured for boron oxide upon cooling and upon heating of a slowly (S) and rapidly (R) cooled glass [34]. (b) Enthalpy and C_p differences between glasses cooled at different rates q ; Sup. liq.: enthalpy of the equilibrium supercooled liquid.

two samples implies that glasses have a residual entropy at 0 K: hence, glasses do not obey the third Law of thermodynamics because of the irreversible nature of the glass transition (cf. Chapters 3.6 and 10.11).

In more detail, the C_p hysteresis results from the observed contrast between a smooth decrease upon cooling and sharp increases upon heating followed by overshoots right at the end of the transition (Figure 12a). The former decrease simply points to the progressive loss of atomic mobility with decreasing temperatures. Upon

heating, the situation is more complicated because relaxation resumes at the temperature at which it vanished on cooling, but its first effect is to lower the enthalpy of the glass to bring it closer to the equilibrium values of the supercooled liquid (Figure 12b). At higher temperatures, the enthalpy curve of the material has already crossed that of the supercooled liquid when relaxation becomes almost complete at the timescale of the experiment. The heat capacity then increases rapidly (Figure 12b) in a way that depends on thermal history. The rise is highest for samples initially cooled down at the slowest rates, whose enthalpy is initially the lowest, or for samples heated at the highest rates. If the heating and cooling rates are increased, the transition shifts to higher temperatures because the decrease of the experimental timescale must be matched by an analogous decrease of the relaxation time (Figure 12b).

Determination of a glass-transition temperature is more complicated in calorimetry than in dilatometry because of the complex shapes of the observed C_p variations or even of the endothermic peaks recorded in thermal analysis. This temperature may, for instance, be taken as the inflection point of the C_p increase upon heating, but it can alternatively be defined in different ways so that is generally needed to specify which particular one has been selected [35].

2.3.5 The Case of Plastic Crystals

This description of the glass transition applies to a variety of kinetically controlled processes in crystals. *Plastic crystals*, characterized by low entropy of fusion and an unusually high plasticity, are good examples of disordered systems with three-dimensional long-range order. When the high-temperature form of cyclohexanol (ChI), for instance, crystallizes at 299 K, the $C_6H_{12}O$ molecules order in a face-centered cubic lattice but their regular shape allows them to maintain orientational mobility by rotations around the lattice points. It is through a transition to the low-temperature polymorph (ChII), which is stable below 265 K, that this dynamics vanishes and the orientational disorder disappears [36]. With rapid cooling rates, the ChI form can be obtained metastably and kept for long periods of time below 180 K. On further cooling, a transition is eventually observed near 160 K (Figure 13). The orientational disorder of $C_6H_{12}O$ molecules is then frozen in within the crystal. In contrast to the ChII form, whose entropy is zero at 0 K, ChI has a residual entropy of 4.7 J/mol K. The similarity with the glass transition phenomenology is such that the name of *glassy crystals* has been proposed for crystals where rotation of molecular groups is freed above a glass-like transition temperature and gives rise to relaxation

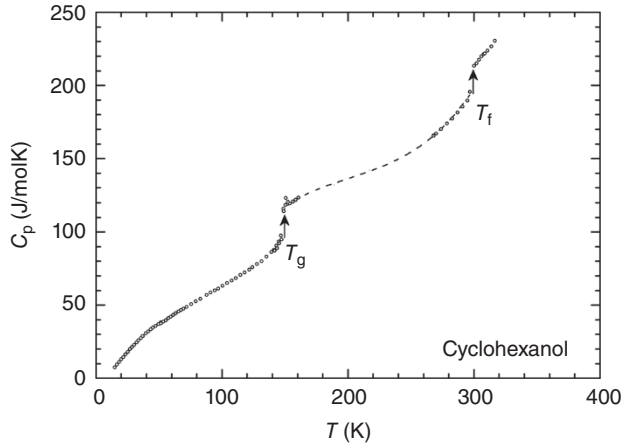


Figure 13 The calorimetric signature of orientational disorder in cyclohexanol plastic crystal. Measurements made upon heating with a gap from slightly above the glass-transition temperature T_g and the melting temperature T_f because of rapid transformation into the stable, ordered polymorph. Source: Data from [36].

phenomena much more complex than summarized here (Chapter 8.6).

2.3.6 Maxwell Model

In view of the continuous pathway between the liquid and glass states, glass-forming liquids cannot be purely Newtonian when they approach the glass transition. In fact, they are *viscoelastic*, with an elastic component that becomes increasingly important near T_g . More precisely, application of a shear stress first causes an elastic strain, which would be recovered if the stress were released, and then a viscous deformation. The response of a viscous melt subjected to stress thus is made up of an instantaneous, elastic response along with a delayed response. By combining the simplest representations of elasticity and viscous flow, Maxwell model has as a mechanical analogue a spring and a dash pot placed in series [37]. Its important result is that, if stresses are applied at low frequencies, as usually the case in viscometry, then a simple relationship holds between the viscosity, relaxation time, and shear modulus at infinite frequency (G_∞),

$$\eta = G_\infty \tau. \quad (7)$$

The fact that the glass transition is observed at values close to 10^{12} Pa.s for widely different kinds of liquids thus indicate that G_∞ also weakly depends on composition, with a mean value of about 10 GPa, which varies by less than a factor of 10 with either temperature or composition at least for oxide glass-forming liquids [38, 39]. Compared with the tremendous variations of viscosity with temperature and composition, G_∞ thus is almost constant. If the viscosity is known, structural relaxation times can be readily estimated from Eq. (7).

2.4 Configurational Properties

2.4.1 Equivalence of Relaxation Kinetics

It is usually more difficult to account for the kinetics of a reaction than for its thermodynamics. Relaxation in glass-forming systems does not depart from this rule. Whereas a single-order parameter such as the fictive temperature may be appropriate for characterizing the volume or enthalpy of a glass, relaxation kinetics requires models much too complex to be discussed here (see Chapter 3.7). One can nonetheless have a first look at the mechanisms involved in relaxation by examining whether their kinetics varies or not with the particular property considered.

As done for viscosity, the kinetics of volume equilibration can, for instance, be measured by isothermal dilatometry experiments. If samples with the same thermal history are studied, comparisons between the relaxation kinetics of different properties can be made in terms of normalized variables

$$Y = (Y_t - Y_\infty)/(Y_0 - Y_\infty), \quad (8)$$

where Y_t , Y_∞ , and Y_0 are the property Y at time t , initial time, and equilibrium, respectively. To within experimental errors, experiments on E glass, for example, show in this way the same kinetics for viscosity and volume (Figure 14).

More general conclusions are readily derived from comparison between different glass-transition temperatures even though these are not necessarily defined in the same way in different kinds of measurements. What is important is that they be defined consistently and refer to samples with the same thermal histories. For volume

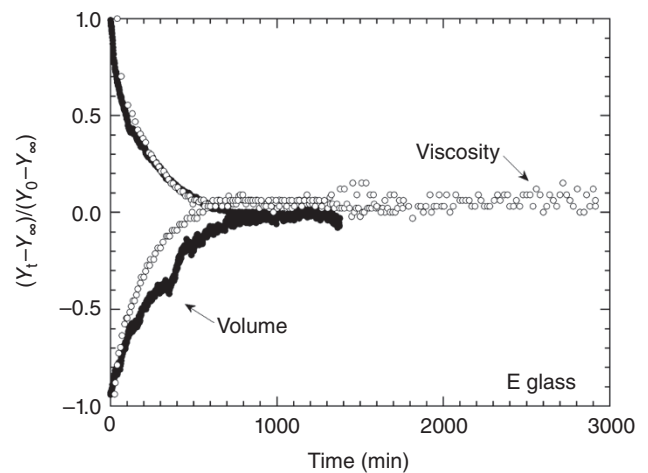


Figure 14 Kinetics of equilibration for the viscosity and volume of E glass. Differences between the ascending branches mainly due to the uncertainties on the Y_0 values caused by unrecorded relaxation during the initial thermal equilibration of the sample. Source: Data from [28].

and enthalpy, the latter condition is fulfilled in dilatometry experiments and differential thermal analyses performed simultaneously, whose results can also be compared with standard glass-transition temperatures (Figure 15). The close 1 : 1 correspondences found in this way for the three temperatures of silicates, calcium aluminosilicates, titanosilicates, and borosilicates over a 400 K

interval thus confirm the equivalence of the relaxation kinetics for differing properties [28]. In other words, one must conclude that the same configurational changes are involved in enthalpy, volume, or viscosity relaxation at least in oxide systems, which illustrates their overall cooperative nature.

2.4.2 Vibrational vs. Configurational Relaxation

The equivalence of relaxation kinetics allows an important distinction to be made between vibrational and configurational contributions to the properties of glass-forming liquids. In preamble, one should note that relaxation in solids does not need to be specifically addressed, as long as macroscopic properties are concerned, because it takes place at the 10^{-14} – 10^{-12} seconds timescale of atomic vibrations. This instantaneous vibrational response persists in liquids where it combines with the configurational response whose timescale markedly decreases with increasing temperatures (Figure 16). For volume, isothermal dilatometry experiments near the glass transition may yield these two contributions (Figure 17) whose relative magnitudes directly reflect the increase in thermal expansion at the glass transition [40]. For the compressibility, another approach may take advantage of experiments made at different timescales. As described above, in certain temperature ranges, ultrasonic measurements yield the equilibrium adiabatic compressibility whereas Brillouin scattering experiments probe only its vibrational part. The configurational compressibility is then given by the difference between these two results [32]. That such determinations are actually scarce is not too problematic for second-order thermodynamic properties because, at least as a first approximation, one can assume that the vibrational contribution is represented by the glass property and the configurational one by the variations of these

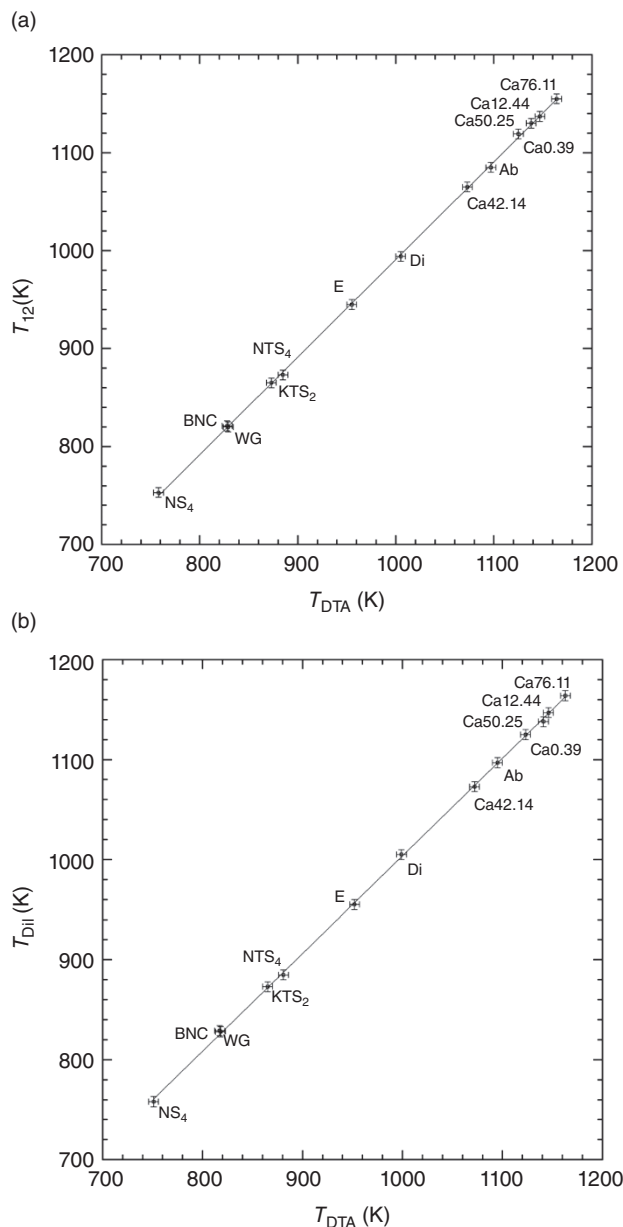


Figure 15 Equivalence of the relaxation kinetics for the enthalpy, volume, and viscosity illustrated by 1 : 1 correlations between the relevant glass-transition temperatures determined by differential thermal analysis (DTA), dilatometry (dil), and viscometry (vis, i.e. standard T_g). BNC: sodium borosilicate; WG: window glass; E: E glass; Ab: NaAlSi₃O₈; Di: CaMgSi₂O₆; N:Na₂O; S: SiO₂; T: TiO₂; Ca.xx.yy: xx mol % SiO₂, yy % Al₂O₃. Source: Data from [28].

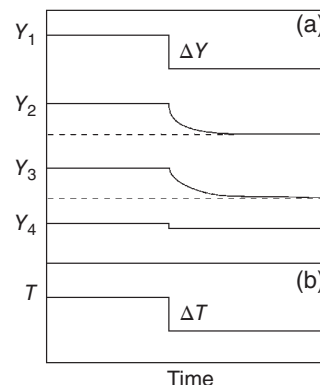


Figure 16 Relative importance of configurational and vibrational relaxation with increasing temperatures for a given property Y(a) after instantaneous temperature jumps ΔT (b). Source: Data from [40].

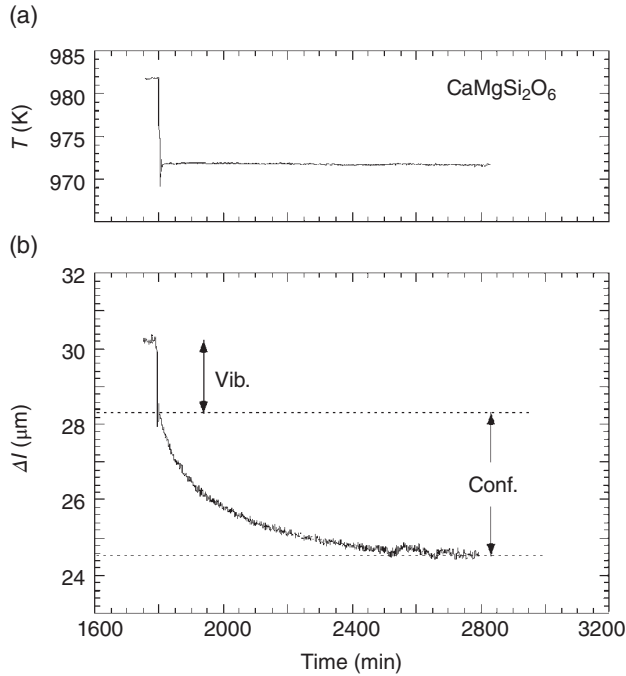


Figure 17 Vibrational and configurational contributions to the volume change of $\text{CaMgSi}_2\text{O}_6$ liquid after an abrupt temperature decrease from 982 to 972 K. Source: Data from [40], cf. Chapter 3.5.

properties at the glass transition. In silicate systems, the configurational heat capacity can thus be written

$$C_{\text{pl}}^{\text{conf}}(T) = C_{\text{pl}} - C_{\text{pg}}(T_{\text{g}}), \quad (9)$$

where the subscripts l and g refer to the liquid and glass phases, respectively, and a further simplification arises from the fact that $C_{\text{pg}}(T_{\text{g}})$ may be considered to be the Dulong–Petit harmonic limit of $3R/\text{g atom}$ (R = gas constant) the isochoric heat capacity [41].

2.4.3 A Microscopic Picture

The vibrational/configurational split can be simply illustrated by a schematic one-dimensional representation of interatomic potentials (Figure 18). Contrary to crystals, where these potentials have a long-range symmetry, glasses have essentially a short-range order because the bond angles and distances between next-nearest neighbor atoms are not constant but spread over a range of values. The minima of potential energy, which determine the glass configuration, are separated by barriers with varying heights and shapes [43]. When thermal energy is delivered to the glass, the subsequent temperature rise is associated only with increasing amplitudes of vibration of atoms within their potential energy wells. Like for any solid, the heat capacity of the glass is, therefore, only vibrational in nature.

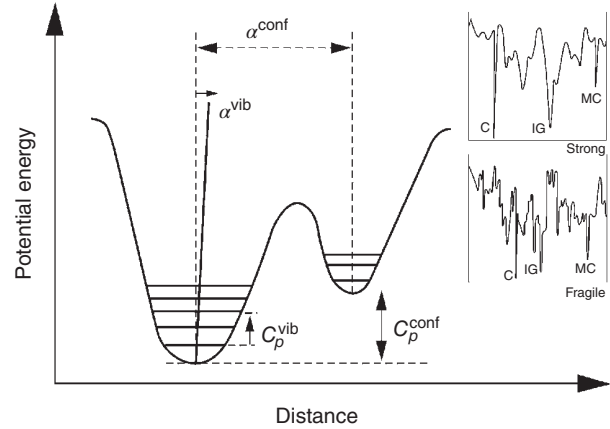


Figure 18 One-dimensional schematic representation of interatomic potentials. Inset: potential-energy landscape for a strong and a fragile liquid (Source: After [42]). C: crystal; IG: ideal glass; MC: metastable crystal.

At sufficiently high temperature, thermal energy increases to the point that atoms can overcome the barriers that separate their own from the neighboring potential energy wells (Figure 18). This onset of atomic mobility signals structural relaxation. If the relaxation time is longer than the experimental timescale, however, only the vibrational heat capacity is measured. If the temperature is increased further, or if time is sufficient for the new equilibrium configuration to be attained during the measurement, then the configurational heat capacity is also measured. When integrated over all atoms, the configurational heat capacity represents the energy differences between the minima of the potential energy wells that are explored as temperature increases (Figure 18).

The glass transition can thus be viewed as the point from which atoms begin to explore positions characterized by higher potential energies. Regardless of the complexity of this process at a microscopic level, this spreading of configurations over states of higher and higher potential energy is the main feature of atomic mobility. As a consequence, configurational heat capacities are positive. This feature, in turn, is consistent with the fact that any configurational change must cause an entropy rise when the temperature increases as required by Le Chatelier principle. As for relaxation times, they decrease with rising temperatures because large thermal energies allow potential energy barriers to be overcome more easily.

Another general feature of interatomic potentials is their anharmonic nature: displacements of the vibrating atoms from their equilibrium positions are not strictly proportional to the forces exerted on them. Because increasing vibrational amplitudes result in increasing interatomic distances (Figure 18), the thermal expansion

coefficient is generally positive for glasses. In the liquid, it increases markedly when even greater interatomic distances result from configurational changes.

2.4.4 Compressibility and Permanent Compaction

An important difference between crystals and liquids concerns the effects of pressure on their structures. The former are stable as long as the variations in their bond angles and distances induced remain consistent with their long-range symmetry. A transition to a new phase takes place when this constraint is no longer respected. In contrast, the lack of long-range order makes a wide diversity of densification mechanisms possible in a liquid, whose structure thus keeps constantly adjusting to varying pressures through changes in short-range order characterized by shorter equilibrium distances and steeper slopes around the minima pictured in Figure 18. The compressibility is thus greater for a liquid than for its isochemical crystal. It is also made up of vibrational and configurational contributions. Because the shape of interatomic potentials determines the vibrational energy levels, compression is termed vibrational for the elastic part of the deformation. As for the configurational contribution, it is related to the aforementioned changes in the potential energy wells.

If a liquid is quenched as a glass at high pressure, the final glass recovered after decompression will be denser than its counterpart formed at room pressure because only the vibrational part of the compression is eventually recovered (Figure 19). But permanent densification can also be achieved at room temperature through compression of a glass at a few tens of kbar (Chapter 10.11). The effects of pressure and temperature on the properties of glasses are thus of a different nature since the kinetics

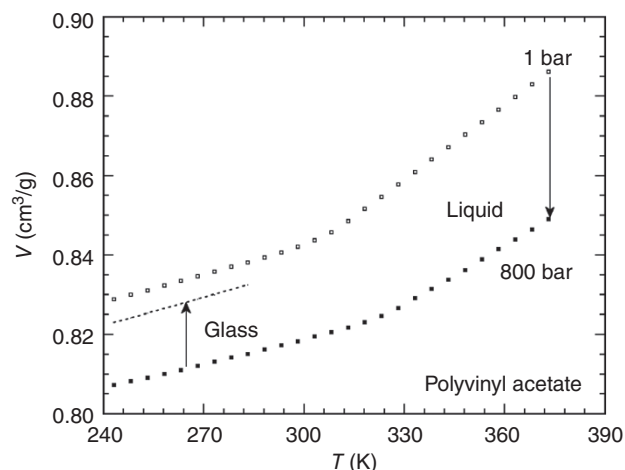


Figure 19 Permanent compaction of polyvinyl acetate after compression at 800 bar (80 MPa) in the liquid state. Source: Data from [44].

of pressure- and temperature-induced configurational modifications are markedly different for given frequencies or experimental timescales. This dissimilarity mainly originates in the fact that the shape of potential energy wells varies little with temperature, but significantly with pressure. If a high kinetic energy is needed to overcome potential barriers at constant pressure, the changes in these barriers with pressure can lead by themselves to new configurational states, at low temperatures, if the pressure is high enough.

2.4.5 Kauzmann Paradox

When viscous liquids escape crystallization, why do they eventually vitrify instead of remaining in the supercooled liquid state? One answer to this question is purely kinetic and relies only on increasingly long relaxation times on cooling. If experiments could last forever, any glass would eventually relax to the equilibrium state. Then, the glass transition would result only from the limited timescale of feasible measurements. A simple thermodynamic argument known as Kauzmann's paradox [45] indicates that this answer is incorrect. At its basis is the existence of a configurational contribution that causes the heat capacity of a supercooled liquid to be generally higher than that of an isochemical crystal and its entropy to decrease faster than that of a crystal when the temperature is lowered (Figure 20). If the entropy is extrapolated to temperatures

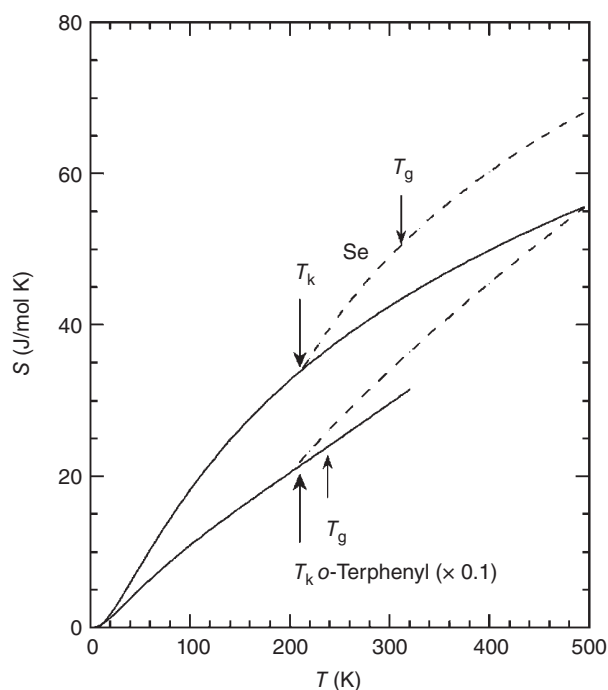


Figure 20 Kauzmann catastrophe for amorphous selenium and ortho-terphenyl (C_8H_{14}). Differences between the glass transition and Kauzmann temperatures indicating the smallness of the C_p extrapolations performed. Source: Data from [46, 47].

below the glass transition range, it becomes lower than that of the crystal at a temperature T_K , which is high enough for such an extrapolation to remain reasonable. Although this situation is not thermodynamically forbidden, it seems unlikely that an amorphous phase could have a lower entropy than an isochemical crystal.

The conclusion is that an amorphous phase cannot exist below T_K . The temperature of such an entropy catastrophe constitutes the lower bound to the metastability limit of the supercooled liquid. As internal equilibrium cannot be reached below T_K , the liquid must undergo a phase transition before reaching it. This is, of course, the glass transition. In its original form, Kauzmann's paradox implicitly neglects possible differences in vibrational entropy between the amorphous and crystalline phases. This simplification is actually incorrect but it does not detract from the gist of the argument, for taking into account such differences would only shift T_K slightly. A more rigorous statement of the paradox is that the catastrophe would occur when the configurational entropy of the supercooled liquid vanishes.

2.4.6 Potential Energy Landscape: Ideal Glass and Fragility

Among the great many statistical mechanical models that have attempted to account for the glass transition and solve Kauzmann's paradox, the early one proposed by Gibbs and Di Marzio [48] is of special interest. It predicts that the supercooled liquid would transform to an *ideal* glass through a second-order transition at the temperature T_0 at which its configurational entropy would vanish. Since then, the existence and the nature of such a transformation have been much debated. This debate notwithstanding, the important point for our discussion is the result subsequently derived by Adam and Gibbs [49] on the basis of a lattice model of polymers. This result is a very simple relationship between relaxation times and the configurational entropy of the melt, viz.

$$\tau = A_e \exp(B_e/TS^{\text{conf}}), \quad (10)$$

where A_e is a pre-exponential term and B_e is approximately a constant proportional to the Gibbs free energy barriers hindering the cooperative rearrangements of the structure.

Qualitatively, this theory assumes that structural rearrangements would be impossible in a liquid with zero configurational entropy so that relaxation time would be infinite. If two configurations only were available for an entire liquid volume, mass transfer would require a simultaneous displacement of all structural entities. The probability for such a cooperative event would be extremely small, but not zero, and the relaxation times would be extremely high, but no longer infinite. When

configurational entropy increases, the cooperative rearrangements of the structure required for mass transfer can take place independently in smaller and smaller regions of the liquid.

Within this picture, relaxation is determined by the topology of potential energy wells in an n -dimensional space and, particularly, by the density and relative depths of these wells as may be illustrated in a 1-d representation of such a *potential-energy landscape* (Figure 18, insets).

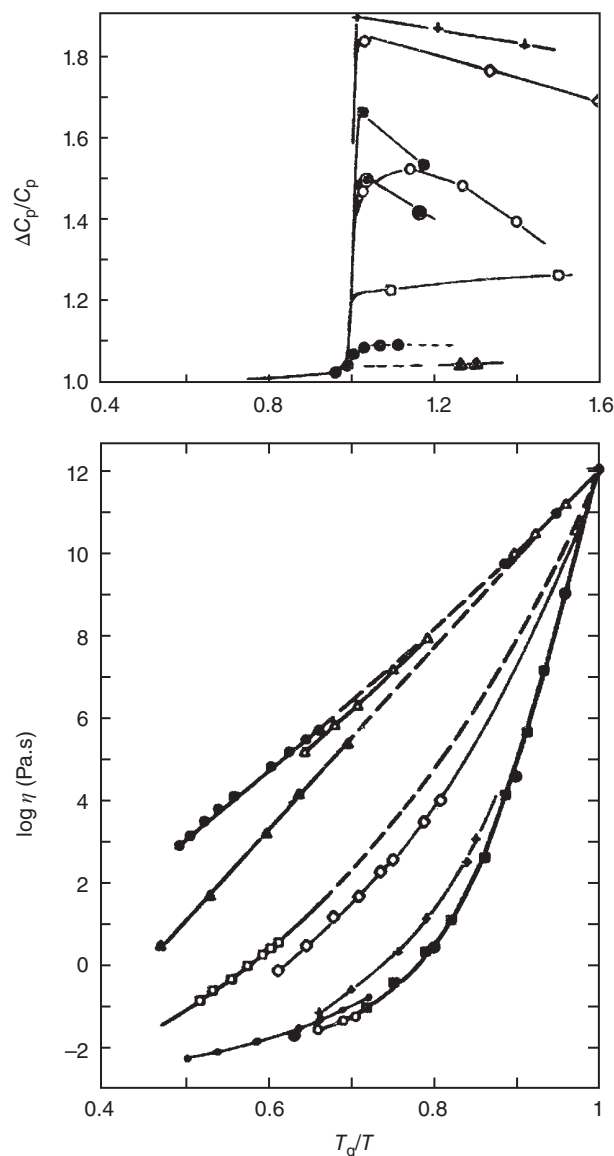


Figure 21 Fragility as a measure of the extent of temperature-induced configurational changes in inorganic and organic glass-forming liquids: correlations between relative C_p increases at the glass transition and deviations of viscosities from Arrhenius laws (Source: After [52]). Lower panel, from top to bottom: SiO_2 , GeO_2 , BeF_3 , ZnCl_3 , LiCH_3COO , $4 \text{ Ca}[(\text{NO}_3)_2] \cdot 4 \text{ H}_2\text{O}$, *o*-terphenyl, glycerol ($\text{C}_3\text{H}_8\text{O}_3$), and $\text{H}_2\text{SO}_4 \cdot 3 \text{ H}_2\text{O}$.

A simple distinction can then be made between strong and fragile liquids [43, 50]. For the former, a low density of wells translates into a small configurational heat capacity and entropy and thus, in small departures from an Arrhenian temperature-dependence of relaxation times as given by Eq. (7); for the former, the high density of wells is in contrast associated with high configurational heat capacities and entropies, and marked deviations from Arrhenian temperature dependences.

Owing to the simple proportionality between relaxation times and viscosity, this difference may be simply visualized in plots of viscosities as a function of T_g/T where T_g is the standard glass-transition temperature [51]. A well-known sketch (Figure 21) illustrates the point for a variety of inorganic and organic glass-forming liquids [52]. As particularly exemplified in Chapter 4.1, this duality between fragile and strong liquids will be a recurrent theme in many other chapters of the *Encyclopaedia* to which the reader is thus referred.

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Appendix A

Table A.1 Coordination numbers, effective ionic radii, field strengths, and electronegativities of some cations and anions of interest in oxide glasses. *Source:* Compilation courtesy J.F. Stebbins.

	Coordination ^a	Ionic radius ^b (Å)	Field strength ^b	Electronegativity ^c
<i>Anions</i>				
O ²⁻	2, 6	1.35, 1.40	—	3.5
F ¹⁻	2, 6	1.29, 1.33	—	4.0
Cl ¹⁻	6	1.81	—	3.0
<i>Cations</i>				
<i>Network formers^d</i>				
Fe ³⁺	4, 6	0.49, 0.55	0.88, 0.82	1.8
Ga ³⁺	4, 6	0.47, 0.62	0.90, 0.77	1.6
Al ³⁺	4, 6	0.39, 0.54	0.98, 0.83	1.5
Te ⁴⁺	3, 4 ^e	0.52, 0.66	1.13, 0.98	2.1
Ti ⁴⁺	4, 6	0.42, 0.61	1.26, 1.03	1.5
Ge ⁴⁺	4, 6	0.39, 0.53	1.31, 1.12	1.8
Si ⁴⁺	4, 6	0.26, 0.40	1.52, 1.29	1.8
B ³⁺	3, 4	0.01, 0.11	1.60, 1.41	2.0
P ⁵⁺	4	0.17	2.14	2.1
<i>Modifier to intermediate: alkalis and alkaline earths</i>				
Cs ¹⁺	8	1.74	0.10	0.7
Rb ¹⁺	8	1.61	0.11	0.8
K ¹⁺	8	1.51	0.12	0.8
Na ¹⁺	6	1.02	0.18	0.9
Li ¹⁺	4, 6	0.59, 0.76	0.26, 0.22	1.0
Ba ²⁺	8	1.42	0.26	0.9
Sr ²⁺	8	1.26	0.29	1.0
Ca ²⁺	6, 8	1.00, 1.12	0.36, 0.33	1.0
Mg ²⁺	4, 6	0.57, 0.72	0.53, 0.46	1.2
Be ²⁺	4	0.27	0.75	1.5
<i>Modifier to intermediate: selected others</i>				
Sn ²⁺	8 ^e	1.26	0.29	1.8
Pb ²⁺	4, 8 ^e	0.98, 1.29	0.37, 0.28	1.9
Mn ²⁺	6	0.83 ^f	0.42	1.5
Fe ²⁺	6	0.78 ^f	0.44	1.8
Zn ²⁺	4, 6	0.60, 0.74	0.52, 0.45	1.6
Ni ²⁺	4, 6	0.55, 0.69	0.55, 0.48	1.9
La ³⁺	8	1.16	0.47	1.1
Nd ³⁺	8	1.11	0.49	1.1
Er ³⁺	8	1.00	0.54	1.2
Y ³⁺	8	1.02	0.53	1.2
Sc ³⁺	6	0.75	0.67	1.3
Sb ³⁺	4 ^e	0.76	0.67	1.9
Zr ⁴⁺	8	0.84	0.83	1.4

Table A.1 (Continued)

	Coordination ^a	Ionic radius ^b (Å)	Field strength ^b	Electronegativity ^c
U ⁴⁺	6	0.89	0.79	1.7
Mo ⁶⁺	4, 6	0.41, 0.59	1.92, 1.58	1.8

^a Common coordination numbers; others may occur. Five-coordinate states are also known for many cations listed with 4 and 6 coordination (e.g. Al, Si, Ti, Ni), which have intermediate radii and field strengths.

^b Cation field strength, valence divided by square of cation–oxygen distance, with the radius of the latter taken as 1.36 Å, the typical value for three-coordinated O.

^c Pauling electronegativity, from Pauling, L. (1970). *General Chemistry*. San Francisco: W.H. Freeman.

^d “Network former” description is generally most appropriate for lower coordination numbers.

^e Lone-pair electronic structure may lead to lower coordination than expected from radius.

^f Radii for high spin electronic state.

^g Effective ionic radius, from Shannon, R.D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* A32, 751–767.

Table A.2 S.I. units and physical constants.

	Symbol	Value	Unit
<i>Universal constants</i>			
Speed of light	c	$2.999\,792\,458\,10^8$	m/s
Gravitation constant	G	$6.674\,08\,(31)\,10^{-11}$	m ³ /kg/s
Planck constant	h	$6.626070\,10^{-34}$	J/s
		$4.135669\,2\,(12)\,10^{-15}$	eV s
<i>Masses</i>			
Electron	m_e	$9.109383\,56\,(11)\,10^{-31}$	kg
Proton	m_p	$1.672621898\,(21)\,10^{-27}$	kg
Neutron	m_n	$1.674927471\,(21)\,10^{-27}$	kg
<i>Physical constants</i>			
Avogadro number	N_A	$6.022140857\,(74)\,10^{23}$	
Faraday constant	F	$9.648533212331001\,84\,10^4$	C/mol
Ideal gas constant	R	$8.3144598\,(48)$	J/mol/K
Boltzmann constant	k	$1.380649\,10^{-23}$	J/K
	k/hc	$69.503\,87\,(59)$	m ⁻¹ /K
Stefan–Boltzmann constant	σ	$5.670367\,(13)\,10^{-8}$	W/m ² /K ⁴
Molar volume of ideal gases (at 273.15 K and 1 atm)	V_m	$22.413\,962\,(13)\,10^{-3}$	m ³
<i>Conversion factors</i>			
Electron-Volt	eV	$1.6021766208\,(98)\,10^{-19}$	J
Standard atmosphere	atm	$101.325\,10^3$	Pa

Numbers in brackets denote the uncertainties in the final decimal places. Reported values by definition exact when no uncertainties are mentioned.

Section I. Glassmaking

Figure 1 The initial melting step in the making of float glass: the 1-m deep bath of raw materials melted by the flames of a cross-fired furnace (Chapter 9.7). Pulls ranging from 500 to 1000 tons/day and mean residence times of at least 24 hours. Electro-fused refractory materials made up of alumina-zirconia-silica in contact with the melt, and of alumina and alumina-silica elsewhere (cf. Chapter 9.8). *Source:* Photo courtesy Simonpietro Di Pierro, Saint-Gobain Research Paris.



Compared with crude steel (1700 million tons/year worldwide) and especially with cement (4300 Mtons), glass (about 120 Mtons) is produced in relatively small quantities. In terms of product value or volume, however, the imbalance is significantly reduced since the cost of cement is about one sixth of that of window glass and steel about three times as dense. But what differentiates glass most from these other two inorganic pillars of modern civilization is the remarkable diversity of its uses illustrated throughout the Encyclopedia.

In Europe, for which the data are the most readily available, the 35 Mtons produced in 2017 were split into container (21.4), flat (10.1), domestic (1.3), reinforcement (0.7), and other (1.1) glass. For both container and flat glass, the world market is estimated to be in the 60–80 billion \$ range and is expected to keep growing in the years to come at yearly rates higher than 5% on average, with large geographical differences (cf. Chapter 9.6). And growth rates should be higher still for new products such as the *smart* glass used in a variety of electronic devices (cf. Chapter 6.10), whose market should increase by a factor of 3 from 2017 to 2023 from the current few billion \$ per year.

Like cement and steel producers, glassmakers sell more than 90% of their production to other industries. Most uses of glass are nonetheless familiar to anyone. These are summarized in the first chapter of this section where R. Conradt points out their strong dependence on chemical composition of the glasses and on their ensuing physical properties, explaining that the reason why the still-dominant soda-lime silicates were empirically found so early in the history of glassmaking is simply because they lie close to the eutectic of the Na_2O – CaO – SiO_2 system.

Even though glass is now made in many different ways for different applications, the traditional procedure of making it by cooling of a batch melted at high temperatures remains by far prevailing. As one readily realizes when looking at the original glazing of late-nineteenth-century buildings, the long-standing problem faced by glassmakers was to achieve chemical homogeneity. The mass production of defect-free glass is a relatively recent achievement. It has resulted from better furnaces (Figure 1; Chapters 9.7 and 9.8), higher melting temperatures, and more carefully selected raw materials. In the Chapter 1.2, S. Di Pierro thus discusses the importance of the specifications, sources, and management of raw materials needed to avoid high rejection costs after

melting operations that must be as fast as possible for economic reasons (Chapter 1.2). Being common to most glassmaking processes, fusion itself is then reviewed by R. Conradt from a dual thermodynamic and kinetic standpoint; the account includes not only the fundamental reaction and dissolution steps of the batch ingredients but also the fining and homogenization of the melt produced (Chapter 1.3).

The second part of the section is devoted to the making of three basic products. Flat glass is dealt with by T. Kamihori. He begins with the first mechanical methods devised at the turn of the nineteenth and twentieth centuries, turns to the famous float process, which revolutionized the flat-glass industry in the 1960s, and ends with the recent drawdown processes widely used to produce new glasses for electronic applications with ever stricter quality specifications (Chapter 1.4). Container glass is considered by C. Roos who briefly presents the first forming devices designed at the beginning of the twentieth century before describing the various ways in which a bottle is now shaped with *Individual Section* machines at extremely high rates and may then be protected by treatments such as coating to enhance resistance to breakage (Chapter 1.5). In the next chapter, the drawing of continuous glass fibers for the relatively small but important reinforcement market is considered by H. Li and J. Watson in terms of both processes and composition evolutions driven by the need to improve chemical and physical properties (Chapter 1.6). That computer modeling of glassmaking has become an important tool to save time and money in the design or improvements of plants is explained by P. Prescott and B. Purnode in the final chapter of this section, which shows that, in industry too, fundamental insights and an accurate knowledge of the physical properties of melts have become badly needed (Chapter 1.7).

Other processes and their products are too diverse to be gathered into a common chapter. Hence, they are described along with some of their important applications: the secondary fabrication of flat glass in Chapter 9.2, the making of thermal insulation fibers in Chapter 9.3, of sol–gel products in Chapter 8.2, of glass tubes in Chapter 7.7, and of light bulbs in Chapter 6.9. Other fabrication issues are dealt with in chapters devoted to modern furnaces (Chapters 9.7 and 9.8), cullet recycling (Chapter 9.9), and the history of glassmaking processes (Chapters 10.5, 10.7, and 10.8).

1.1

Glass Production: An Overview

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1 Introduction

The term “glass” may either refer to a special state of matter in general or to a group of industrially manufactured materials. The chart in Figure 1 presents, from a chemical point of view, an overview of a large number of systems that can be easily transferred into the glassy state. In this chart, special emphasis is given to the industrially relevant group of silicate glasses because, by volume or mass, the vast majority of the glasses produced belong to it. Nonsilicate oxide glasses and other inorganic nonmetallic glasses, nevertheless, play an essential role in the production of highly specialized functional materials such as optical fibers (Chapter 6.4). The group of “other glasses” comprises materials of very different nature. Within this group, metallic glasses (Chapter 7.11) are finding a variety of practical applications whereas organic glasses (Chapters 8.7 and 8.8) have long played a major role at the industrial scale.

No attempt is made here to present a concise definition of the glassy state in general. From a practical point of view, however, glasses comprise a group of noncrystalline homogeneous and isotropic materials characterized by the absence of any microstructure. Thus, in contrast to (poly)crystalline materials, the bulk properties of which are essentially tailored via their microstructure, those of glasses are chiefly designed via their chemical composition; by contrast, thermal treatment has a comparatively small “fine-tuning” effect, which may, nevertheless, become crucial for specific products (e.g. optical or *strong* glasses).

At the atomic scale, the very same bonding interactions are present in isochemical condensed phases, i.e. in liquids, glasses, and crystalline polymorphs. Therefore, the chemical and electronic properties of glasses resemble those of their crystalline counterparts – with the reservation that glasses typically possess larger molar volumes, higher entropies, and higher (less negative) enthalpies of formation. In other words, they are thermodynamically less stable than crystals. Nevertheless, their macroscopic properties reflect in essence the same dependences on chemical composition as their crystalline counterparts. Without mentioning a host of other polymorphs, SiO_2 may, for example, exist under ambient conditions as quartz, cristobalite, or vitreous silica; thermodynamic stability decreases in the given order. The same applies to hydrolytic stability, a macroscopic property for which all SiO_2 polymorphs nonetheless stand out by comparison with other oxides.

In general, information on atomic bond strengths, compound formation energies, and phase equilibria in a system of a given chemical composition may serve as reliable guidelines to explore the relation between the chemical composition of a glass and its macroscopic properties. It would go too far to draw the same conclusion for the relation between the chemical composition and the short-range order structure. Although there is ample experimental proof for such a relation in many systems [1], the general claim may be misleading, even erroneous in specific instances. Yet, in any case, the energetics pertaining to a specific glass structure is in general very close to that of an isochemical crystalline system. Energetics, in turn, is the key factor governing the relation between the chemical composition of a glass and its macroscopic properties. For this reason, equilibrium phase diagrams ([2, 3], Chapter 5.2) and thermochemical databases [4–9] are most helpful tools in the design of glass compositions with desired properties.

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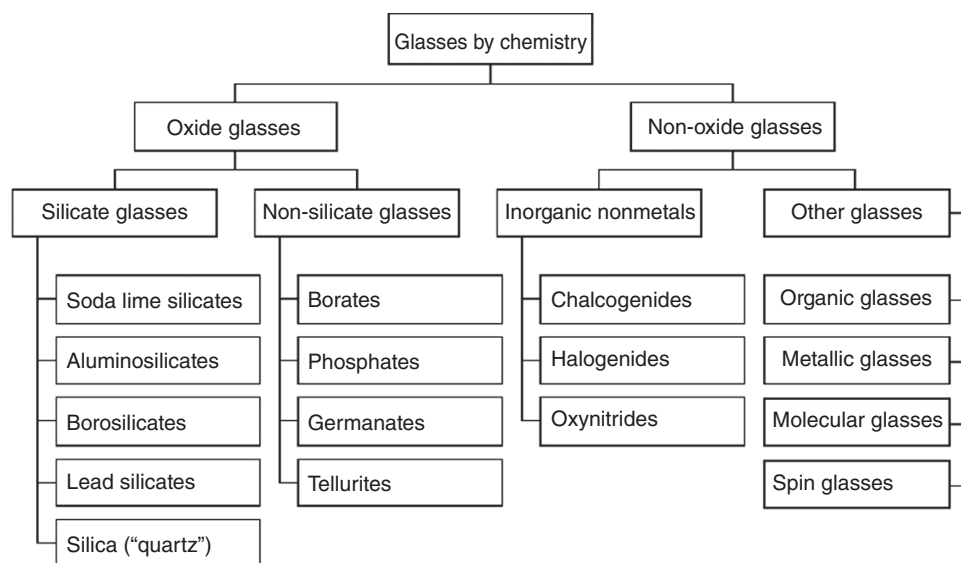


Figure 1 Glass-forming systems, classified by chemical composition.

The industrial synthesis of glasses can also be based on a large systematic collection of experimental data of the properties of glass-forming systems [10–14]. Because at a microscopic level, atomic interactions are primarily pairwise (Chapter 2.7), one can in particular make use of empirical composition–property relations [15–20] of the type

$$P = \sum a_j \cdot p_j + b_j \cdot p_j^2 + \dots, \quad (1)$$

where P denotes a macroscopic property, p_j is the mol or weight fraction of component j , and the a_j and b_j coefficients are sets of empirical parameters representing the contribution of component j to the property P of the glass.

2 Industrially Manufactured Glasses

2.1 Properties of Manufactured Glasses in General

In addition to the influence of chemical composition, it is the homogeneity, isotropy, and absence of any microstructure that brings about the main features shared by most industrially manufactured glasses. This group of materials stands out from others by

- aesthetics; historically, the fact that glass was looking like gems has been the predominant driving force for the invention of glass as a material (Chapter 10.2). Aesthetic requirements today remain an important aspect, technically expressed as *quality* since, for instance, the presence of a single blister calls for the rejection of a 3×6 m sheet of flat glass.
- its suitability for large-scale continuous primary forming as sheets, rods, tubes, and fibers.
- its extreme variability of shapes in discontinuous forming, comprising shapes with undercut.
- optical transparency. By virtue of their electronic and ionic properties, homogeneity, and absence of any microstructure, most glasses have an excellent transparency in the visible range. A standard float glass (4 mm thick) is transparent for light at wavelengths from 300 to 3500 nm, covering the entire visible (400–760 nm) and the near-IR ranges, the reflection losses of a standard glass sheet remaining slightly lower than 8%.
- an extremely wide and continuous compositional variability. Glasses can also easily incorporate functional components such as colorants.
- an extremely smooth surface, which originally allowed glass not to “smell” the odors of the substances it was storing. Today an as-received float glass possesses a roughness (root mean squared [RMS] value) of approximately 0.5 nm on the atmosphere side, and 1 nm on the tin-bath contact side. Even after an extended exposure to water or humid air at room temperature, RMS remains well below 10 nm. This makes glasses ideal substrates for metal and other functional coatings.
- excellent dielectric properties. Lead silicate glasses used in the back part of cathode-ray tubes reach dielectric constants of 20. It is true, this number does not match the extremely high values of functional ceramics (polycrystalline $\text{TiO}_2 \approx 100$, $\text{BaTiO}_3 \approx 1000$). When it comes to breakthrough voltages, however, the lack of any microstructure confers a clear advantage to glasses over polycrystalline materials: polycrystalline alumina withstands less than 8–9 kV/mm, whereas alkali-free

glasses reach 40 kV/mm, like natural mica; glass ceramics doped with BaTiO_3 crystals may even reach values higher than 400 kV/mm.

- excellent chemical durability against most chemicals. This is especially the case for silicate glasses in the low-pH range (i.e. with strong acids), making them excellent materials for chemical-process plants.
- an extremely high stiffness and intrinsic strength, both again by virtue of the absence of any microstructure. With a tensile strength of up to 4000 MPa (glass fibers), glass ranges among the strongest materials available. Its proverbial fragility is not a matter of strength, but of vulnerability of its surface and of low fracture toughness (Chapter 3.11).

It is a combination of the above features which gives glass such a prominent and indispensable place in the world of materials.

2.2 Classification of Glasses by Commercial Branches

From a technical point of view, glasses are classified in terms of applications rather than chemical composition. The following list presents the most important groups of industrial products under this aspect.

Glass hollowware

Container glass	Bottles (flint, green, amber) Preserving jars Flaconnage
Tableware	Stemware, kitchenware, vases

Flat glass

Architectural glass
Glass for personal security and property protection
Glass for photovoltaic application
Fire-resistant glass
Automotive glass
Decorative interior glass and mirrors

Fiber glass

Continuous fibers (textile; reinforcement)	Multi-purpose (E) Acid resistant (A, C, E-CR) Alkali resistant (AR) High strength (R, S) Dielectric (D)
Fibers for thermal and acoustic insulation	Glasswool, stonewool

Other glass, comprising specialty glass

Soluble glass (water glass)	For chemicals and detergents
Foam glass	For thermal insulation
Laboratory and industry	Lab ware glasses Glasses for process plants Electrode glasses
Artificial lighting	Incandescent lamps Gas-discharge lamps Semiconductor light sources Reflectors
Pharmaceutics and medicine	Ampoules and vials Antibacterial glasses Bioactive glasses
Optics	Eyeglasses Cameras, microscopes, telescopes Fiber optics and endoscopy Telecommunication fibers Laser glasses
Electronics and energy generation	Electronic tubes Sealing glasses Soldering and passivation glasses Substrate glasses and display glasses Glasses for thermal power generation
Radiation protection	Radiation shielding windows High-energy radiation detection windows
Silica ("quartz") glass	For high-T processing For silicon crystal growth For silicon-wafer handling For optical fibers

The pie chart in Figure 2 provides a rough overview of the shares of these categories by amounts of worldwide production. The figures given are estimates based on an evaluation of multiple sources for the time span 2003–2008. By absolute amounts, the 2005 world production reached about 124 million metric tons (31 in the European Union, 8 in Germany). Since then, an average annual increase of about 3.5% is observed. Whereas the production is more or less leveling off in most industrialized countries, the PR of China is among the main

driving markets for this increase as its 2005 output of flat glass already accounted for more than 50% of the world production (cf. Chapter 9.6).

For each type of glass products listed above, a typical chemical composition range has been adopted world-wide. The compositions of container and flat glass have never been developed by a scientific approach. Rather, they have remained pretty the same ever since the beginnings of glass makings (Chapter 10.2). Compositions have thus been very early constrained by the availability of affordable raw materials, the need to prevent water corrosion, and the highest temperatures reached in furnaces.

A systematic scientific approach to glass compositions did not begin before the nineteenth century, chiefly promoted by the work of individuals such as Fraunhofer,

Faraday, Harcourt, Abbé, or Schott (Chapter 10.11). Since then, this scientific approach has remained the basis for designing not only the compositions of most specialty glasses but also to improve those of existing products. For example, there is a quest among the producers of continuous fibers for completely new compositions with outstanding mechanical or chemical properties such as high modulus for lightweight construction composites or extreme alkali resistance for concrete reinforcement. In other cases, the driving force for development stems from environmental or health concerns and legislation. As examples, lead and arsenic oxides are being replaced in the formulae of optical glasses, solder and sealant glasses, and even in crystal tableware, whereas insulation-fiber compositions have been reformulated to avoid any confusion with asbestos fibers whose cancerogenic potency is well known. The typical composition ranges of current glass products are summarized in Table 1.

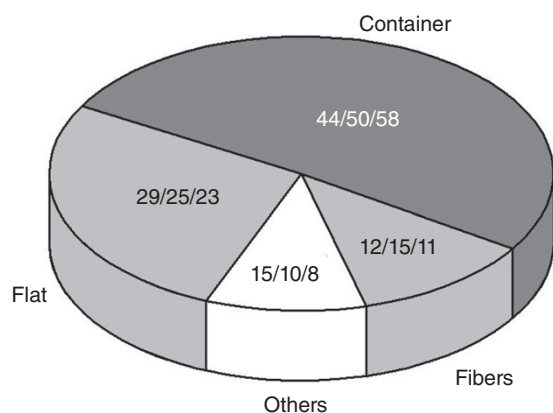


Figure 2 Glass production by branches; figures in % in the sequence world/United States/Europe.

3 Process-controlling Properties

3.1 Viscosity

Among all the properties of a glass-forming substance, the viscosity–temperature relationship is by far the most important practically in glass making. Referring to Chapter 4.1 for an in-depth review of this topic, here we will consider it from a simpler technological point of view. The main feature then is that the viscosity of a glass-forming liquid extends over a range of 12–14 orders of magnitude, which thus involves large rheology changes in the temperature range relevant to glass manufacturing

Table 1 Typical compositions of industrial glasses comprising main oxides only (no colorants or impurities); compositional ranges from multiple sources (e.g. [13]) or typical individual examples (wt %).

Oxide	Container glass	Float glass	Crystal glass	Display glass	E fiber glass	Glass wool	Stonewool	Low- α glass	Soluble glass
SiO ₂	66–75	70–74	66.0	65.0	52–60	56–66	35–48	70–81	66–77
TiO ₂			1.0				0–3		
Al ₂ O ₃	1–3	0.5–1.5	2.0	18.0	12–16	0–6	12–28	2.5–5	
Fe ₂ O ₃							3–12		
B ₂ O ₃				1.0	0–9	3–9		10–15	
MgO	0–4	0–4	4.0	7.0	0.5–4.5	1–5	2–11	1.0	
CaO	8–12	7–10	6.0	6.0	16–24	5–11	10–28	1.0	
BaO			2.0	3.0					
ZnO			3.0						
Li ₂ O	0–1							0–1	
Na ₂ O	11–15	12–14	8.0		0–2	13–17	1–6	4–8	23–34
K ₂ O	0–2	0–1				0–2	1–6	0–3	

Table 2 Viscosity ranges of industrially manufactured glasses.

Viscosity as log η , η in dPa·s	Process range, technological meaning ^a
Melting	
2.0	Typical of a soda-lime silicate glass melt at 1450 °C
3.0	Transfer to forming area Volume relaxation time is <1 s Fixpoint $T(3.0)$ = gob temperature Bushing tip temperature for fiber production ^b
Forming	
4.0.	Upper limit of mechanical working range Fixpoint $T_{WP} = T(4.0)$ = working point
6.0	Lower limit of mechanical working range The difference $T(4.0) - T(6.0)$ is termed the “length” of a glass
Tempering, annealing, and cooling	
7.6	Upper limit of macroscopic shape stability Fixpoint $T_L = T(7.6)$ = Littleton softening point
11.0 ^c	Dilatometric softening point T_D Above T_D , temperature gradients in a glass object no longer cause thermal stresses A related temperature level is $T_d = T(11.5)$ = deformation point Glass objects deform under own weight at rates of a few $\mu\text{m/h}$
13.0	Technical definition of the glass transition Fixpoint $T_g = T(13.0)$ = annealing point Volume strain relaxation time is 60 s
14.5	Technical definition of ultimate transition to a rigid state Fixpoint $T(14.5)$ = strain point Volume strain relaxation time is 30 min

^a In the earlier days of mechanical forming, empirical indicators were in use. They remain worth to be consulted as empirical guidelines when the complex feature of “workability” is to be kept constant under a compositional change; these indicators read: gob temperature, $GT = 2.63 \cdot (T_L - T_g) + T_L$; working range index $WRI = T_L - T_g$; RMS = relative machine speed = $(T_L - 450)/(WRI + 80)$; DI = devitrification index = $WRI - 160$.

^b Some stonewool processes use $T(1.5)$ as fibrization temperature.

^c Approximation, the exact value depending on the load applied by the dilatometer.

(Table 2). Conventionally, technologists do not report viscosities in terms of values found at given temperatures, but rather in terms of temperatures at which given viscosity values are obtained. Thus, $T(n.n)$, the *isokom* temperature, denotes the temperature in °C at which the melt assumes a value $\log \eta = n.n$ in poise CGS units (1 P = 0.1 Pa·s so that all values compiled in Table 1 have to be decreased by 1 if one retains instead the Pa·s SI unit used in many recent publications). The importance of reporting temperatures instead of viscosities rests on the facts that the (Newtonian) rheological response of all substances is by definition the same at the same viscosity and that only the temperature of a glass – not its viscosity – can be operationally regulated during the various forming, tempering, annealing, or cooling steps of glass making.

Viscosity–temperature relationships do vary much with chemical composition: as illustrated in Figure 3 by the data for a soda-lime float glass, a stonewool and silica

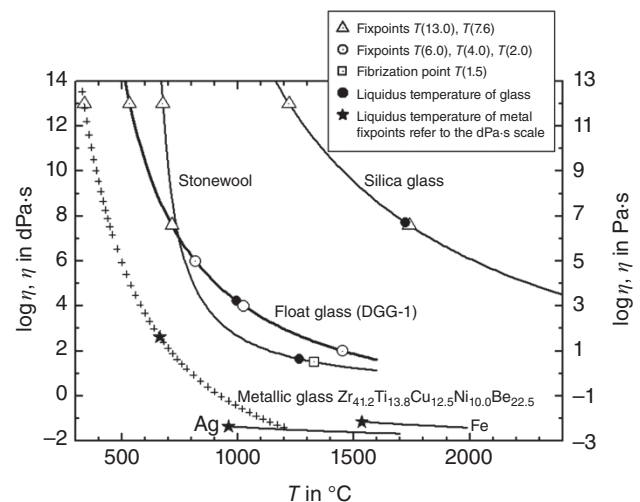


Figure 3 Viscosity–temperature relationship of different glass-forming systems; pure metallic melts of Ag and Fe are displayed for comparison.

glass, and those for a bulk metallic glass and pure Ag and Fe liquids. The fixed points of Table 1 are pinpointed for each glass melt and read in this graph, as just explained, starting from its Y axis. The complete viscosity curves can be reproduced by Vogel–Fulcher–Tamman (VFT) equations,

$$\log \eta = A + B/(T - T_0), \quad (2)$$

where A , B , and T_0 are empirical fit constants and T is expressed here in $^{\circ}\text{C}$. The float glass DGG-1 included in Figure 3 is a certified viscosity standard whose VFT equation has been derived from 44 measurement points. These are reproduced with the parameters $A = -1.601$, $B = 4330.9$, and $T_0 = 246.1$ (η in dPa·s) with a standard deviation of $\delta \log \eta = \pm 0.16$, illustrating that the VFT equation is a valuable tool for any technological purpose.

Viscosities are in addition an indicator of crystallization tendency at the liquidus temperature T_{liq} , which is shown in Figure 3 on the viscosity curves. Melts with $\log \eta(T_{\text{liq}}) < 2.0$ tend to crystallize quickly, thus requiring very high cooling rates, whereas melts with $\eta(T_{\text{liq}}) > 4.0$ may in contrast be vitrified at moderately low cooling rates.

Of great interest, therefore, is the possibility to predict the viscosity of a glass melt as a function of its temperature

and chemical composition. From measurements performed for a variety of samples, sets of incremental factors have been empirically derived by regression analysis for this purpose. The left-hand part of Table 3 presents such a widely used database [19] with which the effect of additions of individual oxides (by weight and molar amounts, respectively) have been calculated for a soda-lime silicate. The temperature $T(\text{n.n})$ at which viscosity reaches $10^{\text{n.n}}$ dPa·s is thus calculated as

$$T(\text{n.n}) = a(\text{SiO}_2) + 100 \cdot \sum a(j) \cdot y(j)/y(\text{SiO}_2), \quad (3)$$

where $y(j)$ is the weight fraction of oxide j .

Helpful guidelines for the design of the viscosity curve of a mass-produced glass may be derived from the graphs of Figure 4. For example, replacement of 1 wt % SiO_2 by 1 wt % Li_2O to yield a glass 73 wt % SiO_2 , 10 CaO, 16 Na_2O , 1 Li_2O lowers the temperature at $\log \eta = 4.0$ and 13.0, relative to the base glass, by 45 and 29 K, respectively. Among the *alkali oxides*, lithia is the strongest liquidus flux; it significantly lowers viscosity at all levels. *Boron oxide* has a similarly strong effect, however, at high-temperature only. So it reduces the working range (the

Table 3 Empirical factors for the calculation of viscosities [19] and elastic properties [21, 22] (units revisited) from composition.

Oxide j	Viscosity				Elastic properties	
	$a(j)$ for			Validity range (wt %)	$V(j)$ (cm^3/mol)	$U(j)$ (GPa)
	$T(2.0)$ ($^{\circ}\text{C}$)	$T(4.0)$ ($^{\circ}\text{C}$)	$T(6.0)$ ($^{\circ}\text{C}$)			
SiO_2	1847.80	1249.70	962.90	60–77 ^a	28.0	64.5
TiO_2	−4.00	−4.00	−4.00	0–8 ^b	29.2	86.7
ZrO_2	8.65	7.96	8.16	0–8 ^b	30.2	97.1
Al_2O_3	8.32	5.23	4.01	0–8 ^a	42.8	134.0
B_2O_3	−21.62	−11.97	−6.42	0–14 ^a	41.6	77.8
– “–”	0.5122	0.3182	0.1900	— ^c	—	—
MgO	−5.87	−0.12	0.91	0–6 ^a	15.2	83.7
CaO	−11.27	−3.99	−0.74	4–13 ^a	18.8	64.9
BaO	−5.67	−3.04	−1.88	0–17 ^b	26.2	40.6
ZnO	−5.37	−1.99	−0.71	0–9 ^b	15.8	41.5
PbO	−4.85	−3.17	−2.24	0–12 ^b	23.4	17.6
Li_2O	−35.54	−30.04	−26.45	0–3 ^a	16.0	80.4
Na_2O	−12.65	−9.19	−7.06	10–17 ^a	22.4	37.3
K_2O	−5.93	−4.17	−3.53	0–9 ^a	37.6	23.4
Error	± 4.7 K	± 3.4 K	± 3.2 K	—	n.s.	n.s.

^a Combinations of these oxides, plus one.

^b Oxide only, keep the error within the given $\pm$ range.

^c For boron oxide, the factors in the second row are square terms; thus, the sum for each $T(\text{n.n})$ has to be expanded by a term $10\,000 \cdot a(\text{B}_2\text{O}_3) \cdot [y(\text{B}_2\text{O}_3)/y(\text{SiO}_2)]^2$.

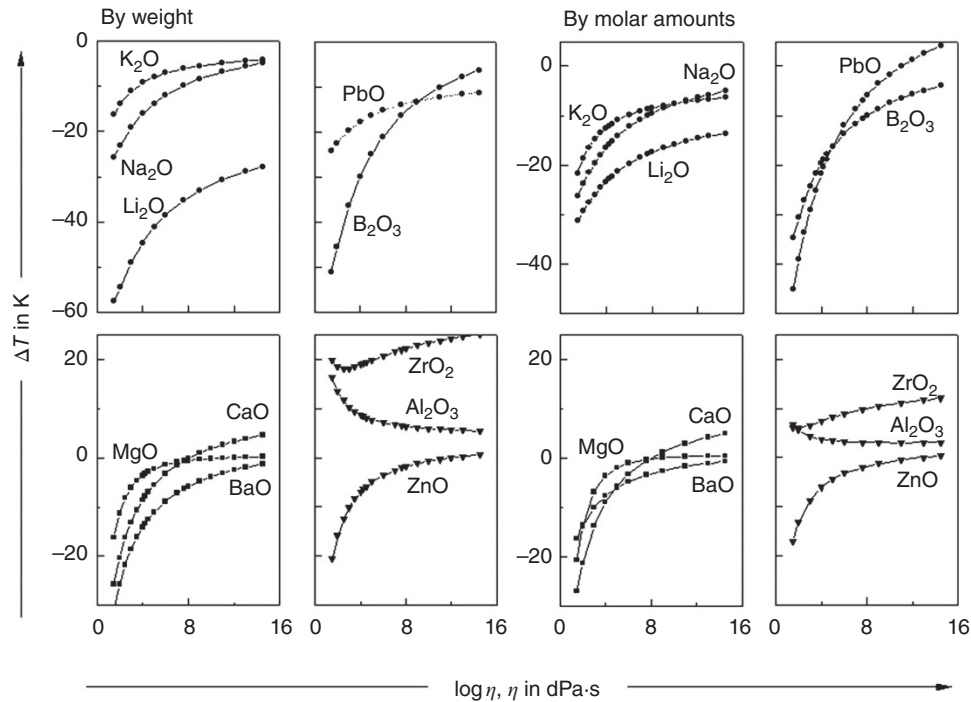


Figure 4 Temperature change brought about by a replacement of 1% of SiO_2 by another oxide in the base glass composition 74SiO_2 , 10CaO , $16\text{Na}_2\text{O}$; left side: for oxide amounts by wt; right side: for molar amounts.

“length”) of a glass. In the language of glass technologists, boron oxide makes a glass “short.” Lime strongly reduces viscosity at high temperatures; the effect is almost as strong as with soda. Thus, if viscosity needs to be lowered in this range, inexpensive limestone as a calcium carrier raw material may be used instead of expensive soda ash as a sodium carrier. Also note that lime, quite in contrast to *magnesia*, makes a glass “short.” One can thus extend the working range of a glass by manipulating its CaO/MgO ratio. *Alumina* makes at the same time a glass more viscous and “longer.” Although not giving any in-depth scientific understanding, these empirical tools undoubtedly have their merits in glass technology.

3.2 Liquidus Temperatures

Most industrial glass-melting processes run in a continuous way 365 days per year over periods of 2–15 years. This operation time depends on the type of glass and on the corrosion wear of both the refractory lining of the melting tank and channels guiding the melt to the working stations. A maximum temperature of about 1500°C is needed to achieve homogenous fusion; at the exit of the furnace, the melt still is at about 1350°C . This temperature makes it necessary to cool steadily the melt down to $T(3.0)$ while keeping a safety margin ΔT above the liquidus temperature T_{liq} of the particular composition to prevent precipitation of crystals. This

yields a constraint of a minimum temperature of $T(3.0) + \Delta T$ required to ensure a crystal-free glass. This constraint is especially critical for continuous glass fiber production (Chapter 1.5), but it applies to any other process as well before the forming step.

Traditionally, liquidus temperatures have been determined experimentally to be represented graphically for simple-enough systems in the form of phase diagrams (Chapter 5.2, [2]). For complex compositions of industrial interest, they are generally determined with a gradient furnace whereby a series of 5–10 samples are heated for typically 24 hours in a temperature gradient spanning the expected range of T_{liq} . After quenching, the samples are examined by optical microscopy. The liquidus temperature is then bracketed by the treatment temperatures of the last homogeneous glass and that of the first sample in which crystallites are observed. In a more accurate approach, samples from the gradient furnace containing tiny amounts of crystals are reheated in a heating-stage microscope at a rate well below 1 K/min , and the temperature at which the last crystal dissolves is adopted as T_{liq} .

Thanks to the progress made in thermodynamic modeling of melts (Chapter 5.3), an increasingly useful approach is to predict liquidus temperatures with one of the dedicated softwares designed to calculate phase equilibria relevant to glass making (e.g. 20). Empirically, however, simple rules have long been known to predict

the effects on a given oxide on liquidus temperatures. Illustrating again the predominantly pairwise nature of atomic interactions, they rely particularly on the topology of binary phase diagrams (Figure 5). The tremendous freezing-point depressions of SiO_2 brought about by addition of alkali oxides as well as by boron and lead oxides are in fact so conspicuous that they have historically been at the basis of the development of glass technology. As illustrated by a comparison made between Li_2O and K_2O (Figures 4 and 5), of particular interest is the fact that

the alkali oxide that most strongly decreases viscosity is the least effective in lowering liquidus. Only boron and lead oxides cause strong decreases of both viscosity and liquidus. This may shed some light on the technological challenge raised by the replacement of lead oxide in the glass formulae of modern tableware and solder glasses.

In ternary systems, the Na_2O – CaO – SiO_2 and CaO – Al_2O_3 – SiO_2 phase diagrams are especially important as they serve as references for soda-lime and most stonewool and reinforcement-fiber glasses, respectively (Figure 6).

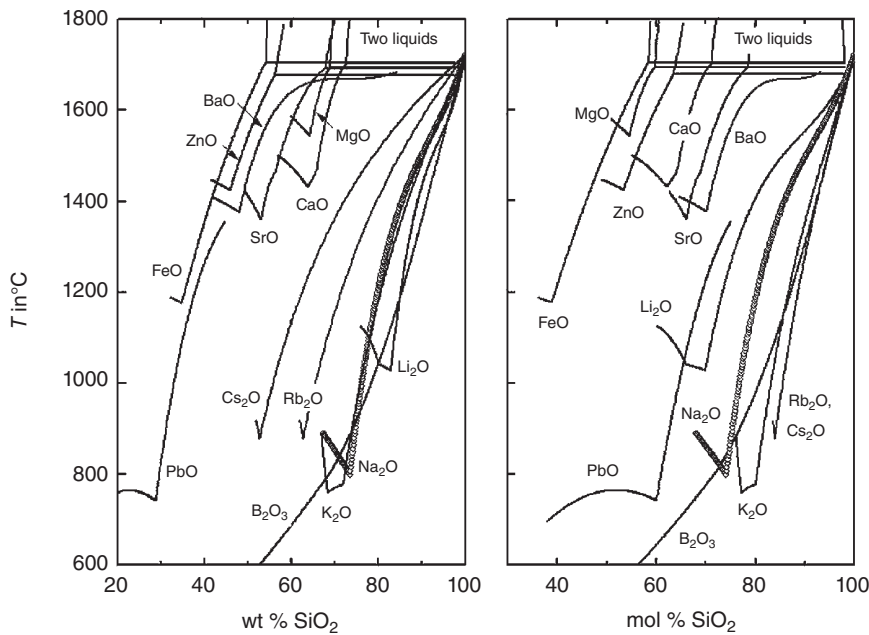


Figure 5 Liquidus lines of binary silicate systems (left: by wt, right: by mol); all systems comprising a divalent oxide, except BaO, show an extended stable miscibility gap; data source [2].

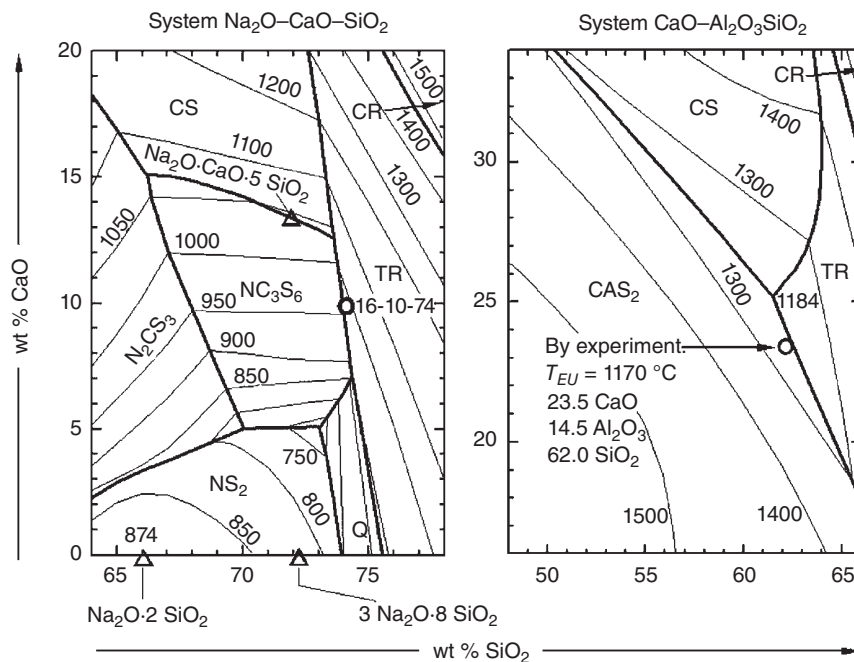
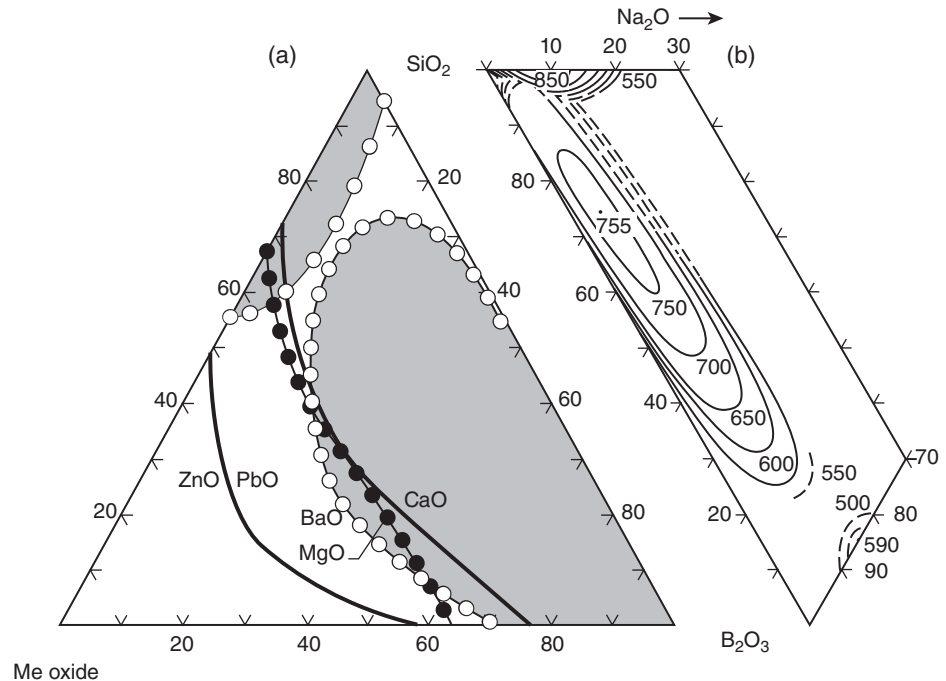


Figure 6 Ternary phase diagrams in versions of technological relevance; shorthand notation: N = Na_2O , C = CaO , A = Al_2O_3 , S = SiO_2 , Q = quartz, TR = tridymite, CR = cristobalite; left: the basic system of all commercial hollowware and flat glasses; the triangles mark the positions of the compounds, $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$; the circle the position of the base glass 74 SiO_2 , 10 CaO , 16 Na_2O ; data source [2]. Right: the basic system of reinforcement-fiber glasses; industrial compositions flock around the eutectic; calculation using FactSage® [23].

Figure 7 Miscibility gaps. (a) Extension of stable gaps in ternary borosilicate systems with different oxides as third component; the area shaded in gray refers to BaO; (b) isotherms of the (metastable) sub-liquidus immiscibility dome in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$.



From Figure 6a, it is easy to understand why, in Antiquity (Chapter 10.3), glasses with silica contents of 70–74 wt % and amounts of lime not exceeding 12 wt % were already mass produced: Thanks to typical $T(3.0)$ values of $1200 \pm 10^\circ\text{C}$, it is comparatively easy to comply for them with the constraint $T_{\min} = T(3.0) + \Delta T$. The particular composition “16-10-74” has been investigated in many scientific studies. It may be considered as a reference and the *mother* of all mass-produced glasses, including of course today’s float glass. That the $T_{\min}$ constraint represents in contrast a real challenge for $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ -based glasses is readily apparent in Figure 6b where only a narrow range around the ternary eutectic between tridymite [SiO_2], wollastonite [CaSiO_3], and anorthite [$\text{CaAl}_2\text{Si}_2\text{O}_8$] qualifies for a successful production. In passing, note that Figure 6b has been calculated by using the thermochemical software and databases FactSage® [23]. The experimental position of the mentioned eutectic is also marked, thus displaying the degree of accuracy that may be expected from the calculation of liquidus for more complex compositions.

3.3 Liquid–liquid unmixing

If phase separation within a condensed system most commonly takes place via partial crystallization, it can also occur as liquid–liquid unmixing (Chapter 5.2). Ternary systems containing boron oxide illustrate that the phenomenon should certainly not be overlooked in glass-forming systems. For ternary borosilicates, the boundaries of the composition domains where such an unmixing

takes place stably, i.e. above the liquidus, are indicated in Figure 7a. If temperature is represented in a third dimension, these domains define the base areas of immiscibility domes that eventually terminate at upper critical points at their tops. The isotherms of the immiscibility dome in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$, which is the base composition of all borosilicate glasses, are drawn in Figure 7b. Here, in contrast to Figure 7a, the entire dome comprising its upper critical point (755°C at composition 25-05-70 by wt) is located below the liquidus surface. Hence, liquid unmixing cannot take place during the initial melting step, but at lower temperatures during the forming process. This is one of the reasons why, in order to minimize phase-separation effects, pharmaceutical and low-expansion borosilicate glasses are designed around a composition of 80 wt % silica. The system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ (not shown here) displays a similar topology.

It is only with glasses known under the trade name *Vycor Glass* that liquid unmixing is exploited on purpose. Here, after forming by conventional technology to the desired shape, phase separation develops upon annealing at an appropriate temperature to yield two interconnected phases, namely an Na_2O - and B_2O_3 -rich glass along with another one that contains more than 96 wt % SiO_2 . Then the former is leached out by a hot strong mineral acid, leaving behind a nanoporous skeleton of high- SiO_2 glass. This material may then be used directly as filter, for example, or sintered at temperatures below 1300°C to fabricate dense and almost pure silica glass articles much more readily than with pure SiO_2 .

The numerical calculation of liquid–liquid immiscibility ranges in multicomponent systems (e.g. by using the software and databases mentioned in Section 3.2) is even more challenging than the calculation of solid–liquid equilibria. This is because available experimental data hardly reach beyond what has been sketched in the present section, and such a narrow base of information does not allow to fine-tune the parameters used in the calculations.

4 Glass Composition – its Relevance to Glass Properties

4.1 Property Optimization

Both search and optimization of glass formulae begin with a given profile of target glass properties. In the following, three properties will be addressed as examples typically targeted in glass development, namely the elastic properties, the thermal expansion coefficient, and the chemical durability. From a scientific point of view, such a task should rest on deep insights on the relationships between chemical composition, glass structure, and glass properties. It is only from such a fundamental approach that ground-breaking developments of novel glasses with outstanding properties may be expected. But this goal is still a matter of fundamental research as expounded in the following chapters where this most challenging issue is pursued.

For the time being, however, only few manageable tools and procedures of this kind are available for the technological community. To optimize properties, technologists thus rely largely on empirical approaches whereby, as applied to glass viscosity in Section 3.1, they use incremental oxide factors derived by statistical means from large numbers of experiments. One has, however, to keep in mind that these approaches represent only interpolations of what is already known. Hence, limited areas in compositional space leading to truly outstanding properties should be easily overlooked so that developments similar to the famous low-expansion metallic alloy *Invar* are very unlikely to be found this way.

4.2 Elastic Properties

Incremental oxide factors for the calculation of the elastic properties from the composition compiled in the right-hand part of Table 3 are taken from a widely accepted earlier publication [21]; for the sake of clarity, they have been adjusted with respect to the units used, i.e. to cm^3/mol for volume, and to GPa for modulus increments. Young's modulus E is then calculated with

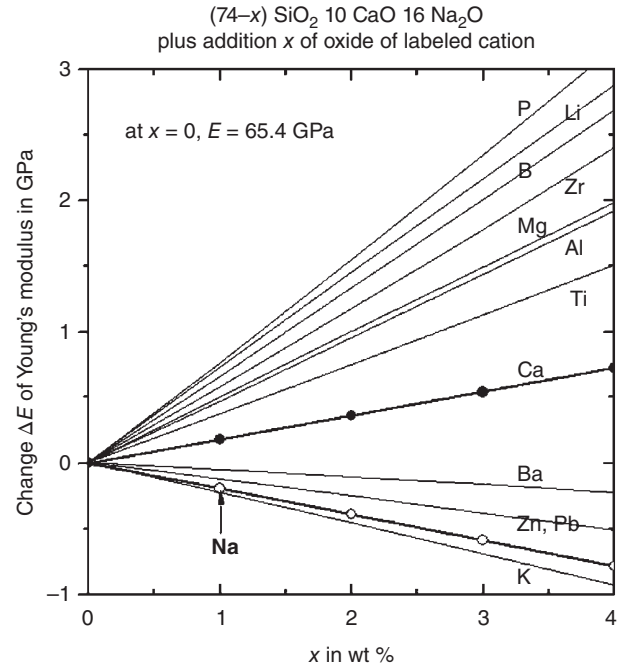


Figure 8 Change of Young's modulus E in the base glass composition 74 SiO_2 10 CaO $16 \text{ Na}_2\text{O}$ upon the replacement of x wt % silica by another oxide.

$$E = [\rho \cdot \sum V(j) \cdot x(j) / \sum M(j) \cdot x(j)] \cdot \sum U(j) \cdot x(j), \quad (4)$$

where $x(j)$ and $M(j)$ are the mole fraction and molar mass of oxide j , respectively, and ρ the density of the glass.

As for Poisson's ratio μ , it is calculated as

$$\mu = 0.5 - 0.278 / [\rho \cdot \sum V(j) \cdot x(j) / \sum M(j) \cdot x(j)]. \quad (5)$$

The manner in which Young's modulus varies when a glass composition of $(74 - x)\text{SiO}_2$, 10 CO , $16 \text{ Na}_2\text{O}$ (by wt) is modified by an addition of x wt % of another oxide is illustrated in Figure 8. Young's modulus can be raised by the addition of P, Li, B, Zr, Mg, and Al oxides, and in contrast lowered by oxides of heavy mono- and divalent ion oxides. True, such small additions do not yield major overall effects but the tendency is clearly shown.

4.3 Thermal Expansion Coefficient

Incremental oxide factors for the calculation of the thermal expansion coefficient are compiled in Table 4. Again, the factors are taken from a widely accepted earlier publication [24], see also [15]. When inspecting the entries in Table 4, the reader will notice a number of conditions that have to be obeyed for specific compositions. These conditions reflect intrinsic structural changes, which

Table 4 Empirical factors for the calculation of the thermal expansion coefficient α_{20-300} in ppm/K; it is calculated from the molar fractions of oxides j like $\alpha_{20-300} = \sum x(j) \cdot \alpha(j)$.

Oxide j	Increment $\alpha(j)$	Condition
SiO ₂	10.5–10· $x(\text{SiO}_2)$	$x(\text{SiO}_2) > 0.67$
	3.8	Otherwise
TiO ₂	10.5–15· $x(\text{SiO}_2)$	$0.5 < x(\text{SiO}_2) < 0.8$
ZrO ₂	–6.0	
Al ₂ O ₃	–3.0	
B ₂ O ₃	–1.26· φ	$\varphi < 4$
	–5.0	Otherwise
MgO	6.0	
CaO	13.0	
BaO	20.0	
MnO	10.5	
ZnO	5.0	
PbO	13.0	$\sum x(\text{R}_2\text{O}) < 0.03$
	13.0	$(1/\psi) \cdot \sum x(\text{R}_2\text{O}) < 3$
	$11.5 + 0.5 \cdot \sum x(\text{R}_2\text{O})$	Otherwise
Li ₂ O	27.0	
Na ₂ O	41.0	in Na ₂ O–SiO ₂
	39.5	Otherwise
K ₂ O	46.5	in K ₂ O–SiO ₂
	42.0	Otherwise

$$\varphi = (\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{BaO} + 0.7 \cdot \text{CaO} + 0.7 \cdot \text{PbO} + 0.3 \cdot \text{Li}_2\text{O} + 0.3 \cdot \text{MgO} + 0.3 \cdot \text{ZnO} - \text{Al}_2\text{O}_3) / \text{B}_2\text{O}_3;$$

$$\psi = \sum (\text{RO} + \text{R}_2\text{O}_3 + \text{R}_2\text{O}_5);$$

Oxide amounts to be inserted as molar fractions.

can be understood only if the chapters in Part II are consulted. As an example, the sophisticated condition for the increment of boron oxide by the factor φ reflects the expected coordination change between [BO₃] and [BO₄] units in the glass (Chapter 7.6). Predictions based on these factors yield estimates of the thermal expansion coefficient within an error margin of ± 0.3 ppm/K. The effect of addition of x wt % of another oxide is shown in Figure 9 for the base glass composition 74 SiO₂·10 CaO·(16– x) Na₂O. Clearly, alkali oxides raise the thermal expansion coefficient whereas especially oxides of highly charged ions decrease it. Iso lines of the expansion coefficient within the ternary sodium borosilicate system are plotted in Figure 10. Optional compositions for so-called “hard” glasses with $\alpha = 4$ ppm/K are marked. The base composition 6 Na₂O·10 B₂O₃·84 SiO₂ may be considered as a starting point for further adjustment. When taking 6 Na₂O $\rightarrow$ 4 Na₂O, 10 B₂O₃ $\rightarrow$ 13 B₂O₃, 84 SiO₂ $\rightarrow$ 81 SiO₂ + 2 Al₂O₃, then the composition obtained is

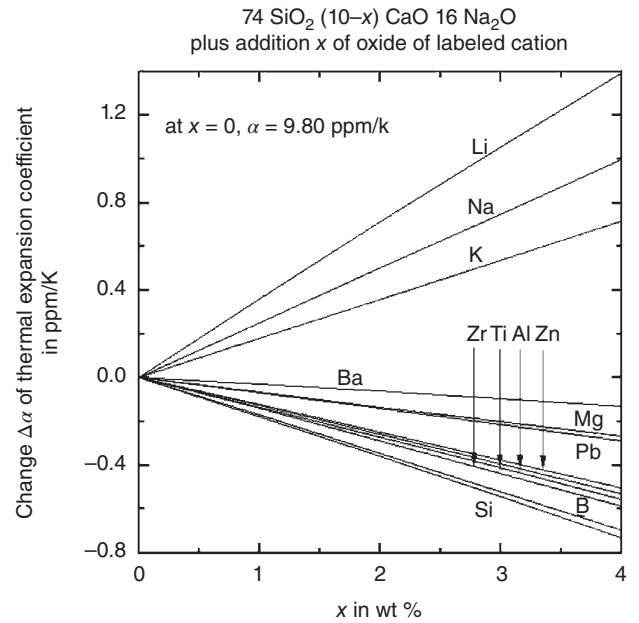


Figure 9 Change of the thermal expansion coefficient α_{20-300} in the base glass composition 74 SiO₂ 10 CaO 16 Na₂O upon the replacement of x wt % of calcia by another oxide.

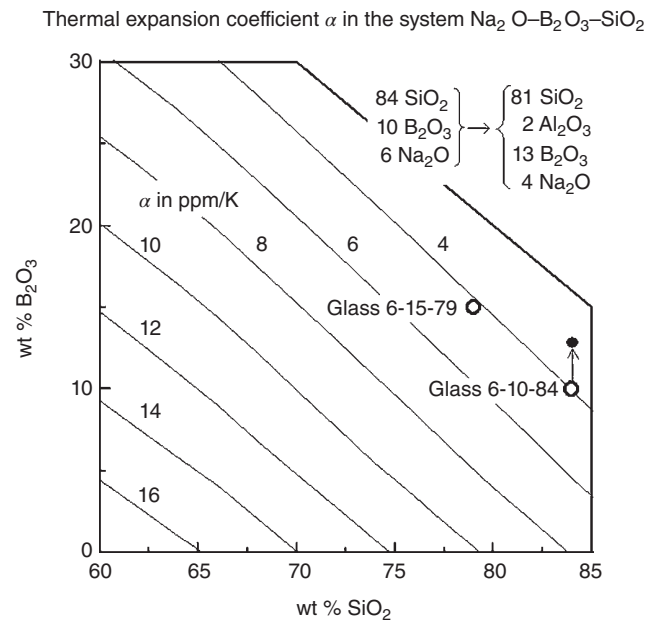


Figure 10 Ternary composition diagram of the system Na₂O–B₂O₃–SiO₂ showing iso lines of the thermal expansion coefficient α_{20-300} ; base glass compositions reaching coefficient $\alpha_{20-300} = 4.0$ ppm/K are highlighted; the further development strategy toward an industrial product is sketched in the upper right corner and indicated by the arrow.

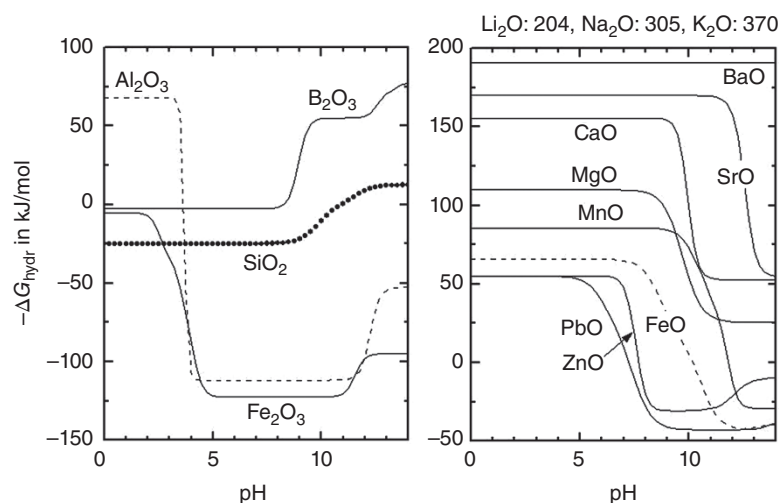


Figure 11 Hydrolytic stability of different pure oxides in aqueous solution as a function of pH; the stability is given in terms of Gibbs energy of hydration ΔG_{hydr} ; negative values of ΔG_{hydr} are plotted against pH to make the most stable cases appear at the bottom of the graphs.

indeed very similar to those of the commercial products *Duran* or *Pyrex* having a thermal coefficient of expansion $\alpha_{20-300} = 3.3 \text{ ppm/K}$ between 20 and 300 °C.

4.4 Chemical Durability

Chemical durability is a very complex property. Attempts at generating an oxide increment system for the prediction of this property are not recommended because the most basic information on chemical durability must reflect the stability of a glass in strong acids, neutral water, and strong caustic solutions. Irrespective of their role in the glass structure, even pure oxides exhibit quite a complicated stability pattern as a function of the solution pH. This is shown in Figure 11 (from [25], revised version). Clearly, a general statement like “alumina enhances the chemical durability of a glass” is erroneous. It is true, alumina enhances the chemical durability under moderately acid to fairly caustic conditions, but it destabilizes a glass exposed to strong acids. Anyway, Figure 11 provides a first guideline of the effect which may be expected from a specific oxide in a given pH range, and hence, to base a first step of development on this information. In Chapter 5.11, the approach is further elaborated.

5 Perspectives

Challenges for future development mainly deal with the extension of both thermochemical and thermophysical databases for glass-forming systems. The usefulness of phase diagrams and of thermochemical calculations for glass development has been demonstrated. Yet, when it comes to the databases on which the calculations of phase diagrams rest, a severe lack of results for multicomponent melts relevant to the glass industry is felt. This situation is

due to the fact that the extension of databases is chiefly driven by the financially potent metallurgical industry whose compositional focus distinctly differs from the needs of the glass industry. A reliable approach to liquidus temperatures, even for the conventional container, float, or fiber glass branches, would open doors for significant process improvements, resulting in enhanced sand dissolution upon melting, higher pull rates, energy saving, enhanced glass quality, and reduced loss of expensive glass contact materials like platinum.

Whereas thermochemical data sets (standard enthalpies and entropies, C_p polynomials) are available for about 6000 mineral substances, thermophysical standard data sets (including stiffness parameters, and their temperature coefficients) hardly exceed a number of a few hundreds only [26]. From such data, glass technologists might learn how the local atomic structure of a material in general influences the resulting mechanical properties. Thus, to date, the intense quest for stronger glasses rests on an extremely narrow scientific basis. The same is true for the adjustment of the thermal expansion coefficient of solder glasses and substrate glasses to contact materials with very high or very low thermal expansion coefficient (like copper, alumina, steel, or silica glass, low-expansion glass ceramics, respectively).

As stated above, as useful as the conventional oxide increment systems may be in the daily routine of industrial glass development, an approach to truly novel glass compositions with outstanding properties must be based on a deep understanding of the relation between chemical composition, structure, and properties. This is where the field of atomistic simulation should play a decisive role in a near future (cf. Chapters 2.7 and 2.8). The challenge for the coming decades thus consists in developing first-principles tools suitable for industrial applications.

Beyond this, new glass-forming systems with a high potential for application as functional materials are being developed. As described in Chapter 8.9, an important group with relevance at the industrial scale (not shown in the scheme of Figure 1) are hybrid glasses combining both inorganic and organic bonds in their structure. Such glasses have been synthesized via a sol–gel route for a long time (Chapter 8.2); recently, systems accessible by melting have been presented [27].

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1.2

Raw Materials for Glassmaking: Properties and Constraints

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1 Introduction

Even though industrial glasses may now be transported across the planet, glassmaking tends to remain a local industry. When selecting their raw materials, glassmakers target specific oxides or elements to fit quantitatively a calculated recipe [1, 2] by paying special attention not only to their composition and quality but, of course, also to their price. Raw materials in effect may represent up to one third of the total cost of glassmaking, strongly depending on local geographical and logistic conditions such as quarry-to-plant distance or transportation mode, which can be by waterways, rail, or truck. This concern holds especially true for commodity products which, like hollow ware, are facing fierce competition from metal or plastic materials.

Natural materials are in principle favored because, like for the mineral resources used in metallurgy or cement industry, their extraction, milling, and transportation are relatively inexpensive operations compared to the fabrication cost of synthetic materials. Some of the raw materials used in glassmaking must nonetheless be man-made when their natural counterparts are rare, geographically restrained, or of an insufficient purity. As such, their price can dramatically increase the overall batch cost. For instance, synthetic sodium carbonate may constitute up to 50 % of the total batch cost for window or bottle glass, whereas it constitutes less than 14 wt % of the recipe.

After batch preparation, melting and subsequent chemical homogenization are complex processes whose kinetics depend on a number of factors. The grain size distribution of raw materials is particularly important in this respect as the main starting product, quartz, dissolves into the forming melt at a rate of only a few hundred μm per hour, so that pull rates tremendously decrease with increasing grain size. The impurity content is another fundamental issue. As natural products, most raw materials are far from being pure chemicals. The infusible minerals they may bring in have a very high likelihood of surviving the glassmaking process and, therefore, of causing unacceptable production losses even when present at the ppb levels. Other impurities such as iron metal originate in the initial processing of the raw materials. In any case, impurities may cause raw materials to depart from the specified physical and chemical properties. Production yield and quality can then be strongly impacted.

Since many parameters may have either positive or negative consequences if not properly mastered, an in-depth knowledge of the chemical and physical properties of raw materials is necessary. In this chapter, the main chemical, physical, engineering, and economic criteria pertaining to raw materials specifications will thus be reviewed. Because high production yields cannot be obtained without high-quality and permanently controlled raw materials, attention will be paid to production problems most commonly met if the specifications and management of raw materials are not respected. The focus will be here on the raw materials used for silicate glasses manufactured in very large quantities. For specialty glasses, the reader is referred to the chapters that deal specifically with optical fibers (Chapter 6.4), chalcogenide (Chapter 6.5) or metallic glasses (Chapter 7.10), sol-gel products (Chapter 8.2), or bioglass (Chapter 8.4).

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2 Raw-material Specifications

2.1 The Specificity of Raw Materials

A very great many different raw materials can be used today for batch preparation (Table 1). On a chemical and mineralogical basis, they can be classified as silicates, carbonates, borates, oxides, and hydroxides. Recycled glass, known as *cullet* (cf. Chapter 9.9), as well as industrial by-products such as metallurgical slags can in addition enter the batch preparation as amorphous and chemically complex materials. As apparent in Figure 1, the compositions of these materials do not match those of the main glass products, which may thus need up to a dozen ingredients for batch preparation. Even the most common soda-lime silica glasses, circled in Figure 1, manufactured for building (windows), automotive (windshields), packaging (bottles), and solar (photo-voltaic panels) applications, require several of them.

Each raw material plays a specific role. Most of them, as oxides, form the building blocks of the glass network as formers or modifiers (see Chapters 20.4 and 2.5), but among the latter some act as fluxes (alkalis), strengthening agents (alkaline earths), refiners (Na sulfate, Sb, Sn, As oxides), reducers (coke, slags), or even as oxidizing, O_2 -releasing ($BaNO_3$), or coloring (Fe, Cr, Mn, Co, etc.) agents.

Raw materials react in specific ways within the batch. Some are strongly hygroscopic, influencing as such the rheology and homogeneity of the still solid batch. As a matter of fact, water is present in most of the raw materials used to produce glass as either free water (moisture) or bound in the crystal structure of minerals. This essential and unavoidable component is crucial in raw-material management since it minimizes the formation of dust at both the batch plant and the dog-house (entrance of the furnace) levels, but it may also contribute to the formation of lumps made of the most hygroscopic materials, increasing the heterogeneity of the batch at the very beginning of melting. Furthermore, as a result, the batch may contain up to few wt % of water, whereas there are less than 1000 ppm H_2O in the final glass. Removing the water in excess may cost much in terms of both energy and furnace refractories, which may be corroded by acids such as HF and HCl formed when water reacts with other volatile components of the batch.

Without taking into account the formation of intermediate products, the overall meltability of the raw materials is highly variable [3]: H_2O is released at around 100 °C; the deshydroxilation of OH-bearing minerals takes place at 400–800 °C; carbonates release large quantities of CO_2 at 700–900 °C; feldspars melt below 1200 °C; the other

silicates are dissolved in the pre-existing glass melt above that range; bauxite has an even stronger refractory character, needing temperature above 1300 °C to be digested by the surrounding liquid (cf. the DSC thermogram of Figure 3, in Chapter. 1.5).

Suppliers of raw materials process their products through several steps to match their customers' specifications [4]. First, rocks containing the desired raw material(s) are blasted or excavated. The bulk material so extracted is then retrieved, crushed, ground, screened, and sorted to achieve the required grain size, washed, dried, or dewatered before being stockpiled and transported in big bags or in bulk. In some cases a physical and/or chemical beneficiation stage may be needed to achieve the required specifications, especially to remove unwanted impurities. All these steps can have an impact on the final quality of the raw materials in terms of presence of impurities and heterogeneities.

2.2 Grain Size

The particle (or grain) size distribution (PSD) is a crucial parameter of individual raw materials. The required PSD may be costly to achieve. It primarily depends on the hardness of the bulk material, which in turn roughly correlates with its melting temperature [5]. As examples, K-feldspar has a hardness of 6 (out of a maximum of 10) on the Mohs scale and melts at about 1200 °C, quartz has a hardness of 7 and melts above 1700 °C (in the form of cristobalite), whereas corundum ($\alpha-Al_2O_3$) has a hardness of 9 and melts above 2000 °C. Hence, the glassmaker determines the final PSD of the raw material as a compromise between meltability, furnace technology, and price (cost) while also limiting the unnecessary fines that generate dust and furnace carryovers. For specific applications, the glassmaker may in addition request the supplier of raw material to cut the lower end of the PSD to get totally rid of dust from fines.

The sieve PSD curves of a variety of important raw materials are compared in Figure 2 to illustrate their variations with composition and overall batch meltability. The median diameter representing 50% of a sieved raw material is termed D50. For quartz, it ranges from 200 to 300 μm when sand is used for standard window or bottle glass but is much lower at 50–100 μm for the flour, for instance, used as SiO_2 -carrier for E-glass fiber, a peraluminous, boron-bearing, alkaline earth silicate (Chapter 1.5). At the other end, the D50 of limestone and dolomite may exceed 1 mm and that of basalt for insulating glass applications may even be 10 times larger because chemical heterogeneities are in this case much smaller than within a mixture of raw materials.

Table 1 Natural and *synthetic* raw materials compositions and prices.

Oxide	Raw material	Bulk chemistry	Overall mineralogy	Sp – Fr – It – De	Price €/T*
SiO ₂	Quartz-sand	>95 % SiO ₂ ; H ₂ O, Al ₂ O ₃ , RO, R ₂ O, Fe ₂ O ₃	Quartz, free-water, mica, feldspars	Arena – Sable – Sabbia – Sand	20–200€/T
	Sandstone	>95 % SiO ₂ ; H ₂ O, Al ₂ O ₃ , RO, R ₂ O, Fe ₂ O ₃	Quartz, mica, feldspars, FeTi-oxides, free-water	Arenisca – Grès – Arenaria – Sandstein	
	Quartzite	>95 % SiO ₂ ; H ₂ O, Al ₂ O ₃ , RO, R ₂ O, Fe ₂ O ₃	Quartz, mica, feldspars, FeTi-oxides	Cuarcita – Quartzite – Quarzite – Quarzit	
Al ₂ O ₃ , R ₂ O	Feldspar (concentrates from greywacke, arkose, pegmatite, granite, etc.)	17–20 % Al ₂ O ₃ ; 11–15 % R ₂ O; <65 % SiO ₂ ; H ₂ O; Fe ₂ O ₃ , TiO ₂ , CaO	Alkali-feldspars [(K,Na)AlSi ₃ O ₈ : orthoclase, microcline, sanidine, albite, and their solid solutions], quartz (15–20%), micas. Li-rich (up to 1.5 wt %) contain spodumene, petalite, or lepidolite (Li-mica), mainly.	Feldespato – Feldspath – Feldspato – Feldspat	80–150€/T
	Nepheline(–syenite)	20–26 % Al ₂ O ₃ ; 15–18 % R ₂ O; <56 % SiO ₂ ; H ₂ O; Fe ₂ O ₃ , TiO ₂ , CaO	Alkali-feldspars [(K,Na)AlSi ₃ O ₈ : microcline, sanidine, albite, and their solid solutions], alkali-feldspatoids [(K,Na)AlSiO ₄ : nepheline, kalsilite, and their solid solutions], micas, titanite, perovskite, garnet, zircon, apatite, REE-silicates. Silica undersaturated = no quartz	Nefelina – Néphéline – Nefelina – Nephelin	100–130€/T
	Phonolite	20–26 % Al ₂ O ₃ ; 15–18 % R ₂ O; <56 % SiO ₂ ; H ₂ O; Fe ₂ O ₃ , TiO ₂ , CaO	Alkali-feldspars [(K,Na)AlSi ₃ O ₈ : sanidine, albite, and their solid,solutions], alkali-feldspatoids [(K,Na)AlSiO ₄ : nepheline, kalsilite, and their solid,solutions], leucite KAlSi ₂ O ₆ , sodalite, haiüyne, carnegeite, micas, amphibole, pyroxene, titanite, ilmenite, perovskite. Silica undersaturated = no quartz	Fonolita – Phonolite – Fonolite – Phonolith	60–70€/T
	Anorthosite	<30 % Al ₂ O ₃ , <15 % CaO, <45 % SiO ₂ , Fe ₂ O ₃ , R ₂ O, MgO	Anorthite CaAl ₂ Si ₂ O ₈ , pyroxene, amphibole		
Al ₂ O ₃	Bauxite (raw or calcined)	40 % < Al ₂ O ₃ < 80 %; 10–15 % Fe ₂ O ₃ ; H ₂ O; SiO ₂	Gibbsite Al(OH) ₃ , diaspore α-AlO(OH), boehmite γ-AlO(OH), bayerite, corundum, goethite, hematite, kaolin, anatase	Bauxita – Bauxite – Bauxite – Bauxit	250–400€/T
	Hydrated alumina	>60 % Al ₂ O ₃ , H ₂ O, Fe ₂ O ₃ , SiO ₂	Al(OH) ₃ polymorphs		250–300€/T
	Calcined alumina	99 % Al ₂ O ₃ , Fe ₂ O ₃ , SiO ₂	Corundum		500–600€/T
	Kaoline	>45 % SiO ₂ , >35 % Al ₂ O ₃ , 13–14 % H ₂ O, Fe ₂ O ₃	Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄ , quartz	Caolín – Kaolin – Caolino – Kaolin	100–300 €/T
	Pyrophyllite	>65 % SiO ₂ , >25 % Al ₂ O ₃ , H ₂ O	Pyrophyllite Al ₂ Si ₄ O ₁₀ (OH) ₂ , quartz		

(Continued)

Table 1 (Continued)

Oxide	Raw material	Bulk chemistry	Overall mineralogy	Sp – Fr – It – De	Price €/T*
Na ₂ O	<i>Na-carbonate (soda ash)</i>	58 % Na ₂ O, 42 % CO ₂	<i>Natrite</i> Na ₂ CO ₃ , <i>natron</i> Na ₂ (CO ₃) · 10 H ₂ O, <i>trona</i> Na ₂ CO ₃ · NaHCO ₃ · 2 H ₂ O	<i>Soda</i> – <i>Na-carbonate (Soude)</i> – <i>Soda</i> – <i>Soda</i>	150–300 €/T
	Albite	67 % SiO ₂ , 20 % Al ₂ O ₃ , 11 % Na ₂ O, K ₂ O	Albite NaAlSi ₃ O ₈		
K ₂ O	<i>K-carbonate</i>	58 % K ₂ O, 42 % CO ₂	K ₂ CO ₃	<i>Potasa</i> – <i>Potasse</i> – <i>Potassio</i> – <i>Pottasche</i>	500–1500 €/T
CaO	Limestone	56 % CaO, 44 % CO ₂ , MgO, SiO ₂	Calcite CaCO ₃ , dolomite, quartz	Caliza – Calcaire – Calcare – Kalkstein	20–40 €/T
	<i>Burnt lime</i>	>98 % CaO, H ₂ O	CaO, Ca(OH) ₂	<i>Cal</i> – <i>Chaux</i> – <i>Calce</i> – <i>gebranntes Kalk</i>	
	Marble	56 % CaO, 44 % CO ₂ , MgO, SiO ₂	Calcite CaCO ₃ , dolomite, quartz	Marmol – Marbre – Marmo – Marmor	
MgO	Wollastonite	48 % CaO, 52 % SiO ₂	Wollastonite CaSiO ₃		80–450 €/T
	Dolomite	30 % CaO, 22 % MgO, 47 % CO ₂ , SiO ₂	Dolomite CaMg(CO ₃) ₂	Dolomie – Dolomie – Dolomia – Dolomit	20–40 €/T
	Magnesite	48 % MgO, 52 % CO ₂ , CaO	Magnesite MgCO ₃		250–400 €/T
	Talc	32 % MgO, 63 % SiO ₂ , <5 % H ₂ O	Talc Mg ₃ Si ₄ O ₁₀ (OH) ₂	Talco – Talc – Talco – Talk	100–300 €/T
	Basalt	<10 % MgO, <15 % Al ₂ O ₃ , <12 % Fe ₂ O ₃ , <12 % CaO, <44 % SiO ₂ , TiO ₂ , R ₂ O	Olivine, pyroxene, plagioclase, amphibole	Basalto – Basalte – Basalto – Basalt	10–20 €/T
Li ₂ O	<i>Li-carbonate</i>	40 % Li ₂ O, 60 % CO ₂	<i>Zabuyelite</i> Li ₂ CO ₃ , <i>Li(OH)</i> ₂		5000–5020 k €/T
	Spodumene (concentrate from pegmatite)	7 % Li ₂ O, 27 % Al ₂ O ₃ , 65 % SiO ₂	Spodumene LiAlSi ₂ O ₆ , quartz		900–1000 €/T
	Petalite (concentrate from pegmatite)	4 % Li ₂ O, 16 % Al ₂ O ₃ , 78 % SiO ₂	Petalite LiAlSi ₄ O ₁₀		800–900 €/T
B ₂ O ₃	Colemanite	50 % B ₂ O ₃ , 27 % CaO, 20 % H ₂ O, SiO ₂	Ca ₂ B ₆ O ₁₁ · 5 H ₂ O, Ca ₂ B ₆ O ₈ (OH) ₆ · 2 H ₂ O		400–600 €/T
	Ulexite	42 % B ₂ O ₃ , 13 % CaO, 35 % H ₂ O, 7 % Na ₂ O	NaCaB ₅ O ₆ (OH) ₆ · 5 H ₂ O		350–450 €/T
	<i>Borax</i>	35 % B ₂ O ₃ , 45 % H ₂ O, 15 % Na ₂ O	<i>Na₂B₄O₇ · 10 H₂O</i> , <i>Na₂B₄O₅(OH)₄ · 8 H₂O</i>	<i>Borax</i> – <i>Borax</i> – <i>Borace</i> – <i>Borax</i>	350–500 €/T
	<i>Boric acid</i>	56 % B ₂ O ₃ , 44 % H ₂ O	<i>Sassolite</i> H ₃ BO ₃	<i>Acido borico</i> – <i>Acide borique</i> – <i>Acido borico</i> – <i>Borsäure</i>	650–1000 €/T
BaO	<i>Ba-nitrate</i>	58 % BaO, 42 % NO _x	BaNO ₃		1200–1300 €/T

	<i>Ba-carbonate</i>	78 % BaO, 22 % CO ₂	<i>Witherite BaCO₃</i>		350–800 €/T
F	Fluorspar	49 % F, 72 % CaO equivalent	Fluorite CaF ₂	Fluorita – Spath Fluor – Fluorite – Flußspath	300 €/T
SO ₃	<i>Na sulphate</i>	56 % SO ₃ , 44 % Na ₂ O	<i>Thenardite Na₂SO₄</i>	<i>Sulfato – Solphate – Solfato – Sulfat</i>	100 €/T
	Gypsum	46 % SO ₃ , 32 % CaO, 21 % H ₂ O	Gypsum CaSO ₄ ·2H ₂ O	Yeso – Gypse – Gesso – Gips	10 €/T
	<i>Anhydrite</i>	59 % SO ₃ , 41 % CaO	<i>Anhydrite CaSO₄</i>	<i>Anhidrita – Anhydrite – Anidrite – Anhydrit</i>	30 €/T
Fe ₂ O ₃	Iron-oxide	>98 % Fe ₂ O ₃ , FeO	Hematite Fe ₂ O ₃ , magnetite	Hierro – Fér – Ferro – Eisen	100–2000 €/T
Cr ₂ O ₃	Chromite	68 % Cr ₂ O ₃ , 32 % FeO	Chromite FeCr ₂ O ₄ , (Fe,Mg)(Cr,Al,Fe) ₂ O ₄ magnesio-chromite – spinel solid solution	Cromita – Chromite – Cromite – Chromit	300–500 €/T
TiO ₂	Rutile	>98 % TiO ₂ , Fe ₂ O ₃	Rutile TiO ₂ , anatase, ilmenite, titanite	Rutilo – Rutile – Rutilo – Rutil	1400–1500 €/T
	Ilmenite	52 % TiO ₂ , 48 % FeO, SiO ₂	Ilmenite FeTiO ₃		150–200 €/T
ZrO ₂	Zircon	70 % ZrO ₂ , 30 % SiO ₂ , HfO ₂ , REE, Fe ₂ O ₃ , TiO ₂	Zircon ZrSiO ₄	Circón – Zircon – Zircone – Zirkon	1100–1200 €/T
P ₂ O ₅	Ca-phosphate	35 % < P ₂ O ₅ < 45 %, 35 % < CaO < 45 %, R ₂ O, H ₂ O, F	Apatite Ca ₅ (PO ₄) ₃ (OH, F, Cl)	Fosfato – Phosphate – Fosfato – Phosphat	500–1000 €/T
V ₂ O ₅	<i>Vanadium-oxide</i>	>98 % V ₂ O ₅			15,500 €/T
C	Coke	>90 % fixed-C	Coke		100–200 €/T
<i>Reducers</i>	<i>Slag</i>	30–40 % CaO, 30–40 % SiO ₂ , 10–15 % Al ₂ O ₃	<i>Glass</i>		50–200 €/T
O ₂	Cassiterite	>98 % SnO ₂	Cassiterite SnO ₂		16,000 €/T
	<i>As-oxide, As acid</i>	>98 % As ₂ O ₅			>2500 €/T
	<i>Sb-oxide</i>	>98 % Sb ₂ O ₅			
<i>Colorants</i>	<i>Se, Co, Cu, Cd, Mn</i>				

Prices only indicative as actual quotations strongly depend on quality (grain size distribution, iron content, and overall impurities), volumes, transportation costs (quarry-to-plant distance and transportation mode) and, of course, market-price fluctuations. RO = CaO and MgO; R₂O = Na₂O + K₂O.

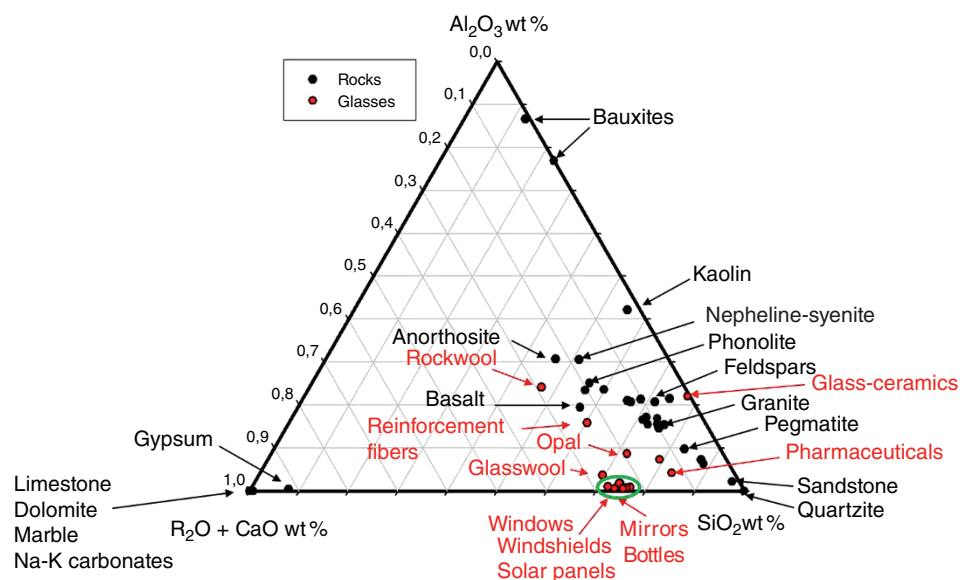


Figure 1 Comparison between the compositions of the main raw materials used in glassmaking and those of some important glass products as projected in the pseudo-ternary $\text{Al}_2\text{O}_3\text{--R}_2\text{O} + \text{CaO--SiO}_2$ diagram.

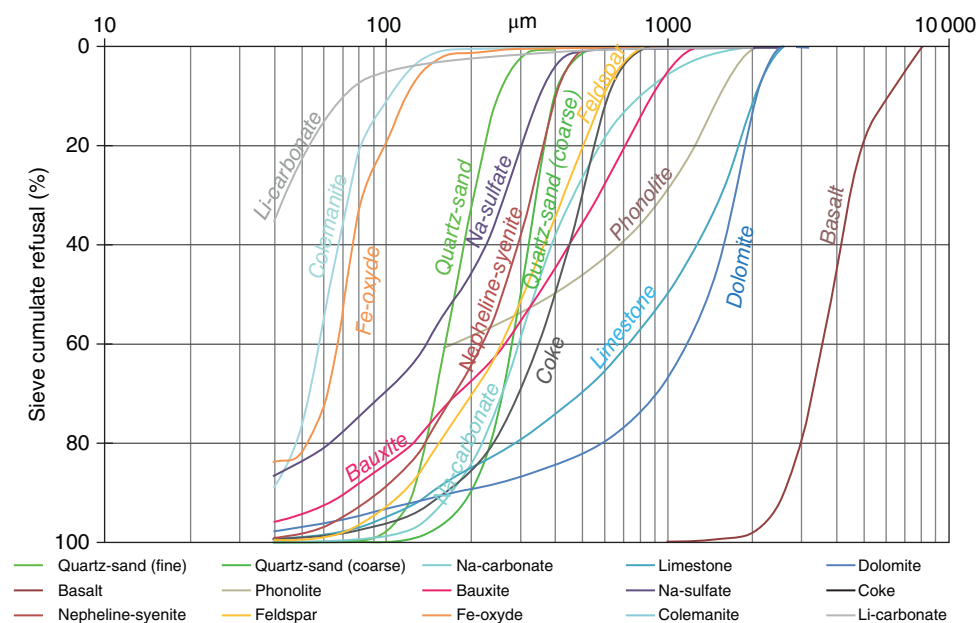


Figure 2 Sieve particle size distribution (PSD) curves of the main raw materials used in glassmaking ($<40\ \mu\text{m}$ laser PSD domain). The D50 is the median diameter representing 50% of a sieved raw material. The steeper the curve, the more homogeneous is the PSD.

2.3 Operational Parameters

Another crucial feature the glassmaker has to consider for raw-material management is the mass budget. It is common knowledge that to produce 1 ton of new, cullet-free glass, one needs around 1.2 tons of raw materials. The $\sim 20\ \text{wt}\%$ mass loss is mostly due to CO_2 released by Na, Ca, and Mg carbonates. Besides free or bound water, raw materials may in addition contain other volatile components such as unbatched carbon, fluorine, chlorine,

sulfur, or boron. When present in traces, these components are not detected through standard chemical analyses (Chapter 5.1) but can nonetheless be quantified as loss on ignition (LOI) above 1000°C . It is an important specification negotiated with the raw-material supplier since the glassmaker needs it to calculate the total mass budget of the process, including the chimney emissions that are most frequently submitted to regulatory obligations.

Because the large majority of industrial glasses are oxides, they are manufactured under oxidizing conditions. The oxygen budget is a key element to control the combustion process and, thus, melting temperatures, as well as the overall color and optical transmission of the glass, which markedly depend on redox conditions ([6], Chapter 5.6). This feature is particularly important for applications such as solar panels, and is essential for glasses made with O_2 -sensitive raw materials such as coloring agents and those that contain a significant fraction of multivalent elements.

For these reasons the glassmaker must take particular care of the total chemical oxygen demand (COD) whose proper analysis is mandatory for certain raw materials entering the batch calculation. The cullet may, for instance, contain significant amounts of organic components, such as PVC, paper, or any other residues from the downstream industrial chain. Metals, besides being detrimental to the overall quality of the glass, are oxygen sinks so that they may locally shift the overall redox budget of the process when they are oxidized. For iron as a coloring agent, for example, one cannot use iron metal, whatever its grain size, but iron oxides instead. Bearing only Fe^{3+} , hematite (Fe_2O_3) is generally selected along with magnetite [Fe_3O_4] whose mixed Fe^{3+} , Fe^{2+} valence states make it suitable for reduced compositions such as amber-glass bottles. In contrast, wüstite [FeO_{1-x}] is generally of very limited use.

Finally, the apparent density is another factor needing to be specified simply because it must be known to dimension the silos where the raw materials are stockpiled at the plant site. As an example, the bulk density of quartz is 2.65 g/cm^3 . Depending on grain shapes and contact angles, that of dry quartz sand is in contrast lower than 2 as a result of a high open porosity. Practically this means that a sand-storage silo must be at least 32% bigger than estimated from the quartz density.

3 From Raw Materials to Melt

3.1 Effects of Digestion Kinetics

The sum of the oxide contents listed in Table 1 (column “bulk chemistry”) is always lower than 100 wt %. The missing few percent mainly relate to impurities. Although it would be tempting to consider them as negligible for the overall glassmaking process, these are actually significant as illustrated by building and automotive glasses, which are manufactured with the float process (Chapter 1.3). Under standard market conditions, a float line averages 600–700 tons of daily production. This pull rate requires to introduce between 500 and 600 tons of quartz sand daily into the melter. With a SiO_2 content

of 99%, about 5 tons of impurities are then introduced at the same time. Even with an expensive 99.9% quartz, there remains about half a ton of impurities. These include different minerals, highly dispersed and diluted in the bulk, some of which may simply be incompatible with the glassmaking process because refractory materials are too slowly digested by the surrounding alkali-rich molten glass.

Even quartz does not melt during the glassmaking process, but is digested at rates of a few hundred μm per hour at 1400°C [7]. It follows that 1 mm-sized quartz grain will need hours to be completely digested. That is why raw-material suppliers sieve and sort their products, and why the maximum PSD of quartz sand is fixed at less than 1 mm by glassmakers. But dissolution rates are typically as low as a few μm per hour for commonly found heavy minerals such as corundum [$\alpha\text{-Al}_2\text{O}_3$]; zircon [$ZrSiO_4$]; kyanite, sillimanite, and andalusite [the Al_2SiO_5 polymorphs]; spinel [$MgAl_2O_4$]; and chromite [$FeCr_2O_4$]. Now, corundum, for instance, melts at above 2000°C whereas the glass temperature does not exceed 1500°C at the hottest point in a melter where the average residence time of the batch is at most a few hours. As a consequence, part of the corundum introduced as mm-sized grains would survive the glassmaking process and occurs in the final product as tiny inclusions, causing mechanical stress and impairing the optical quality. Such a product would not reach the customer to be discarded instead to the internal recycling circuit or, in the worst cases, to be dumped.

The impact of such impurities may indeed be very serious. Consider a 20 m^2 , 5-mm thick float-glass slab. With a volume of about 0.1 m^3 , its weight is 200 kg and requires 170 kg of quartz sand to be made. If on average a single mm-sized grain of chromite was present in 1 kg of the sand, then the 20 m^2 slab would display 170 dot-like defects of chromite. It would clearly be unsellable since current specifications dictate that at most one dot-like defect be present in 100 m^2 of glass. To meet glassmaking specifications, raw materials thus have to be purified by the suppliers through flotation and other costly operations [4].

3.2 Quantification of Heavy Minerals

One finds approximately 150×10^6 grains of quartz in 1 kg of fine sand [4]. In such a population it is obvious that one cannot detect one grain of chromite or other impurity by routine chemical analysis. To detect these minerals at the part-per-billion (ppb) level, one rather takes advantage of the fact that they are denser, or even much denser than quartz (e.g. corundum: $\sim 4 \text{ g/cm}^3$; chromite: $\sim 5 \text{ g/cm}^3$). One can thus concentrate them by immersing the test powder in a liquid with a density slightly higher than that

of quartz, which will then float while heavier minerals will sink, allowing the harmful ones to be identified and quantified with standard methods such as optical microscopy, Raman spectroscopy, or electron microscopy [8]. For this purpose, the most frequently used liquids have long been bromoform (CHBr_3) and diiodomethane [CH_2I_2 , also called methylene iodide], whose room-temperature densities of 2.9 and 3.3 g/cm^3 , respectively, can be slightly lowered through mixing with lighter ethanol [$\text{C}_2\text{H}_6\text{O}$]. Because strict precautions must be observed to handle these toxic liquids, however, sodium polytungstate [SPT, $3\text{Na}_2\text{WO}_4 \cdot 9\text{WO}_3 \cdot \text{H}_2\text{O}$] has become an efficient alternative [9], thanks to the fact that this salt can readily dissolve in distilled water to yield liquids with a maximum density of 3.1 g/cm^3 .

Proper sampling of raw materials [4] thus is needed to guarantee their conformity with regard to possible geological heterogeneity and product variability at the quarry level. It relies on suitable quartering techniques to obtain a true fingerprint of the mineralogy of all raw materials from which incorporation of harmful species may be ruled out or at least minimized. In other words, heavy-mineral content is an overwhelming and crucial specification concerning the physical and chemical properties that must be guaranteed by a producer of raw materials, especially when fabrication of a new glass has to be tested. Not complying with these specifications can generate long-lasting yield drops and large financial losses for the glassmaker. Since glassmakers constantly need to diversify and secure their supplies of raw materials, heavy-mineral characterization must routinely be operated by well-equipped internal or academic laboratories.

Of course, the bulk chemistry must also be determined on a daily basis at the plant by XRF, ICP-MS, or wet chemistry (cf. Chapter 5.1) to monitor the variability of moisture and oxide content, especially for multielement raw materials, and thus to allow batch adjustments needed to keep the glass recipe constant to be calculated (cf. Chapter 1.3). As indicated above, the PSD, LOI, and COD parameters must in addition be included in the almost daily control of raw materials at the plant. In this way it is possible to anticipate possible drifts away from the targeted specifications of the raw-material feed. As for the overall meltability, energy demand, and expected quality, they may be tested less routinely through differential scanning calorimetry (DSC) measurements, while it should be compulsory to test the actual batch incrementally, first in the laboratory (few kg), then in a pilot furnace (~1 ton), and finally at the industrial scale (<1000 tons).

3.3 Impurity-related and Other Melting Defects

Melting quality first and foremost depends on appropriate digestion rates. *Batch stones* can, for instance, readily

occur when market requirements push glassmakers to increase pull rates and, consequently, to reduce the average residence time of the raw materials in the furnace. They also form in case of errors in batch calculation or of scale malfunction. The problem is illustrated with the overall texture and microstructure of the silica batch stone shown in Figure 3. Noteworthy are former quartz grains, whose shape have been preserved although they have been totally replaced by cristobalite (as a pseudomorph) from which newly formed tridymite lath-shaped crystals have grown radially in a groundmass of silica glass [10]. These textural features are typical of an insufficiently dispersed quartz sand within the batch.

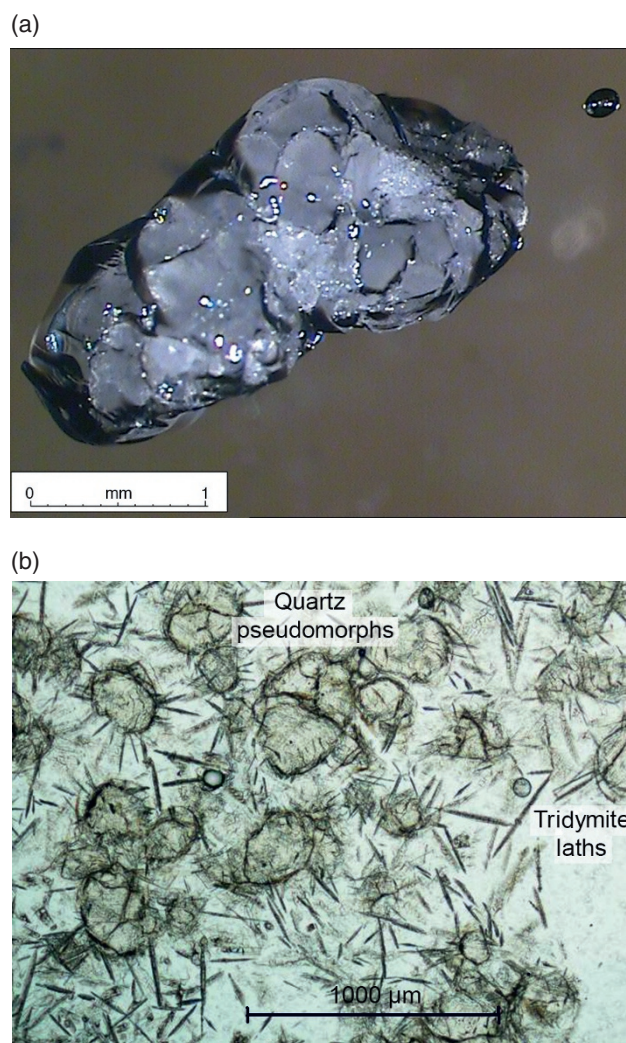


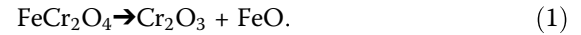
Figure 3 Silica batch stone in a soda-lime silica glass, resulting from incomplete digestion of a lump of quartz grains as viewed under an optical microscope (a) and as observed in a thin section under transmitted light (b), where rounded grains of cristobalite formed as quartz pseudomorph are sluggishly digested while generating radially growing tridymite laths in a vitreous groundmass showing an overall open-porosity.

Regardless of the actual pull rate, the overall moisture content and distribution can provoke the formation of lumps when grains stick together at the batch plant and quickly sinter at the dog-house level, preventing natural convection within the melter from properly stirring the melt under formation. Moisture is of special concern in regions facing very wet or very cold (ice) seasons. Preheating or protecting the raw materials yard can then be an effective, but somewhat costly solution.

Quartz batch stones can also result from an inadequate overall PSD when other raw materials contain up to several weight % of free silica as impurities, whose size distribution differs from that of quartz sand. Limestone, dolomite, and feldspars are typical examples, the two carbonates having a $d_{\max}$ for quartz as high as 2 mm or more

(Figure 2). Given the aforementioned digestion rates of quartz, such large grains will end up as unmolten stones in the production process.

Refractory minerals, of course, raise special difficulties as illustrated in Figure 4 by an incompletely dissolved chromite inclusion. Its core is preserved as FeCr_2O_4 , but it is surrounded by newly formed laths of eskolaite [Cr_2O_3] radially growing from it according to the decomposition reaction:



Although Fe^{2+} then diffuses in the melt, the highly refractory eskolaite crystals (melting at 2435°C) passivate the chromite core, which will thus remain throughout the production process.

Incomplete digestion can alternatively cause the existence of vitreous inclusions called *knots* in the glassmaker jargon. The example shown in Figure 5 is that of an mm-sized pocket of alumina-rich glass within the normal soda-lime silica matrix, which represents the ghost of a feldspar crystal. As already stated, feldspar minerals melt at temperature below 1200°C , therefore early in the process, i.e. already at the dog-house level. When they do so, they generate an alumina-rich liquid phase whose viscosity of 10^5 dPa s at 1000°C is 10 times higher than that of the soda-lime silica glass [11]. At high pull rates this difference prevents rapid enough interdiffusion from taking place to ensure complete mixing between the two liquids, whence the presence of knots. A simple solution to avoid them when Al-carriers are feldspars thus is to control the PSD of these minerals. But, with very different PSD ranges, feldspars can also be present as impurities in a variety of materials such as quartz-sand, limestone, and dolomite. Likewise, a proper

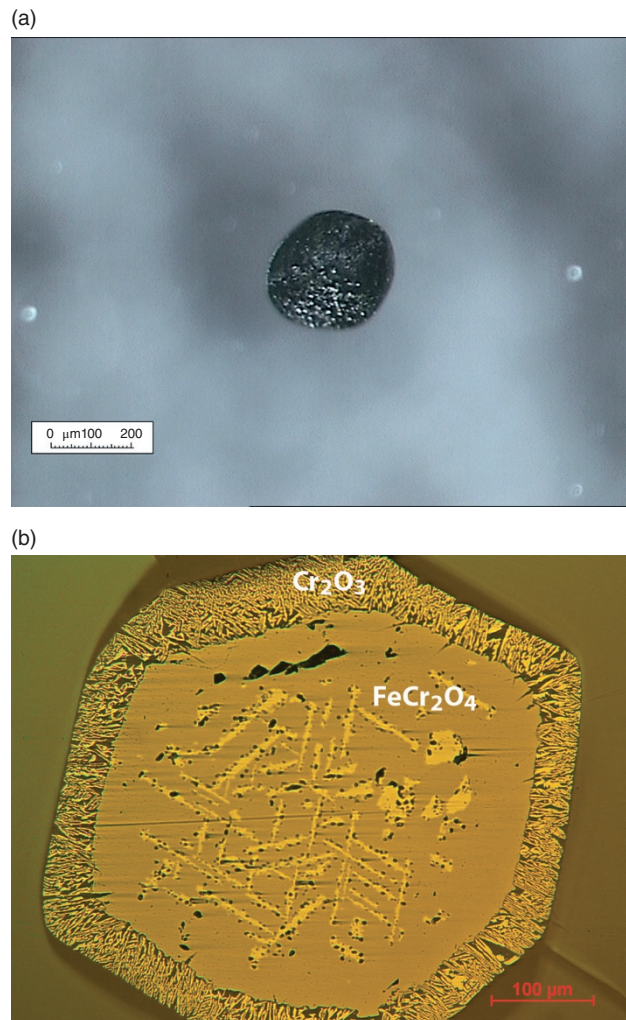


Figure 4 Undissolved chromite crystal in a soda-lime silica glass as seen under a binocular microscope (a) and in a polished thin section photo under reflected light (b). The chromite grain shows a preserved FeCr_2O_4 core, exsolution lamellae, and radially growing eskolaite Cr_2O_3 laths in the outer shell.

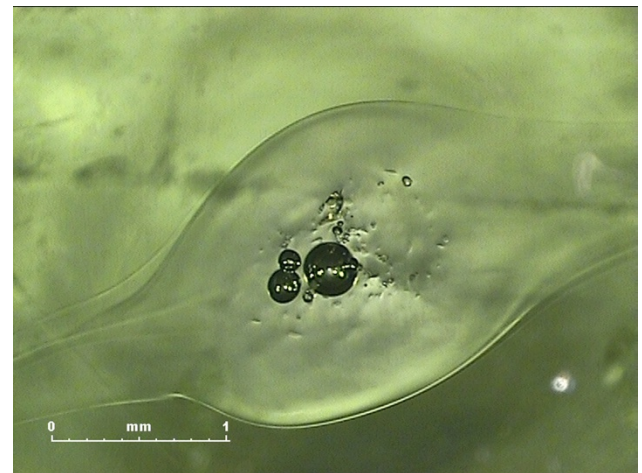
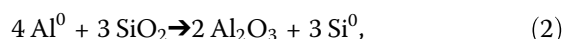


Figure 5 A feldspar knot with about 20 wt % Al_2O_3 , enclosing bubbles (gas inclusions) in a soda-lime silica glass as seen under a binocular microscope.

PSD helps minimizing the presence of alumina-rich knots in the final product when the Al-rich phonolite and nepheline syenite rocks are used as raw materials.

Even cullet may be a source of defects, which has important practical consequences since it accounts for up to 80–90 % of the total batch for tinted soda-lime silica glasses used for packaging, and up to 30 % for standard-window and windshield glass production. In this case, the culprit is metallic aluminum from soda-drink cans that pollutes household cullet or from framework residues of window cullet coming from building demolishing sites [10]. Through the redox reaction [12]



metallic silicon forms while hydrogen is liberated by the reduction of OH-group from the glass network. The result is a sub-mm-sized silicon bead surrounded by H₂-rich gas inclusions (Figure 6), which are virtually indestructible because they are digested at rates of the order of a few μm per hour. Appropriate cullet management is thus needed to reduce this risk in glass production. For similar reasons, the absence of ceramic, porcelain, and glass-ceramic shards polluting the external cullet must also be checked carefully to avoid stones, knots, and slowing down of the production.

Another special case arises from the presence of nickel in raw materials. In sulfate-fined glasses, reduction of NiO yields nickel metal, which can react with trace amounts of sulfur to form small inclusions of NiS [mill-erite] [13]. The problem here is that this sulphide in principle undergoes near 390 °C a phase change from a high-temperature α-polymorph to a denser low-temperature β-polymorph. The kinetics are slow

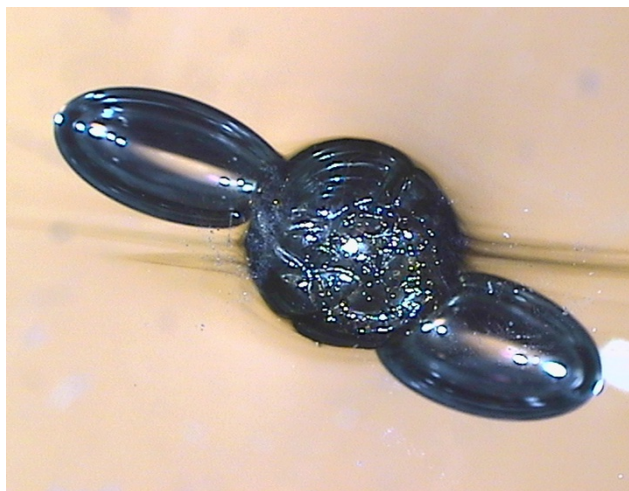


Figure 6 A sub-mm-sized silicon bead surrounded by H₂-rich gas inclusions in a soda-lime silica glass, resulting from aluminum-metal contamination of recycled cullet.

enough, however, that the phase transition can take place at room temperature several days to several months or even years after tempering (Chapter 3.12). When it eventually does so, the 2–4% volume expansion generates cracking and sometimes the explosion of the finished glass product. Hence, both Ni metal and oxides are nowadays proscribed in raw-material specifications.

3.4 The Problem of Dolomite Decrepitation

Even when all chemical, physical, and mineralogical specifications are respected, some raw materials may pose special difficulties upon heating. Decrepitation is such a special case affecting mainly dolomite [14] and, albeit to a lesser extent, limestone. It occurs at 300–400 °C, hence well before the onset of decarbonation and decomposition of the (Ca, Mg) carbonate. Although it is still poorly understood [14], decrepitation appears to result from a sudden change in the overall PSD of dolomite, and an overall increase of fines, when dolomite grains locally burst into smaller grains. The decrepitation factor is defined as the increment in the fraction of grains smaller than 60 μm after heating at 1000 °C. It can range from a few to several 10% depending on geological history and, in particular, on the thermal pathway followed by the dolomite after its formation. High-decrepitation dolomites are detrimental to the glass process because they contribute to further increase in dust and carryover in the furnace atmosphere. The latter in turn contribute to clogging phenomena at the level of regenerator chambers, drastically decreasing their energy-recovery efficiency. Furthermore, dolomite dusts may increase the overall wear of the furnace-superstructure refractories through the formation of new Mg-bearing phases that decrease their overall durability. When a local supply of good-quality dolomite is lacking, glassmakers may thus find safer to produce Mg-free glass.

4 Special Raw Materials

4.1 Sodium Carbonate

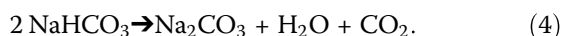
Originally known as natron, sodium carbonate hydrates have been the main flux used ever since the beginnings of glassmaking. As exemplified by the celebrated Wadi el Natroun deposits in Egypt (Chapter 10.3), very pure Na₂CO₃ hydrates did form naturally but such deposits currently satisfy only about 30 % of 50 million tons used annually in industry, half of which for glassmaking. The cheapest source of sodium would be NaCl, but this salt is quite unfit for production of oxidized glasses in view of chlorinated emissions that would in particular dramatically degrade the wearing resistance of the furnace

refractories. Soda [NaOH] would be a much better alternative, but its price on an Na₂O basis is twice that of synthetic Na₂CO₃ as manufactured with the Solvay process [15], which currently supplies 59% of the market.

Sodium is most conveniently added to the batch as Na₂CO₃, whereas CaCO₃ is the most common source of carbonate ions. Hence, the goal of the Solvay process is to achieve the overall reaction:



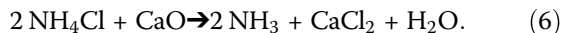
Now, this reaction could not proceed directly in the solid state even if its Gibbs free energy of about 100 kJ/mol were not positive. But Na₂CO₃ is readily obtained through heating of NaHCO₃ precipitates at around 200 °C:



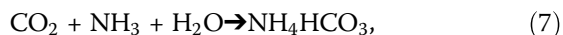
The trick of the Solvay process thus is to produce sodium bicarbonate in an aqueous solution from an NaCl brine with the reaction



which, as a by-product, yields calcium chloride, a valuable compound:



The first step then consists in producing a solution of ammonium bicarbonate with



such that NH₃ and CO₂ are in the end “totally” recycled within the process.

4.2 Raw Materials with Very Low Iron Contents

Given its strong absorption bands (Chapter 6.2), iron badly needs to be present at the lowest possible concentrations in a variety of glasses for which optical transmission must be optimized. This is, for instance, the case of the sheets protecting silicon wafers from oxidation in solar panels or of the mirrors used for concentrating solar energy in thermal solar plants. Such solar glasses are currently the most transparent available on the market with an optical transmission that can be as high as 91–92%, against values lower than 90 % for standard glasses used in windows or car windshields. Although it might appear small, this difference is in practice significant so that it is worth the subsequent increases in the cost of the raw materials. Here, two factors must be considered, namely the total iron content and the iron redox state. Whereas the latter can be controlled through various process parameters, the former is, of course, determined by the batch

composition. Specifically, the total iron content of extra-clear glasses for solar applications must be below 100 ppm [16], compared to the 600–1000 ppm of clear glass for windows. Natural raw materials with so low iron contents are rare, however, so that suppliers need beneficiation processes to reach them [4]. Grinding then becomes an issue because of potential iron contamination by the steel of the machines. Magnetic separation then is a convenient way to remove any added iron as the last step of raw-material preparation (Figure 7).

4.3 Globetrotting Raw Materials

Like other capital-intensive activities, glassmaking plants traditionally are local industries so as to minimize transportation costs of both raw materials and finished products. Although not necessarily rare geologically, however, certain minerals are not commonly found in commercially exploitable amounts with the consequence that they have to be procured globally, national policies sometimes applying heavy, protectionist custom fees to limit exportations. This situation applies, for instance, to lithium, boron, and some aluminum carriers.

In glassmaking, lithium occasionally serves as an additive (flux) for the production of standard soda-lime silica glasses, but it is mainly used for glass-ceramics to form the β -spodumene [LiAlSi₂O₆] phase that gives them very low thermal expansion coefficients (Chapter 7.11). But the price of Li₂O raw materials has been boosted – it has actually almost tripled – during the last decade, driven by the dramatically increasing demand for Li-ion batteries (Chapter 9.5). Among the available Li₂O raw materials (Table 1), Li from brines is mostly used to manufacture Li-carbonate or hydroxide (battery-grade raw materials), whereas mineral Li is incorporated into glass and ceramics. Concentrates of both minerals, spodumene and petalite, are actually crucial sources for the glass industry [17, 18], which does not require as high a purity as Li-ion battery makers. These Li-silicate sources are abundantly available in Australia, China, the United States, and Canada, but much rarer and mostly unexploited in Europe (Austria, Finland, Ireland, Portugal, and Spain) where most of the glass-ceramic industries are in fact located.

As for boron, this element is important for the production of reinforcement fibers (Chapter 1.5) and for insulation (Chapter 9.3) and textile glasses. Borates are found in Turkey, the United States, China, Russia, and South America. Turkey is the world's biggest producer and holds the largest reserves. The United States ranks second both in terms of reserves production, with about 40% of the market [19]. In this case too, the heterogeneous distribution of boron sources translates into high transportation costs as a component of the raw-material supplies.

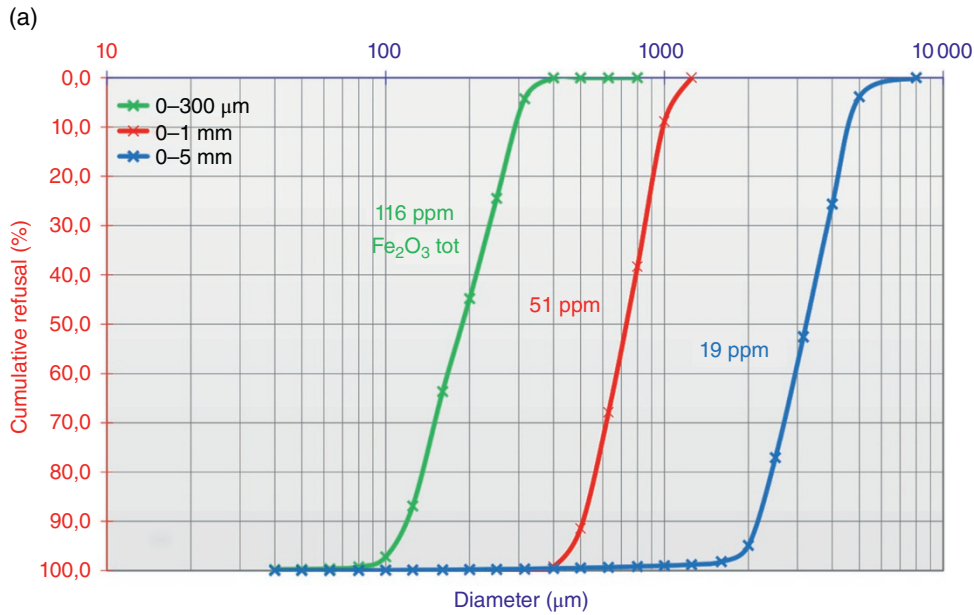


Figure 7 Increases of iron contamination caused by grinding of quartz made with steel-bearing jaws to shift the particle size distribution. (a) Iron contents associated with the PSD curves of quartz sand and flour ground. (b) Alignment of steel particles in the magnetic field of the separator during the deferrization step of raw-material beneficiation. Picture scale of 0.5 m.

Concerning aluminum, bauxites and laterites are used as Al-carrier in standard industrial glasses. The main and largest exploited ores, representing more than 90% of the reserves, are located in Western Africa (especially Guinea), Brazil, Central America and the Caribbean (Jamaica, Trinidad and Tobago, Suriname) and Australia [20]. In this market, however, glassmakers are very distant followers of alumina-ceramics makers and especially of metallic aluminum producers whose needs are several orders of magnitude higher than theirs. In instances when relatively high contents of both aluminum and alkalis are required, it may be advantageous to use instead nepheline

syenite, a rock consisting mainly of alkali feldspars and nepheline $[\text{NaAlSiO}_4]$, which is exploited and exported from Norway, Russia (Kola Peninsula), South-Africa, Brazil, India, and China.

5 Perspectives

More than 100 million tons of glass (container, flat, fiber, and specialty) are produced yearly. In a society moving toward a CO₂-less or -free economy, extra-clear glasses

will play a key role for the development of an efficient solar energy market. As the availability of extra-pure raw materials is not infinite [16], however, beneficiation techniques will need to be improved in order to meet cost-efficient requirements adapted to the forthcoming societal challenges. In terms of both volumes and quality, middle- and long-term availability of raw materials is a major challenge for sustainable, cost-related production. But a successful low-carbon society implies the fast development of infrastructures and commodity products, which contribute to the overall industrial minerals' demand in direct competition with the glass raw materials supply chain [16]. Governmental initiatives, such as the European Union ERA-MIN Program [21] and the EIT Raw Materials, intend to build an EU-wide network linking industry, academia, and research institutes capable of sustaining the domestic supply chain of non-energy mineral resources. In parallel, efforts are made to improve batch recipes through either the use of standard raw materials with lower energy consumption [22], or totally new ways exploiting the huge potential of the recycling supply chain. Food and agriculture wastes, for instance, could allow making glass with "exotic" sources such as eggshells for Ca-carbonate, banana peels as K-carrier, or rice husk for silica [23]. Major changes are likely on the way.

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1.3

Fusion of Glass

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1 Introduction

Fusion is of course the high-temperature process through which a glass is synthesized from the relevant raw materials. In this chapter, fusion and melting will be used synonymously as no preference for either term obtains in glass manufacturing. Nevertheless, the matter deserves a few comments because both are used to describe different processes under conditions of constant pressure. They may denote:

- 1) A first-order phase transition of a single-component system (such as pure H_2O , SiO_2 , or $\text{CaAl}_2\text{Si}_2\text{O}_8$) from the solid to the liquid state. This transition occurs at a unique melting (or fusion) temperature T_m where the solid and liquid coexist; between them, however, there exist discontinuities in enthalpy and entropy, which are the enthalpy (ΔH_m) and entropy ($\Delta S_m = \Delta H_m/T_m$) of melting (or of fusion).
- 2) The transition of a thermodynamically stable assemblage of different crystalline phases to the liquid state. Upon heating, such a system passes through a temperature range at which the solid and liquid phases coexist; the solidus (T_{sol}) and liquidus (T_{liq}) temperatures are the lower and upper bounds, respectively, of this interval.
- 3) The transition of any mixture of crystalline phases to the liquid state upon heating. Since such phases are not in thermodynamic equilibrium, they begin to react mutually in the solid state so that the actual path of fusion may be unpredictably complicated.
- 4) A special technique, often used by artists, to join pieces of glass together to form an object. It makes use of the fact that a glass, upon heating, undergoes gradual softening from a rigid condition below the

glass transition temperature T_g to the liquid state at $T > T_g$. At sufficiently high temperatures, glass pieces may then be joined together by viscous flow. The transition from a crystalline state is here nonexistent, which distinguishes clearly this special meaning of *fusion* from the three others.

In glassmaking, it is of course case (3) that matters, which is why it will be exclusively dealt with in this chapter. It begins with the heating of a mixture of granular solids, the *batch*, and is completed when a homogeneous liquid state is reached. Regardless of the complexity of its chemical composition, any glass is associated with a liquidus and a solidus temperature between which crystals and melt can coexist in thermodynamic equilibrium. Upon not too fast heating, a liquid for instance begins to form at the liquidus temperature of the system as determined by its overall chemical composition.

At the industrial scale, the fusion of glass is a most complex energy-intensive, high-temperature process. The transformations involved in are multiphase, multicomponent chemical reactions, which are quite different from a student's simple concept of chemical reaction. The goal of the fusion process consists in delivering a workable glass melt of high quality at high production rates and low specific-energy consumption, thereby abiding with environmental legislation. It brings together the issues of reactor technology, bulk solid melting, particle dissolution, as well as redox and acid–base chemistry of the melt. Fusion takes place in specifically designed glass furnaces. Small amounts of specialty glass are melted discontinuously in crucible, pot, or day tank furnaces; the melting compartments may be considered as crucibles of different size, ranging from a few kg to a few 100 kg. For continuous melting of small amounts of some specialty glasses, rotary kilns are used. But the vast majority of glasses is

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continuously melted in large glass furnaces whose production capacities range from a few tons to 1000 t per day.

Regardless of this diversity, fusion involves the same steps that will be successively described in this chapter. The first is the careful preparation of the batch from the appropriate raw materials. The second takes place at high temperatures through the various reactions that lead to a melt through complete dissolution of even the most refractory starting materials. The third step aims at producing a homogenous, bubble-free product by physical and chemical fining. Finally, this chapter will briefly discuss the economically and environmentally important energetics of the fusion process. A review of earlier work dealing with these issues is the feature article by Cable [1].

2 Overview of Industrial Processes

A continuously operated industrial melting process can be split into two distinct room- and high-temperature parts within which well-defined different steps may generally be identified. Their main features are as follows:

Preparation (at room temperature)

P1	Acquisition and storage of raw materials
P2	Chemical analysis of raw materials
P3	Calculation of the proportions of the batch raw materials
P4	Weighing and then mixing of the batch raw materials
P5	Intermediate storage of the batch in a buffer silo
P6	Batch charging

Glass melting (at high temperatures)

M1	Primary batch-to-melt conversion, yielding a <i>rough melt</i> still containing considerable amounts of gas bubbles and undissolved solids Time demand: about one hour Intrinsic energy demand: about 2000 MJ/t of produced glass (3.6 GJ = 1 kWh) Temperature range: 600–1200 °C
M2	Sand dissolution (comprising the dissolution of any other crystalline solids) Temperature range: 1200–1400 °C Intrinsic energy demand (mostly for heating up the melt): approx. 280 MJ/t of glass
M3	Fining, i.e. physical removal of residual bubbles via the thermochemical generation of an adequately high-volume fraction of large bubbles of a fining gas Temperature range: 1400–1500 °C Intrinsic energy demand (for heating-up): approx. 140 MJ

M4	Refining, thermal, and chemical homogenization, whereby refining denotes the resorption of residual gas bubbles upon steady cooling Target temperature: 1350 °C Heat released: –220 MJ.
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At the end of step M4, the melt is finally conveyed to the forming area where it is transformed into hollow ware (Chapter 1.5), or flat glass (Chapter 1.4), or any other type of product. To maintain a high glass quality, the filling level of the melting compartment must be kept constant. Therefore, the sequence of process steps P1 to M4 must be well balanced logistically. This constraint puts a stringent time interval to act for online corrections to steps P4–P6; the buffer silo between steps P5 and P6 thus serves the sole purpose of widening this interval. Along the path from P6 to M4, no action for correction is possible at all.

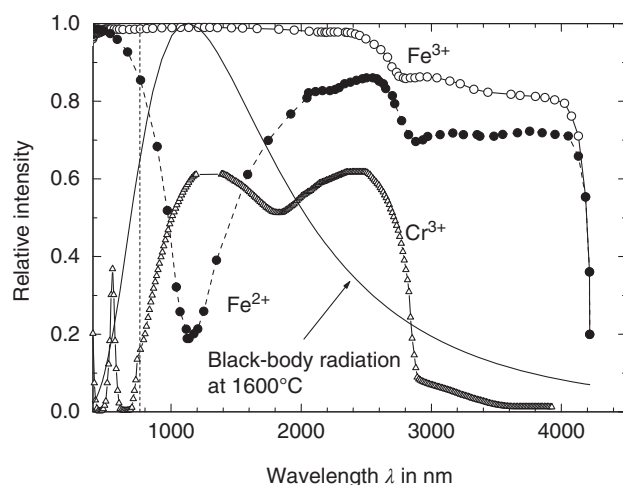
3 Batch Preparation

3.1 Raw Materials

The fusion of a glass of a given composition requires a suitable set of raw materials (Chapter 1.2). These are selected according to their availability and quality, which, in turn, determine their price. The issue of availability may be complex since it includes geological occurrence (for natural materials), production capacity (for manufactured materials), infrastructure for recycling and upgrading (for cullet) as well as transport distance, number of tenders, political stability at the source, etc. Quality is likewise a manifold issue as it concerns chemical composition (from impurities to the main component), mineralogical composition (special attention being paid to side minerals difficult to melt), and grain size distribution (with a particular concern to under- and oversized grain fractions). Among chemical impurities, iron is a critical factor. It is present in virtually every natural raw material but is generally tolerated in glass only at very low levels (Table 1) except, of course, when it is itself a major component of the product as in fire-resistant glass fibers (Chapter 9.3). Here, the iron content is given in terms of stoichiometric Fe_2O_3 irrespective of its actual valence state. Yet, iron is generally present as Fe^{2+} and Fe^{3+} whose relative abundances depend on the redox state of the melt. Owing to the strong absorption bands of both cations, iron has a strong impact on the color of the glass even at low concentrations (Chapter 6.2). And because of its strong absorption in the 600–4000 μm wavelength range, which is that of the heat radiation in the furnace, Fe^{2+} acts as a blinding agent to limit tightly the

Table 1 Maximum iron contents in various types of glasses, given in ppm of stoichiometric ferric iron (Fe_2O_3).

Glass type	ppm Fe_2O_3
Optical glass	10
Ultra-white glass	100
Continuous fibers	200
Flint container glass	250
Standard float glass	300
Amber container glass	2 500
Cr-green container glass	10 000

**Figure 1** Absorption bands of Fe^{2+} , Fe^{3+} , and Cr^{3+} in a glass melt, and radiation intensity in the combustion space of a furnace illustrated in a simplified way by black-body radiation emitted at 1600°C from the upper lining (the crown) of the furnace; relative intensities.

transparency of the melt to IR radiation (Figure 1). In Figure 1, the furnace radiation is illustrated by a black-body-type curve. This is an oversimplification. The actual flame radiation spectrum in a furnace is characterized by strong emission lines of the H_2O and CO_2 molecules in the flame (H_2O : $0.9\text{--}1.1$, $1.8\text{--}2.0$, $2.5\text{--}3.2\ \mu\text{m}$; CO_2 : $2.7\text{--}3.0$, $4.2\text{--}4.7\ \mu\text{m}$) and by black-body radiation from soot particles. The radiation enters the melt directly to a certain extent; however, chiefly via emission (emission coefficient $\varepsilon \approx 0.5$) and diffuse reflection from the top lining (the crown) of the furnace. The curve shown in Figure 1 is an envelope of the actual radiation only. Irrespective of the above details, furnaces in which glasses with high Fe^{2+} contents are melted thus exhibit large vertical temperature gradients and low bottom temperatures; heat transfer from the combustion space has then to be brought about by the convective motion of

the melt. By contrast, melts with very low amounts of Fe^{2+} weakly absorb energy from the combustion space since Fe^{3+} does not influence IR absorption. As a consequence, they display high temperatures at the bottom of furnaces. Controlling the redox state of the melt thus is important not only for color generation but also for furnace operation, a general conclusion that also applies for instance to green glasses colored by Cr^{3+} .

3.2 Calculation of Batch Composition

An accurate chemical analysis of every raw material is a prerequisite for batch preparation (Chapter 1.2). On this basis, one swiftly determines the batch composition by solving a system of linear equations where data are arranged in a specific way (Table 2). First, the total number of different oxides in the raw material basis is determined (6 in the example shown). The target glass composition is entered as an oxide column vector Y_{TARGET} . The large matrix shaded in gray contains the results of raw-material analyses. It is arranged in the order of carriers of the respective glass oxides. For each oxide that is not represented by a specific raw material, the entry 1 is filled in the matrix. If an oxide has more than one carrier raw material (in the example, Al_2O_3 has two carriers, namely feldspar and Calumite®), then their ratio has to be specified, and the respective column entries are merged to a single column in proportion of this ratio. Through these operations, the gray area takes the form of a square matrix M . Next, a preliminary vector R_{PRE} of the batch composition is obtained from the product $R_{\text{PRE}} = M^{-1} \cdot Y_{\text{TARGET}}$. It may contain negative figures since it is impossible to make for example an iron-free glass from iron-containing raw materials. To derive the actual batch-composition vector R , these negative figures are thus set to zero. The real glass composition is then given by the product $Y_{\text{REAL}} = M \cdot R$ before Y_{REAL} is normalized to 100 wt % and R to 1000 kg of resulting glass, or 2000 kg of sand (see following paragraph), or to any other convenient reference mass.

Final adjustment of the batch composition still requires allotments of the appropriate agents for controlling glass color, fining (as described in Section 5.2), redox conditions, and, thus, valence states and oxygen complex formation of polyvalent ions (cf. Chapter 5.6) at the industrial scale. For adjustment of the redox state, the so-called redox number concept [2] is widely accepted and empirically applied in industry. This incremental system assigns a specific redox factor R_i to every member of a set of redox-active ingredients i (Table 3). In the example of Table 4, the batch composition from Table 2 is complemented by 4 kg of sulphate (the amount of soda ash being reduced accordingly to maintain an identical amount of Na_2O in the glass). Then the batch

Table 2 Batch calculation scheme.

The glass			The raw material basis									
			Raw material	Sand	None	Feldspar	Calumite®	None	Dolomite	Limestone	Soda ash	None
			For oxide	SiO ₂	TiO ₂	Al ₂ O ₃	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O
			Ratio			0.5	0.5					
Y _{TARGET}	Y _{REAL}											
Oxide	wt %	wt %	Oxide	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg	kg/kg
SiO ₂	72.00	71.80	SiO ₂	0.9960		0.6920	0.3550		0.0002	0.0040		
TiO ₂	0.00	0.04	TiO ₂	0.0001	1.0000		0.0080					
Al ₂ O ₃	1.50	1.50	Al ₂ O ₃	0.0009		0.2010	0.1250					
Fe ₂ O ₃	0.00	0.03	Fe ₂ O ₃	0.0002			0.0020	1.0000		0.0007		
MgO	3.00	2.99	MgO				0.0650		0.2160	0.0057		
CaO	9.50	9.47	CaO				0.4090		0.3070	0.5502		
Na ₂ O	14.00	13.96	Na ₂ O			0.0620	0.0170				0.5868	
K ₂ O	0.00	0.21	K ₂ O			0.0370	0.0110					1.0000
Sum	100.00	100.00	Sum	0.9972	1.0000	0.9920	0.9920	1.0000	0.5232	0.5606	0.5868	1.0000
			Batch composition vector R in kg raw material per t of glass.									
			kg/t	674.28	0.00	44.02	44.02	0.00	123.39	70.61	231.99	0.00

The results of the considered raw-material analysis is reported in the shaded gray area of the matrix.

Table 3 Redox factors $R(i)$ of selected active raw materials i ; these factors refer to batch compositions normalized to a sand amount of 2000 kg.

Raw material i	Chemical formula	$R(i)$ per 2000 kg sand
Carbon	C : 100, 85, 65%	-6.70
Iron sulfide	FeS	-1.60
Pyrite	FeS ₂	-1.20
Fluorspar	CaF ₂	-0.10
Calumite	Multicomponent slag	-0.073
Iron red	Fe ₂ O ₃	+0.25
Chili saltpeter	NaNO ₃	+0.32
Heavy spar	BaSO ₄	+0.40
Gypsum	CaSO ₄ ·2 H ₂ O	+0.56
Potassium dichromate	K ₂ Cr ₂ O ₇	+0.65
Salt cake; sulfate	Na ₂ SO ₄	+0.67
Gypsum anhydrite	CaSO ₄	+0.70
Sodium dichromate	Na ₂ Cr ₂ O ₇	+0.77
Manganese oxide	MnO ₂	+1.09

composition is normalized to amounts $m_{III}(i)$ per 2000 kg of sand, and the total redox number of the batch is calculated from the weighted sum $R = \sum R_i \cdot m_{III}(i)$. It is true that this number R does not have a straightforward scientific meaning but it allows one to set in a well-defined way the redox state to a desired level. For redox numbers in the

interval $-25 < R < 25$, a fair estimate of the Fe^{2+}/Fe_{total} ratio for is given by $0.4 - 0.015 \cdot R$. Because the chemical composition of the batch can no longer be corrected after charging, these rather simple calculations are mandatory for any successful melting process.

Finally, the raw materials are automatically weighed in proportions determined by batch calculations, conveyed to a mixer, and thoroughly mixed. During mixing, typically 2–3% of water is added to suppress dust formation and segregation induced either originally by transportation or subsequently by mixing. In batches containing soda ash, small amounts of this product dissolve in the water before reprecipitating on other batch grains. This process termed “impregnation” actually enhances the kinetics of batch melting.

4 The Conversion of Batch into Melt

4.1 The Basic Importance of Convection

In principle, the melting compartment (the *tank*) is a shallow basin whose typical dimensions (length $L \times$ width $W \times$ depth D) are $10 \times 6 \times 1 \text{ m}^3$ for medium-size container-glass furnaces and $30 \times 10 \times 1.4 \text{ m}^3$ for float-glass furnaces. The required energy is delivered in a combustion space right above the melting compartment and transferred to the melt chiefly by black-body radiation. Additional energy (5–20%) is delivered by direct electrical heating (*boosting*) of the melt.

The very melting process, i.e. steps M1–M3, takes place in one single box-shaped compartment as sketched in Figure 2a, b. The sketches illustrate some essential

Table 4 Scheme for final batch adjustment with sodium sulphate set to 4 kg/t glass for a targeted redox number R of -24.

Raw material i	$m_i(i)^a$	$m_{II}(i)^b$	$m_{III}(i)^c$	$R(i)$	$R(i) \cdot m_{III}(i)$
	kg/t glass	kg/t glass	kg/2000 kg sand		
Sand	674.28	674.28	2000.00		
Feldspar	44.02	44.02	130.57		
Calumite	44.02	44.02	130.57	-0.073	-9.53
Dolomite	123.39	123.39	365.99		
Limestone	70.61	70.61	209.44		
Soda ash	231.99	229.01	679.26		
Sulfate		4.00	11.86	0.67	7.95
Carbon		1.13	3.35	-6.70	-22.46
Redox number $R = \sum R_i \cdot m_{III}(i)$					-24.04

$\sum R_i \cdot m_{III}(i)$ matches the target value $R = -24$.

^a Batch composition as calculated in Table 2.

^b Batch composition with 4 kg of sulfate added, soda ash reduced accordingly.

^c Batch composition normalized to 2000 kg of sand; amount of carbon varied until the sum.

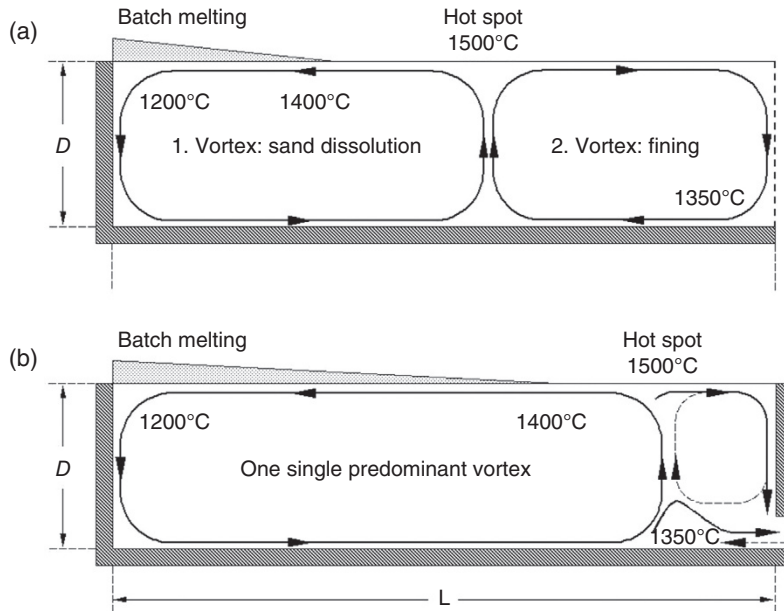


Figure 2 Convection cells (vortices) in the melting tank of a glass furnace (vertical projection): (a) float glass furnace (side port firing), transit to the refining zone indicated by the dotted vertical line on the right-hand side; (b) end port fired container glass furnace, transit to the refiner through a narrow opening at the lower right (the “throat”); D = depth of the tank.

features only (see Chapter 9.7 for details). Spatially, the individual process steps are separated – not in a rigorous but effective way – by two convective vortices. In furnaces with transversal flame direction (so-called side port fired furnaces; flow pattern Figure 2a), these are mainly generated thermally by an appropriate distribution of fuel input to a series of burners arranged along the L axis above the melt. This results in two well-developed vortices with a well-localized hot spot at the position of maximum energy input. In furnaces with longitudinal flame direction (end port fired furnaces; flow pattern Figure 2b), the energy input via combustion along the L axis cannot be controlled at the same distinction as in a side port fired furnace. Here, the flow pattern is typically dominated by a single predominant vortex; the hot spot is shifted toward the end of the furnace. Local stabilization of the vortices is achieved by electrical heating from below, and – for the second type of furnaces – also mechanically by the action of air bubblers or by implementation of a solid barrier (a *wall*) at the bottom of the tank. As seen from Figure 2, the batch floats on the surface of the molten phase and melts continuously in the L direction, thereby typically covering an area whose length is about $L/3$, or more than $2L/3$ for side and end port firing, respectively. Processes M2 (sand dissolution) and M3 (fining) then take place in the first and second vortices, respectively. Note that the first vortex conveys very hot melt right underneath the batch, helping to satisfy the very high intrinsic energy demand of melting. As for the second, it transports a very hot (hence low-viscosity) melt along the surface area, thereby facilitating the escape of rising bubbles. This effect is especially pronounced in the pattern shown in

Figure 2a while in Figure 2b, a large portion of the melt does not reach the surface at all.

At a given pull rate p in t/h, the nominal overall dwell time of the melt in the furnace is

$$\tau_{\text{NOM}} = \rho L W D / p \quad (1)$$

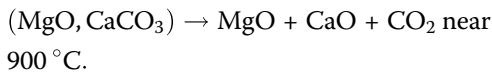
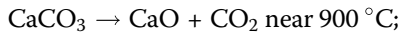
where ρ is the density of the melt and $L \cdot W \cdot D$ the volume of the melting tank. Depending on the size of the furnace and the targeted glass quality (in terms of residual bubbles), τ_{NOM} ranges from 20 to 40 hours. During this time, the average volume element circles 2–6 times in vortex 1, and about twice in vortex 2. For a detailed analysis of the role of the flow pattern on melting and fining, see [3, 4]. The process of refining (M4) already starts at the descent of vortex 2; it is completed in a subsequent compartment termed *refiner*, which is thermally separated from the *melter*. Thermal separation is accomplished either with a vertical wall leaving an opening of about $0.5 \times 0.3 \text{ m}^2$ cross section (the *throat*) at half width right above the bottom of container-glass furnaces (Chapter 1.5), or by an area of moderately narrowed width (the *waist*) in float glass furnaces (Chapter 1.4). For the sake of glass quality (i.e. homogeneity), it is mandatory to keep the position of the hot spot constant at any pull rate.

4.2 The Chemistry of Melting

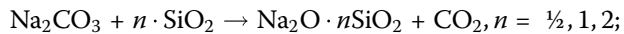
The first high-temperature process is primary melting of the batch. It is typically accomplished within one hour and is characterized by a very high energy demand and

the release of CO_2 from the carbonated raw materials. For a glass batch, the individual reactions involved are the following ones:

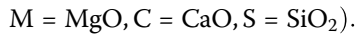
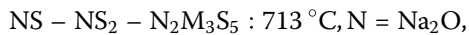
- 1) *Physical melting of salt-like raw materials*, Na_2CO_3 , Na_2SO_4 , NaNO_3 , NaOH , NaCl , etc.
- 2) *Evaporation of batch and hydrate water* in the temperature range $100\text{--}600^\circ\text{C}$.
- 3) *Decomposition of limestone and dolomite*:



- 4) *Formation of a double carbonate*: $\text{Na}_2\text{CO}_3 + \text{CaCO}_3 \rightarrow \text{Na}_2\text{Ca}(\text{CO}_3)_2$ near 785°C ; in conventional batches, this is a side reaction of only minor importance.
- 5) *Formation of silicate melts*. These reactions assume noticeable turnover rates only after actual melting of soda ash:



Formation of ternary melts (eutectic $\text{NS}\text{--}\text{NS}_2\text{--}\text{N}_2\text{CS}_3$: 821°C , eutectic



- 6) *Sulphate coal reaction*: $\text{Na}_2\text{SO}_4 + 4\text{CO} \rightarrow \text{Na}_2\text{S} + 4\text{CO}_2$ at approx. 900°C .

- 7) *Reactions with cullet*. Although it appears as a neutral post in the energy balance, cullet vigorously react with soda ash; very fine cullet compete with sand for soda ash, delaying sand dissolution.

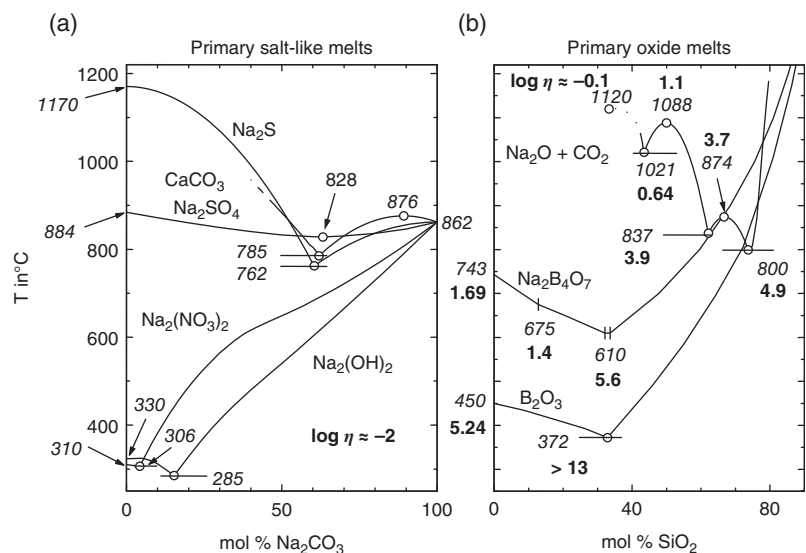
The liquidus temperatures and viscosities of the primary melts forming during the early stages of batch melting are plotted in Figure 3 in the cases of binary salt-like melts formed from soda ash and another compound (Figure 3a) and of the systems $\text{Na}_2\text{O}\text{--}\text{SiO}_2$, $\text{Na}_2\text{B}_4\text{O}_7\text{--}\text{SiO}_2$, and $\text{B}_2\text{O}_3\text{--}\text{SiO}_2$ (Figure 3b).

Owing to their extremely low viscosities, the salt-like primary melts play an important role in bringing about high turnover rates during batch melting. When they are lacking, as in alkali and boron-free continuous fiber glasses, the products in contrast remain in a granular state until they reach their lowest eutectic temperature (compare with Figure 6b in Chapter 6.1).

These different stages of early batch melting are sketched in Figure 4 for a soda lime silicate glass batch. Before a soda-ash melt forms, the batch remains in a granular state (Figure 4a). Then, a primary salt-like, low-viscosity melt rapidly spreads throughout the batch, thereby wetting the solid grains (Figure 4b). This stage is characterized by a large ratio between the liquid interface and the melt volume. It is predominantly at this time that diffusion paths for oxygen exchange are short and that the surrounding atmosphere effectively interacts with the melt to determine its final redox state.

Upon further melting (Figure 4c, d), the melt becomes increasingly viscous and the ratio of liquid interface to melt volume decreases. In a real batch heap, stages (a) to (d) proceed longitudinally along the L axis (see Figure 2) and vertically from the outside to the inside of the batch. The batch melts from both its top and

Figure 3 Liquidus temperatures and viscosities (dPa·s) of primary melts formed during the early stages of batch melting. (a) Binary salt-like melts formed from soda ash and another compound. (b) Primary oxide melts in the systems $\text{Na}_2\text{O}\text{--}\text{SiO}_2$, $\text{Na}_2\text{B}_4\text{O}_7\text{--}\text{SiO}_2$, and $\text{B}_2\text{O}_3\text{--}\text{SiO}_2$. Invariant points indicated by open circles.



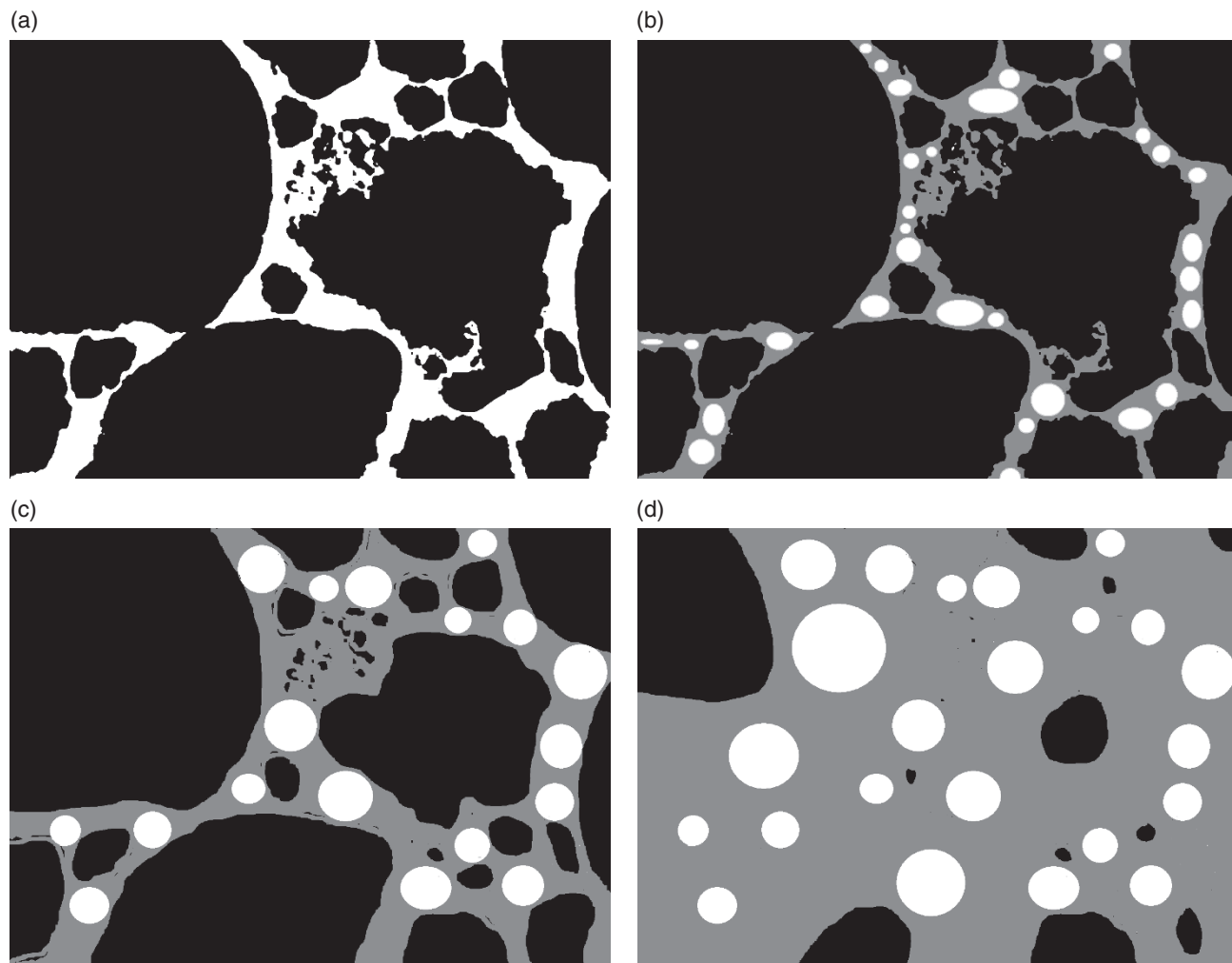


Figure 4 Early stages of batch melting, manually sketched after the scanning electron microscopy micrograph. (a) Open-pore stage with granular solids and gas, the gas composition being dominated by the equilibrium between CO_2 and O_2 from trapped air and the furnace atmosphere. (b) Closed-pore stage with the development of a widespread primary liquid, a large ratio s of effective liquid interface (solid/liquid and solid/gas) and liquid volume, and a gas composition dominated by CO_2 , redox active materials, and polyvalent ions in the primary melt. (c) Reaction-foam stage characterized by large volumes of granular solids, bubbles, and melt, and by progressive melting of solids and decreasing s ratios. (d) Rough-melt stage, the melt being the predominant phase coexisting with considerable amounts of bubbles and undissolved grains and showing on top a seam of the primary foam formed.

bottom side, typically in an almost symmetrical way as the heat fluxes from above and below are of the same order of magnitude. The release of gases is in contrast asymmetric since those from the upper parts readily escape whereas those coming from the lower parts remain trapped below the batch. In a successful primary melting process, the majority of solids are digested, only a minor part being released to the rough melt. This requires good batch mixing and a well-balanced granulometry of the raw materials. The issue can be tested at the lab scale by so-called batch-free time crucible tests. In these simple tests, batch samples of 50–100 g are exposed to a laboratory furnace at 1400°C and the progress of melting is inspected visually after a given time.

4.3 Sand Dissolution

All solids surviving primary batch melting have to dissolve in the viscous rough melt by slow diffusion processes under comparatively low driving chemical forces. This is one of the reasons why, even today, long dwell times are required for the fusion process. By mass, the sand represents the major part of solids that have to dissolve in this way. The process suffers from an especially unfavorable feature (Figure 5): the decrease of the silica concentration from the sand grain to the melt phase represents a strong chemical gradient that causes the grain to be surrounded by a seam of melt with a high viscosity and a low basicity. This gradient affects not only

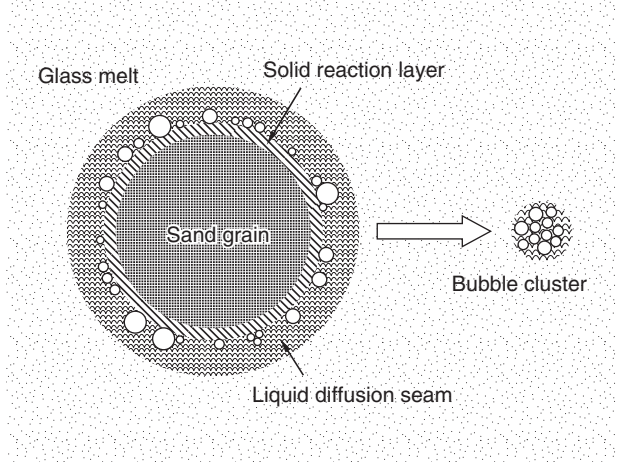
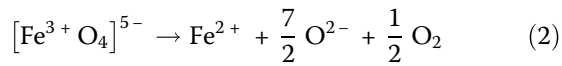


Figure 5 Schematic view of a dissolving sand grain; the grain is surrounded by a solid reaction layer (e.g. tridymite) followed by a liquid high-viscosity diffusion seam with decreasing SiO_2 concentration, hence decreasing acidity, from inside to outside; gas bubbles – mostly O_2 – precipitate at the interface solid/liquid; upon complete dissolution of the sand grain, a bubble cluster remains in the melt.

mass transport but also the solubility of gases, which generally decreases with decreasing basicity (cf. Chapter 5.7). Thus, gases dissolved in the rough melt tend to form bubbles around a dissolving sand grain.

In addition, temperature-induced reduction of ferric iron takes place as described by the reaction



describing how firm $[\text{Fe}^{3+}\text{O}_4]$ oxygen complexes give rise to the weak $[\text{Fe}^{2+}\text{O}_6]$ complexes formed by ferrous iron. The equilibrium constant of the reaction is given by

$$K_p = \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \cdot [\text{O}^{2-}]^{7/2} \cdot P(\text{O}_2)^{1/2} \quad (3)$$

so that, at constant redox state, tiny oxygen bubbles emerge at the boundary of the dissolving grain. Any dissolving sand grain leaves behind it a cluster of small bubbles, removal of these bubbles makes sense only if their generation is over. This is one of the reasons why sand dissolution and the fining process need to take place in separate parts of the furnace.

In summary, successful sand dissolution is a prerequisite for successful fining. Even apparently small differences in the grain-size distributions of sands have a big impact in this respect. This statement will be demonstrated for two different sands. Let us assume that a spherical sand grain with radius r dissolves according to Jander's kinetics:

$$\alpha(r, t) = 1 - \left(1 - \sqrt{\frac{t}{t^*(r)}}\right)^3, \quad t^*(r) = \frac{r^2}{4 \cdot D}. \quad (4)$$

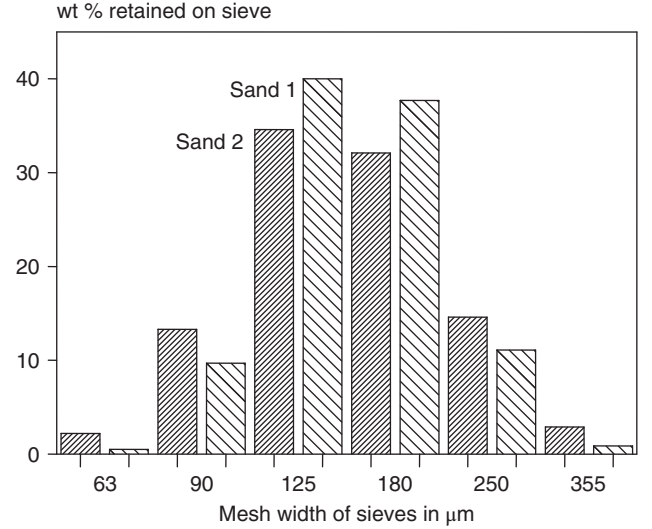


Figure 6 Grain-size distributions of two different glass-grade sand qualities as determined with sieves of increasing mesh width.

Here, $\alpha(r, t)$ denotes the turnover, with $0 \leq \alpha(r, t) \leq 1$ and D a diffusion coefficient. The grain-size distribution is mathematically represented by a log-normal distribution, the differential form of which reads

$$q(r) = \frac{1}{\sqrt{2\pi} \cdot \sigma \cdot r} \cdot \exp \left[- \left(\frac{1}{\sqrt{2} \cdot \sigma} \cdot \ln \frac{r}{r_{50}} \right)^2 \right], \quad (5)$$

where r_{50} is the median radius of the particle size distribution and $\sigma = \frac{1}{2} \cdot \ln(r_{84}/r_{16})$ is the standard deviation denoting the width of the distribution; 16 and 84% by mass of the sand are contained in the fraction smaller than r_{16} and r_{84} , respectively. The values of r_{50} and σ are determined by an evaluation of the sieve analysis (Figure 6). Both sand qualities have an identical median $d_{50} = 2 \cdot r_{50} = 180 \mu\text{m}$, but different σ . An ensemble of grains with a size distribution $q(r)$ then dissolves according to the equation

$$A(t) = \int_0^{\sqrt{4Dt}} q(r) dr + \int_{\sqrt{4Dt}}^{\infty} \alpha(r, t) q(r) dr \quad (6)$$

where $0 \leq A(t) \leq 1$ denotes the reaction turnover of the entire ensemble. The results for the two selected sand qualities upon isothermal dissolution are shown in Figure 7 as obtained with the solution of Eq. (18) given in the Appendix. At first sight, both kinds of sands dissolve in about the same manner. But on closer

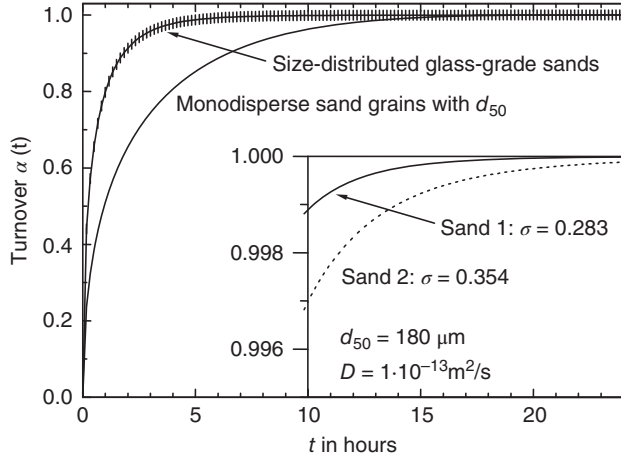


Figure 7 Dissolution turnover of the two sands of Figure 6 as a function of process time for isothermal diffusion with $D = 1 \cdot 10^{-13} \text{ m}^2/\text{s}$. Inset: magnification of the results for nearly complete dissolution.

inspection (see inset), the difference does become large toward the very end of the process since Sand 2 needs significantly many more hours than Sand 1 to reach a 99.9% dissolution level, which is crucial for glass quality.

5 Fining, Refining, Homogenization

5.1 Physical Fining

As noted above, the ideal onset of fining takes place when sand dissolution is complete. Physically, fining relies on two simultaneous processes, namely bubble removal by buoyancy and coalescence of small bubbles to form larger ones. The latter is driven by the release of energy associated with the excess internal pressure of a bubble relative to ambient. As given by Laplace's formula, this excess pressure is $\Delta P = 2\sigma/r$ for a bubble of radius r with a surface tension σ so that the energy gained amounts to about $3.5 \cdot \sigma \cdot r$ when two bubbles of identical size merge. As for the buoyancy velocity v_0 of a single bubble in a melt of viscosity η , it is given by a modification of Stokes' law for dispersed phases with mobile boundaries known as Hadamard's law:

$$v_0 = \Delta \rho g r^2 / 3\eta, \quad (7)$$

where g is the gravitation constant and $\Delta \rho$ the density difference between the melt and bubble.

For a melt with a volume fraction ϕ of bubbles, the effective viscosity becomes

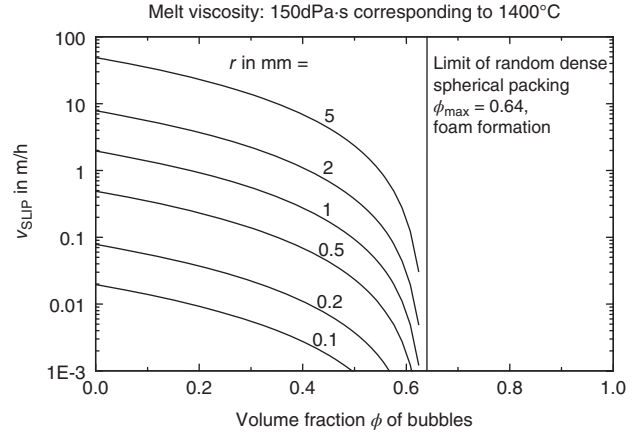


Figure 8 Rising velocity v_{SLIP} of bubble swarms in a melt at a viscosity of 150 dPa·s as a function of bubble radius r and volume fraction ϕ of bubbles.

$$\eta_{\text{eff}} = \eta (1 - \phi / \phi_{\text{max}}) \quad (8)$$

where $\phi_{\text{max}} = 0.64$ is the maximum value of ϕ as given by random close spherical packing. But the density decrease caused by the presence of bubbles, which is proportional to $1 - \phi / \phi_{\text{max}}$, must also be taken into account. The rising velocity v_{SLIP} of an individual bubble within a bubble swarm of volume fraction ϕ thus is

$$v_{\text{SLIP}} = v_0 \eta / \eta_{\text{eff}} = \Delta \rho g r^2 / 3\eta (1 - \phi / \phi_{\text{max}})^2. \quad (9)$$

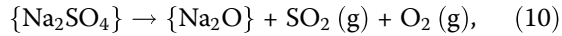
The situation is illustrated in Figure 8 for a viscosity of 150 dPa·s, which is that of a typical float glass melt near 1400 °C. Up to a volume fraction of 0.4, bubbles bigger than 0.5 mm in radius safely escape during the available process time, whereas those smaller than 0.1 mm hardly reach any noticeable rising velocity. They rather rest relative to the environment. An especially critical situation occurs when the volume fraction approaches the limit ϕ_{max} . In this case, bubbles of any size become stagnant so that a foam forms on top of the melt in the fining area as observed in a glass of beer. Hence, this problem calls for utmost care in the design of the chemical part of the fining process, and especially of the amount of fining agent used.

5.2 Chemical Fining

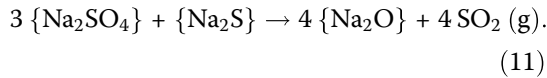
As indicated by old glass specimens, bubbles cannot be completely eliminated with only physical fining. In a somewhat paradoxical way, better results are achieved if additional bubbles are produced within the melt at a sufficiently high, yet not too high, volume fraction to coalesce with the bubbles formed or entrapped during

melting. The process is known as *chemical fining* as it involves reactions with gas-releasing substances.

For reasons of cost, chemical compatibility, and effectiveness, the most widely used agent is sodium sulphate (Na_2SO_4). By experience, 4 kg of Na_2SO_4 are added per ton of produced glass. During the early stages of batch melting, the sulfate dissolves in the melt. Under oxidizing conditions, it decomposes at 1400–1450 °C according to the reaction



where the braces $\{-\}$ denote the state “dissolved in the melt.” Under reducing conditions, sodium sulphate reacts with the Na_2S formed during primary batch melting as follows:

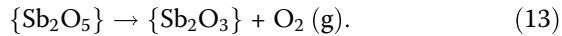


The latter reaction already occurs at temperatures slightly below 1400 °C.

Oxygen fining is an alternative option. The agent typically used is Sb_2O_3 ; it is added to the batch in amounts of 3–5 kg per 1000 kg of sand, in combination with a four- to eightfold amount of NaNO_3 [5]. At the moderately low temperatures of primary batch melting, Sb_2O_3 converts to $\{\text{Sb}_2\text{O}_5\}$ provided that a sufficiently high oxygen partial pressure in the batch is established (Figure 4, stage b). This is achieved by the action of NaNO_3 , which decomposes at batch melting temperatures to release oxygen:



At increasing temperatures, the higher valences of polyvalent ions become increasingly unstable (see Chapter 5.6) so that the fining reaction actually reads



The release of oxygen bubbles reaches its maximum at about 1300 °C and extends beyond 1400 °C. The negative side effect of this procedure is the formation of the NO_x pollutant.

A simple calculation will finally explain why experience and empirical knowledge still play the predominant role in the allotment of fining agents. As used in the batch in Table 4, a mass of 4 kg of Na_2SO_4 represents 56.3 mol of SO_2 , which, at 1400 °C, 1 bar, would fill a volume of 7.6 m³. Now, 1 ton of melt, by contrast, fills 0.4 m³ only. Obviously, only a very minor part of the nominal SO_2 ends up in gas bubbles otherwise a foam instead of a clear melt would be obtained. The major part of SO_2 is in fact lost during batch melting, by evaporation from the melt surface, or is retained in the glass. Thus, the proper

allotment of fining rests on the small difference between sulfate input and the above losses. One of the rare attempts to perform a detailed sulfur balance of a glass furnace revealed that approximately 0.25–0.3 kg of the sulfate added per t of glass are released in the form of fining bubbles [6].

5.3 Homogeneization

After the fining process, the melt is cooled down and homogenized thermally in a steady way. Small residual bubbles resorb themselves because the solubilities of most volatile species strongly decrease with increasing temperatures (Chapter 5.5). For this reason, care has to be taken to prevent local temperature rises from happening during the homogenization process otherwise the so-called *reboil bubbles* would form in the melt and could not be removed in any way. Among dissolved gases, N_2 distinguishes itself by its decreasing solubility with decreasing temperatures. Thus, N_2 -containing bubbles escaping the fining process appear as very tiny bubbles called *seeds* in the final glass. Their number per unit mass of glass represents an important quality criterion. In container glass, a few tens of seeds per 100 g of glass are accepted. Float glass requires a much higher quality (one visible defect per 20 m² already is considered a high defect density) and hence, much longer dwell times (approx. 1.5–2 days vs. 1 day for container glass) in the melting compartment.

6 Energetics of Glass Melting

The amount of energy involved in the fusion of glass is an issue of great interest to the glass industry. Referring to comprehensive quantitative treatments ([7, 8] and Chapter 9.8), we will give only a brief sketch of this issue within the scope of this chapter. The approach rests on the fact that, at constant pressure, the heat (enthalpy) transferred to or drawn from a system is thermodynamically the variation of a state function: as such, the intrinsic energy demand depends only on the initial and final states of the system and it can be determined without any consideration of what is going on along the process road.

The initial enthalpy state is given by the sum of standard enthalpies H°_i at 25 °C, 1 bar, of the individual raw materials i , weighted by their respective amounts m_i in the batch:

$$H^\circ_{\text{BATCH}} = \sum m_i \cdot H^\circ_i. \quad (14)$$

The final enthalpy is given by the standard enthalpies of the batch gases g , $H^\circ_{\text{GASES}} = \sum m_g \cdot H^\circ_g$, and of the glass,

H°_{GLASS} , plus the heat content $\Delta H(T_{\text{ex}})$ of the glass at the exit temperature T_{ex} . The standard enthalpy difference between inputs and products constitutes the chemical energy demand

$$\Delta H^\circ_{\text{chem}} = H^\circ_{\text{BATCH}} - H^\circ_{\text{GASES}} - H^\circ_{\text{GLASS}}. \quad (15)$$

The heat content of the melt at T_{ex} is given by $\Delta H(T_{\text{ex}})$. For convenience, all enthalpy values are inserted in absolute figures, disregarding the minus sign given in thermochemical tables. The overall intrinsic heat demand H_{ex} (exploited heat of the process) is given by

$$H_{\text{ex}} = (1 - y_{\text{CULLET}}) \cdot \Delta H^\circ_{\text{chem}} + \Delta H(T_{\text{ex}}), \quad (16)$$

where y_{CULLET} denotes the weight fraction of cullet per amount of glass produced.

It is true, real raw materials typically do not contain their main mineral phase only, but also contain minor amounts of side minerals. For example, a real quartz sand may contain, beside its main phase quartz, minor amounts of feldspar minerals, magnetite, spinel, etc.; a natural dolomite is typically composed of different minerals forming solid solutions in the system Ca–Mg–Fe^{II}–CO₃ with an overall composition not too far from the pure phase CaMg(CO₃)₂. An accurate determination of the enthalpy values H°_i of real raw materials would thus require the evaluation of multicomponent phase diagrams. However, such an approach would hardly be accepted by the technological community. Beyond this, the gain of accuracy against a simpler approach is minor only. Thus, with the reservation to a more rigorous treatment [7, 8], only the enthalpy values H°_i of pure raw materials are given here in units of MJ/kg:

Raw material <i>i</i>	Enthalpy H°_i in MJ/kg
Pure quartz sand	15.150
Pure albite (NaAlSi ₃ O ₈)	14.952
Pure dolomite CaMg(CO ₃) ₂	12.549
Pure calcite CaCO ₃	12.058
Soda ash	10.659
Sodium sulfate	9.782
Carbon	0.000
Calumite®	13.561

For the batch gases, the following values hold:

CO₂: 8.941; H₂O: 13.422; SO₂: 4.633; O₂: 0.000.

The energy calculation for the real glass composition of Table 2 (where the tiny amount of TiO₂ has been allotted to SiO₂) is summarized in Table 5. The position of the

glass composition in the phase diagram in units of kg of equilibrium compounds per t of glass is found by the following simplified procedure:

$$\begin{aligned} \text{NAS}_6 &= 51.440 \text{ Al}_2\text{O}_3 - 55.697 \text{ K}_2\text{O}, \\ \text{KAS}_6 &= 59.102 \text{ K}_2\text{O}, \\ \text{hm} &= 6 \text{ Fe}_2\text{O}_3, \\ \text{FS} &= 7.345 \text{ Fe}_2\text{O}_3, \\ \text{MS} &= 24.907 \text{ MgO}, \\ \text{NC}_3\text{S}_6 &= 35.112 \text{ CaO}, \\ \text{NS}_2 &= 29.386 \text{ Na}_2\text{O} + 19.346 \text{ K}_2\text{O} - 17.867 \text{ Al}_2\text{O}_3 \\ &\quad - 10.824 \text{ CaO}, \\ \text{S} &= \text{difference to 1000 kg}. \end{aligned}$$

Oxide amounts are to be inserted in wt %. For the components *k*, the shorthand notation hm = FeO·Fe₂O₃, F = Fe₂O₃, M = MgO, C = CaO, N = Na₂O, K = K₂O, S = SiO₂ is used. Column m(*k*) in Table 5 lists the resulting amounts of the constitutional components of the glass. By this procedure, one finds that the standard enthalpies of formation of the glass and melt are 14 189.7 MJ/t at room temperature and 12 665.9 MJ/t at 1300 °C, respectively. The enthalpy physically stored in the melt at 1300 °C relative to the glass at 25 °C is thus 1523.8 MJ/t. By the weighted sum of the heat capacity of compounds *k*, the latter value can be adjusted to any other exit temperature of the melt. For the batch given in Table 4, column “ $m_{\text{II}}(i)$ ”, a chemical energy demand of $\Delta H^\circ_{\text{chem}} = 461.8$ MJ/t is obtained. Fusion of the selected batch with 50% cullet ($y_{\text{CULLET}} = 0.5$) thus requires an intrinsic energy demand of

$$\begin{aligned} H_{\text{ex}} &= (1 - y_{\text{CULLET}}) \cdot \Delta H^\circ_{\text{chem}} + \Delta H(T_{\text{ex}}) \\ &= 1745.7 \text{ MJ/t}. \end{aligned} \quad (17)$$

A well-constructed and operated melting furnace (end port, air-gas fired) reaches an efficiency of heat exploitation η_{ex} of 48%. Thus, the actual energy demand H_{in} of the melting process amounts to $H_{\text{in}} = H_{\text{ex}}/\eta_{\text{ex}} = 3637$ MJ/t. This result is very much in line with industrial experience. Calculations of this kind are of high importance for the evaluation of glass furnace performance [9], for furnace design, as well as for the energy optimization of batch and glass compositions.

7 Perspectives

Although the energetics of the fusion process may be considered as satisfactorily assessed, the kinetic aspects of fusion are not yet well enough understood. The efficiency of heat exploitation η_{ex} of a furnace varies according to a hyperbolic law of the type $\eta_{\text{ex}} = 1/(A + B \cdot p)$ with the production rate *p* (t/h). Thus, furnaces are preferentially operated at the highest achievable rates. The limits for *p* are determined by the rate of heat transfer or the time

Table 5 Calculation scheme for the energetics of a soda-lime silicate glass (composition in wt %).^a

Oxide	wt %	Compound <i>k</i>	$H^{\circ}_{k,GL}$	$H_{k,1300}$	$c_{p,k,L}$	$m(k)$	$m(k) \cdot H^{\circ}_{k,GL}$	$m(k) \cdot H_{k,1300}$
			MJ/kg	MJ/kg	kJ/kg·K	kg/t	MJ/kg	MJ/kg
SiO ₂	71.84	hm	4.4313	3.0196	0.9217	0.18	0.8	0.5
Al ₂ O ₃	1.50	FS	8.7888	7.3999	1.0589	0.22	1.9	1.6
Fe ₂ O ₃	0.03	MS	14.9599	13.2740	1.4582	74.47	1114.1	988.5
MgO	2.99	NS ₂	13.4194	11.6862	1.4335	284.99	3824.4	3330.4
CaO	9.47	NC ₃ S ₆	14.0278	12.6137	1.3301	332.51	4664.4	4194.2
Na ₂ O	13.96	NAS ₆	14.7131	13.2234	1.2358	65.46	963.2	865.6
K ₂ O	0.21	KAS ₆	14.0258	12.5775	1.3755	12.41	174.1	156.1
Sum	100.00	S	15.0023	13.6179	1.4347	229.75	3446.9	3128.8
						Sum	H°_{GLASS}	$H_{1300,MELT}$
						1000.00	14 189.7	12 665.9
							ΔH_{1300}	
							1523.8	

^a $H^{\circ}_{k,GL}$ = standard enthalpy of component *k* in the glassy state; $H_{k,1300}$ = enthalpy of *k* in the liquid state at 1300 °C; $c_{p,k,L}$ = isobaric heat capacity of liquid *k*; $m(k)$ = equilibrium amount of *k* in the multicomponent phase diagram; H°_{GLASS} = standard enthalpy of the resulting glass;

$H_{1300,MELT}$ = enthalpy of the melt at 1300 °C; ΔH_{1300} = heat content of the melt at 1300 °C relative to the glass at 25 °C.

^b hm = FeO·Fe₂O₃, F = Fe₂O₃, M = MgO, C = CaO, N = Na₂O, K = K₂O, S = SiO₂.

demand of the fusion process required to achieve an acceptable glass quality. As of now, however, one does not even know which of the above constraints controls the melting rate. As a matter of fact, the answer depends on both furnace and batch design.

A better understanding of redox and acid base reactions in real furnaces is also desired. Although these reactions are well understood at the laboratory scale, the transfer to a real production situation is still set by experience rather than by scientific principles. In view of the large impact of these reactions on glass quality, progress in this area would be highly appreciated.

Finally, the glass industry is engaged in a quest to lower its overall energy consumption to decrease its operating costs and to satisfy increasingly stringent legislation imposed on high-temperature industrial processes. The design of faster conversion batches is becoming important in this respect. Conventional glass formulae and batch recipes are no longer taken for granted. Efforts are in particular made to design batches that would melt along reaction pathways ensuring higher turnover rates than current randomly mixed batches. Progress may be achieved with selective batching, granulation processes bringing the reaction partners into close contact at the μm scale, preparation of core-shell type pellets, or selective preheating of specific raw-material combinations of the batch. In each case, of course, a prerequisite would be that the obtained energy savings are not offset by increased batch costs.

Appendix

The results plotted in Figure 7 for the dissolution of an ensemble of grains have been obtained from the analytical solution to the integral $A(t)$ of Eq. (6) given by:

$$\begin{aligned}
 A(t) = & 1 - \frac{1}{2} \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y\right) + \frac{3y}{2} \cdot \exp\left(\frac{s^2}{4}\right) \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y + \frac{s}{2}\right) \\
 & - \frac{3y^2}{2} \cdot \exp(s^2) \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y + s\right) \\
 & + \frac{y^3}{2} \cdot \exp\left(\frac{9s^2}{4}\right) \cdot \operatorname{erfc}\left(\frac{1}{s} \cdot \ln y + \frac{3s}{2}\right), \\
 y = & \frac{\sqrt{4 \cdot D \cdot t}}{r_{50}}, \quad s = \sqrt{2} \cdot \sigma
 \end{aligned}
 \tag{18}$$

Here, $\operatorname{erfc}(z)$ denotes the complementary Gaussian error function of argument z , while y and s are used as abbreviations in the formula. It is true that sand dissolution does not proceed isothermally at a constant diffusion coefficient D in a real fusion process, but the utmost importance of the grain-size distribution for a successful fusion process is nonetheless demonstrated clearly.

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1.4

Primary Fabrication of Flat Glass

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1 Introduction

Flat glass is ubiquitous in the modern world, from the facades of high-rise buildings to the large windows of automobiles, the solar power generation systems, and the various kinds of displays that are now integral components of daily life. Not only did these new applications cause a tremendous increase of the world production from less than 7×10^5 in the early 1960s to 59×10^6 metric tons in 2014 (then with an annual growth rate of 7%), but they have also yielded dramatic improvements in glass quality and functionalities. For a glass material that had been manufactured for 2000 years with very little change, the industrial evolution observed during the last 50 years has been incredibly rapid indeed!

As experienced by ancient Roman glassmakers, flat glass made by pouring the melt on a solid substrate has a surface that is not smooth enough to ensure good transparency. Until the beginning of the twentieth century, flat glass had for this reason to be produced out of hollow glass to keep the defect-free surface conferred by fire polish. As made in this way with either the crown or the cylinder process (Chapter 10.8), production of flat glass was very labor-intensive, restricted to relatively small sheets and subject to wastage when cut into pieces for use. Besides, it did not yield high-quality products as is obvious to anyone looking at an old window where objects are often seen distorted through the glass in which defects and streaks are also generally present as a result of the detrimental effects of temperature or composition heterogeneities that could not be avoided during the melting and forming processes.

Mechanization was pioneered from 1894 to 1916 by J. H. Lubbers at the American Window Glass company. Glass cylinders of constant diameter and wall thickness began in 1904 to be blown successfully with a well-controlled low-pressure air flow issued for 15–18 minutes from a machine that was dubbed *iron lung* [1]. Making much bigger cylinders, which eventually reached 1 m in diameter and more than 13 m in length (Figure 1), did reduce considerably cost and labor (whence the very strong Union opposition met by the new process), but did not result in consistently good quality because of the wavy surface and optical distortion induced by the flattening stage. Thanks to *updraw* processes designed in Belgium and in the United States, it then became possible in the following decade to bypass the hollow-glass step. But these processes remained discontinuous because devitrified material had to be removed periodically from the production line.

A true revolution in glass producing thus occurred when the float process was introduced in the 1950s to produce sufficiently good flat glass to make the grinding and polishing steps ensuring high-quality sheets obsolete. Production became in addition completely continuous, which allowed the productivity to be considerably increased without affecting surface quality. Because of the very large amount of glass produced, however, the float process may be impractical when production volumes are small or the glass composition has to be changed frequently. For specialties such as crown glass for niche markets or new glass for electronics markets, older processes are thus still used or new ones have been designed to achieve in particular a high flexibility of throughput and broad ranges of thickness and width.

In this chapter, we will review the various processes that have been designed to achieve these goals, beginning with the first developed ones whose interest is now only historical. The early processes are denoted as *updraw* because

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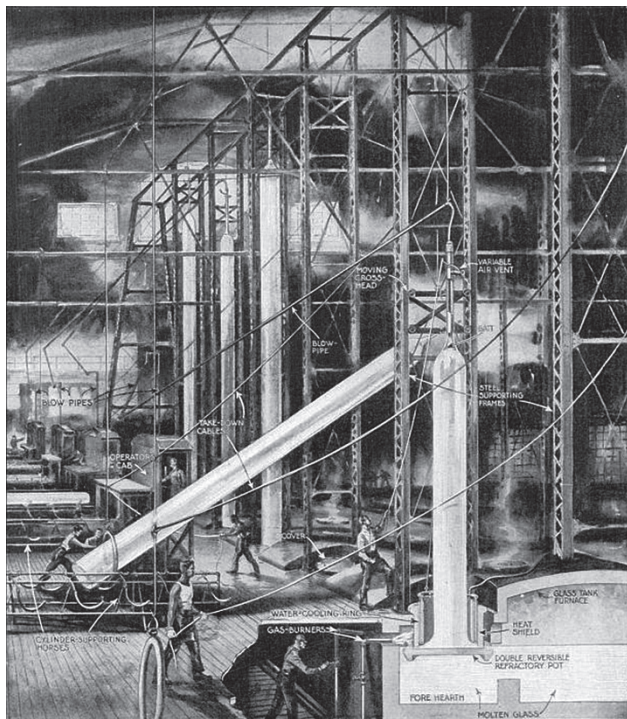


Figure 1 Very large glass cylinders blown mechanically with the Lubbers process for flat-glass production [2].

the glass was drawn upward, in contrast to the *downdraw* processes, which have subsequently been developed for specialty glasses. No attention at all will be paid to the synthesis of the glass itself, which is described in Chapter 1.3. The emphasis will thus be put on the forming process and on the material parameters such as viscosity, density, heat capacity, and surface tension that control it. For more detailed descriptions, the reader will be referred to the available technical literature [1–9].

2 Overview

The main features of past and current processes are summarized in Table 1. Although updraw processes are no longer used for commodity applications, it remains worthwhile to examine their mechanisms and forming principles from a technological viewpoint. For flat-glass forming, the essential requirement is to achieve the constant desired thickness, which now ranges from around 25 mm to less than 50 μm , with the specified width at a commercially admissible cost. Additionally, a flatter and smoother surface is requested. The essential forming defects are mainly of two kinds depending on whether they are derived from locally uneven deformation or undesirable stress. The former is caused by viscosity heterogeneity of glass originating from chemical impurities

or temperature irregularity, and the latter is caused by fluctuation of forming condition or stress imbalance.

Architectural glass must, for instance, satisfy appropriate transparency and reflection, but glass for automobiles and electronics products has to meet much more demanding quality specifications even for thinner glass whose production becomes increasingly difficult.

In all forming processes, two distinct steps are involved once the glass has been melted at about 1500 °C, refined, and homogenized in the melting tank. The first is its delivery under conditions at which the temperature, thickness, and flow rate must be as stable and uniform as possible throughout its whole width at a viscosity of about 10^2 – 10^3 Pa·s (i.e. at 1200–1000 °C for soda-lime silicate). In the second step, the more viscous molten glass cooled down to a temperature at which the viscosity is 10^3 – $10^{6.65}$ Pa·s (i.e. at 1050–700 °C for soda-lime silicate) is stretched in the longitudinal direction, while minimizing simultaneous narrowing of the glass ribbon.

In both glass delivering and stretching systems, properties of the molten glass such as surface tension, gravitational force, and tensile stresses are critical factors, whereas the kinetic aspects of the process are tightly controlled by means of drawing chambers, *débiteuses*, draw bars, rolls, float baths, slots, fusion pipes, etc. Besides, heat management through variously devised heaters and coolers is another fundamental aspect because glass properties vary very strongly with temperature. In addition to physical effects, one must also take into account chemical factors such as possible devitrification and chemical reactions between the glass and other materials, which may themselves depend on glass composition.

Since annealing follows forming, the conditions of the former process are greatly influenced by those of the latter. The formed glass ribbon is cooled down and conveyed to an annealing *lehr* where the decreasing glass temperature is carefully controlled so that residual stresses caused by viscoelasticity are relaxed between the annealing and strain points (10^{12} Pa·s, 570 °C, and $10^{13.6}$ Pa·s, 530 °C, respectively, in soda-lime silicate), and breakage caused by thermal stresses is minimized upon cooling down to room temperature. Finally, optical devices are installed at the downstream part of production line to detect in the glass at room temperature any visible defects such as bubbles, stones, streaks, etc., which originate either from the melting tank or the forming process. These defects are at once clearly marked on the glass ribbon and their positions are usually electronically recorded for optimized cutting either at the end of the production line or by the user according to its specific application. For flat glass to be used in buildings, any 10 m^2 -sheet must, for instance, have fewer than three defects with a maximum size of 1 mm (which would be tantamount to finding fewer than three coins on a football field!).

Table 1 Comparison of forming processes.

Category	Process	Mechanism		Advantage	Disadvantage	Current situation
		Step 1: Preliminary forming (Molten glass delivering)	Step 2: Main forming (Stretching)			
Updraw process	Fourcault process	Glass flow toward débiteuse and upward flow through débiteuse slot	Upward drawing against gravity by pairs of rolls	Earliest continuous production Smaller investment	Quality (Draw lines) Cyclic operation	Almost obsolete for commodity applications Customized/modified process operating for specialty glass
	Colburn process	Glass flow toward drawing point and upward flow from free surface	Upward drawing against gravity by pair of knurled rolls and bending roll	Higher output Wide range of thickness	Low surface quality Complex operation	
	Pittsburg Pennvernon process	Glass flow around draw bar and upward flow above draw bar	Upward drawing against gravity by pairs of rolls	Better surface quality Longer cycle	Distortion Thickness deviation	
	Asahi process	Glass flow toward Asahi blocks and upward flow through gap between Asahi blocks	Upward drawing against gravity by pairs of rolls	Smaller investment Longer cycle	Cyclic operation	
Roll out process	Continuous double roll process	Horizontal glass flow through forehearth	Pressing by pair of rolls	Value added with patterns and wires Versatility Smaller investment	Limited applications	Popular for patterned glass, wired glass, and specialty glass
Float process	For thinner sheet (Top roll process)	Viscous flow with equilibrium thickness in upstream area of bath	Horizontally stretching by conveyor rolls and top rolls	Large-scale production (productivity) Quality (flatness) Flexibility for thickness and width	Large investment Constraint of chemical elements in glass	Widely operating in the world for various applications
	For thicker sheet(Fender process)	Viscous flow with restricted width by pair of fenders	Cooling to appropriate temperature in fender area (without stretching)	+ Thicker and larger sheet		
Downdraw process	Slot downdraw process	Glass flow toward slot and downward flow through slot	Stretching by pairs of rolls and gravity with anchored to slot	Thinner glass Small-scale production	Flatness and surface quality Limited width	Customized/modified process operating for specialty glass
	Fusion downdraw process	Glass flow through trough and over weirs, downward flow on both sides of fusion pipe	Stretching by pairs of rolls and gravity with anchored to root	Thinner glass High surface quality	Minute control required (temperature, glass flow) Constraint of liquidus viscosity	Popular for specialty glass

3 Updraw Processes

3.1 Fourcault

The first manufacturing method successfully industrialized and commercialized was invented from 1901 in Belgium by É. Gobbe and É. Fourcault and finally implemented industrially in 1912 by É. Fourcault in his family company in Charleroi. With this process, the molten glass was drawn vertically through a débiteuse into a continuous glass ribbon. The débiteuse, a rectangular refractory piece with a spindle-shaped slot at the center, was immersed into the molten glass. The molten glass flowing up from the slot was drawn upward and immediately cooled by the coolers while conveyed upward by pairs of rolls in a such a manner that its width was kept constant. The formed glass was annealed along the way and finally cut off at the top of the 8–10 m drawing tower (Figure 2). The flow rate was controlled by the immersion depth of the débiteuse, the shape of the slot, and the cooling exerted, whereas the thickness of the sheet was determined by the drawing speed.

The advantages of this process were many. Not only could production be made with several drawing machines for a single glass tank, but wide ranges of thickness (1–8 mm) and width (1.5–2.5 m) were possible for glass sheets formed with a relatively uniform thickness. In terms of disadvantages, continuous operation was impossible because of the need after about two weeks of operation to remove the devitrified glass that was accumulating around the slot of the débiteuse and on the inner surfaces of the drawing kiln. Whereas the former devitrified

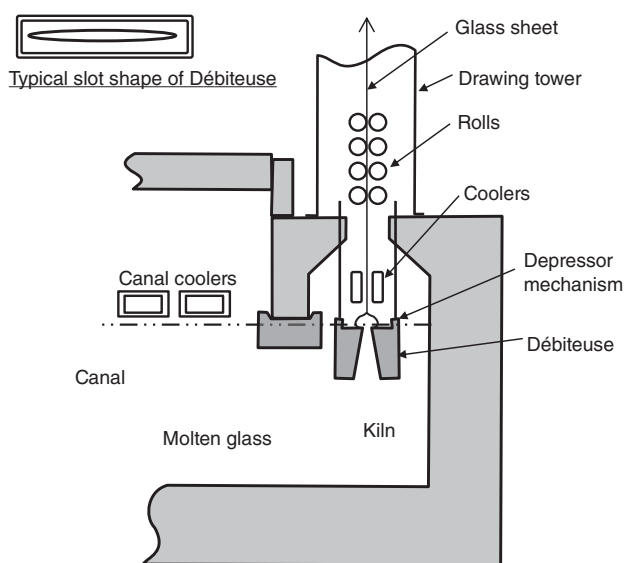


Figure 2 Sketch of Fourcault process in cross section. The molten glass flows up through the débiteuse slot and is drawn upward [3].

material was causing draw lines, the latter changed the flow rate and flow pattern toward the débiteuse. In addition, it was impossible to maintain a completely stable throughput because of bubble formation at the beginning of a drawing cycle and draw-line problems and instability toward the end [1, 3–6].

3.2 Colburn

At the same time the Fourcault process was being developed, the American inventor I. W. Colburn (1861–1917) was experimenting vertical drawing without a débiteuse. His first patent was taken in 1902 but the company he founded in 1906 to produce glass went bankrupt five years later. Working thereafter for the Toledo Glass Company, which had bought his patent, Colby was eventually successful in 1913. With his process, the molten glass introduced into a shallow drawing chamber was drawn upward from the free surface, its edges being gripped and driven by pairs of knurled rolls, and cooled immediately. After being reheated by a gas burner, the formed glass was brought horizontally by a bending roll and conveyed to a horizontal annealing lehr (Figure 3). Since the surface condition and flatness of the bending roll directly determined the quality of the glass sheet, the choice of an appropriate metal as well as the surface treatment and temperature control of the bending roll were crucial. Typically, two drawing chambers were mounted on one glass tank. The 0.9–6 mm thickness range obtained was similar to that of the Fourcault process, but devitrification on the débiteuse was avoided and a much larger width of up to 4.2 m could be obtained, thanks to the horizontally conveying process. But the price to be paid was a lower glass quality because of thickness variations, optical distortions, and surface defects [1, 3–6].

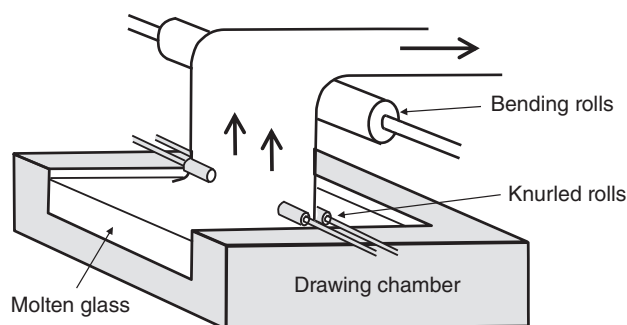


Figure 3 Sketch of Colburn process in a bird's-eye perspective. The molten glass is drawn upward from the free surface and bended horizontally by a bending roll [6].

3.3 Pittsburgh Pennvernion

A process similar to that of Fourcault was developed and introduced by the Pittsburgh Plate Glass Company in 1926. In this Pittsburgh Pennvernion process, the molten glass was not drawn through a *débiteuse* but upward from the free surface right above a drawbar, which was a long and thin refractory part immersed below the glass surface. The ribbon width was kept constant because the glass was cooled by edge folks and coolers. After being annealed and cooled in the drawing tower, the glass ribbon was cut off at the top of the tower (Figure 4). The drawbar served to anchor the drawing point and to ensure uniform temperature and glass flow rate across its width. In addition, ell blocks served to homogenize the drawing temperature by keeping the glass melt covered. The operation cycle was much longer than that of the Fourcault process with a better surface quality and without devitrification complications. Typically, the thickness range was 1–8 mm with a width of up to 3.2 m, but the disadvantages were thickness variations resulting from temperature fluctuations and inhomogeneities in chemical composition caused by drawing of the glass directly from its surface [3–6].

3.4 Asahi

The most recent updraw process has been developed by Asahi Glass Company around 1970 to overcome in a new way the disadvantages of the Fourcault process [5, 6, 8]. With it, a pair of hourglass-shaped rolls, called “Asahi blocks,” is immersed into the molten glass instead of a *débiteuse*

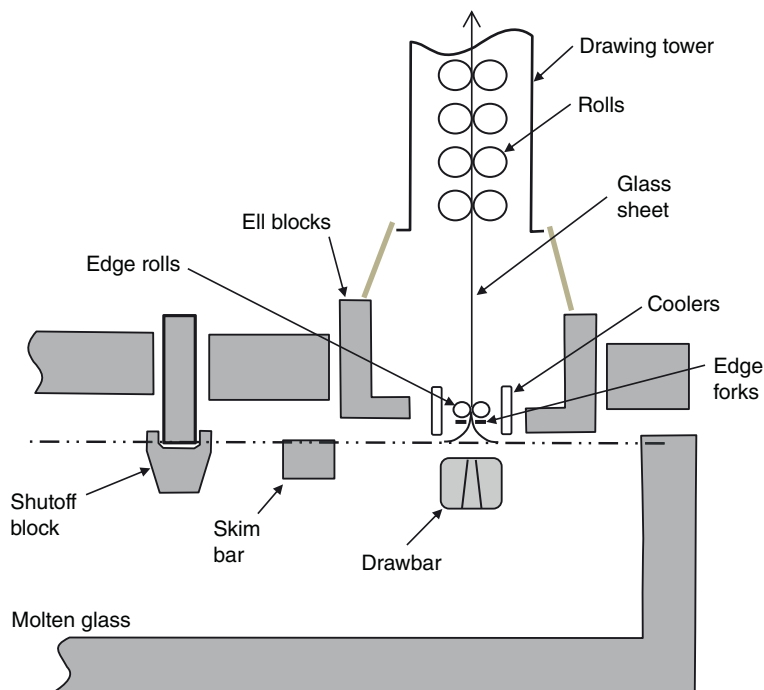
(Figure 5). The trick then is to make the Asahi blocks rotatable to renew the parting line where the glass leaves from the refractory and devitrification takes place. As a result, much longer drawing periods of up to 2–4 months can be achieved. An additional advantage is that thinner sheets down to 1.1–0.7 mm can be produced, especially for electronics applications, with a width of 1.5–2 m, thanks to the forming stability derived from the Asahi blocks.

4 Roll Out Process

The continuous double-roll process was developed in the United States in an effort led by the Ford Motor Company to meet a growing demand from the automotive industry. As delivered from the forehearth, the molten glass was pressed to a given thickness, cooled rapidly by a water-cooled pair of rotating rolls, and then conveyed into a horizontal annealing *lehr*. The thickness was determined mainly by the gap between the rolls, whereas the output was fixed by the rotating speed of the rolls.

As made by Pilkington Brothers in the 1920s, this process was then improved to manufacture plate glass through online grinding after annealing, followed by polishing of the cut plates. The process was further developed by Saint-Gobain in the 1950s to grind *and* polish on line the glass ribbon (Chapter 10.9). Along with a waste of about 20% of the glass, very high investment and operating costs were major disadvantages of these mechanical methods, however, which in fact prompted Pilkington to develop the float process as described in Section 5.

Figure 4 Sketch of the Pittsburgh Pennvernion process in cross section. The molten glass is drawn upward from the free surface right above the drawbar immersed below the glass surface [3].



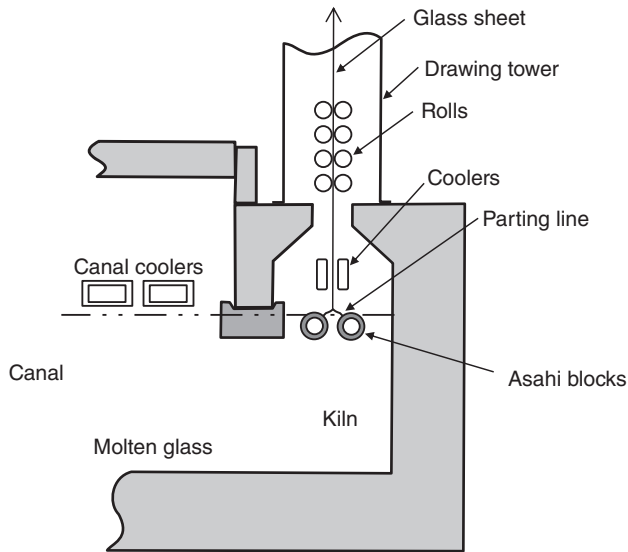


Figure 5 Sketch of the Asahi process in cross section. The rotatable Asahi blocks are immersed into molten glass instead of the *débiteuse*, and enable the parting line to be renewed where devitrification takes place [6].

Because the float process was not designed at all for patterned and wire-reinforced glass, the continuous roll out process, with which these products have been produced since the 1920s, has escaped oblivion (Chapter 10.9). Thanks to its versatility and facility for customization, it has even found new special applications, for instance, to make cover glasses for solar cells with excellent light diffusion through patterned textures on the surface. Usually the pattern is impressed on the lower surface by the lower roll, which is engraved. Generally the thickness range is 2–7 mm for the patterned and 8–25 mm for the polished glass.

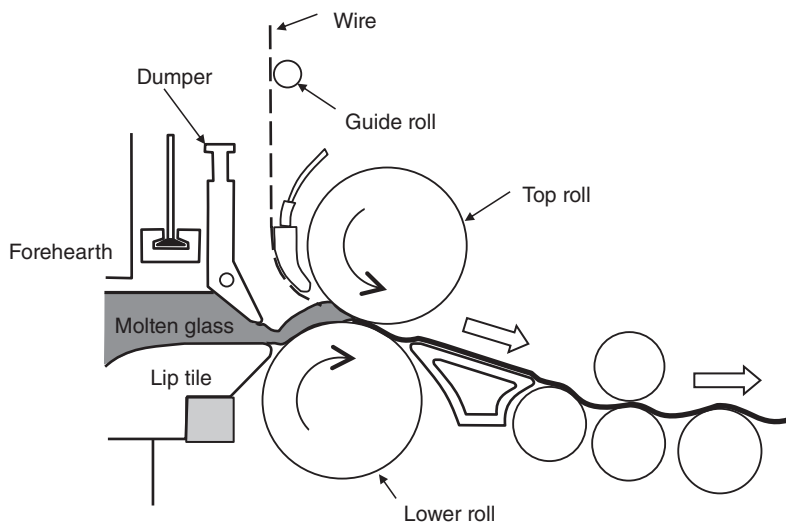


Figure 6 Sketch of single-pass wire roll out process (upper part insertion process). The wire is inserted into the molten glass, which is pressed and cooled by rotating water-cooled rolls [8].

As to wire-reinforced glass, it is produced in two ways depending on whether the wire is simply inserted into a molten glass (single-pass process, Figure 6) or sandwiched between two glass layers (double-pass process). Although more complex, the latter process has advantages over the former in terms of larger output, wider width, and higher quality, and better suitability for subsequent conversion into polished wired glass because the wire mesh is always precisely located at the center in the thickness direction [1, 3–8].

5 Float Process

5.1 Principle

When it was invented in the 1950s, the float process turned out to be an epoch-making method to produce flat glass with a smooth surface without any additional polishing. Its production cost was low enough to make possible an extensive use of the material in buildings and automobiles, which is one of the hallmarks of current civilization. The basic process of making flat glass on a molten metal was in fact patented in various ways as early as in 1848 in England by H. Bessemer, of steel-converter fame, and then several times in the United States by W. Heal and J. H. Forrest (1902 and then in 1925), and by Halbert K. Hitchcock (1905 and 1925), but a great many technical problems had to be solved before the process could be made practical. Through a seven-year expensive research program of Pilkington Brothers in the United Kingdom, which in its last stage included 13 months of production that had to be discarded, all these problems had eventually been overcome in July 1958 by a team led by L.A.B. Pilkington (no relationship with the Company's owners) and K. Bickerstaff. The following year it

even became possible to produce with the same process the distortion-free glasses needed for mirrors, thus abolishing the long-standing distinction between window and polished-plate glass (Chapter 10.9).

Although the float process became continuously profitable only in 1963, the previous year it began to be licensed all over the world by Pilkington Brothers in rapidly expanding markets. Within a decade, the good optical quality of float glass resulted in a vanishing share for other sheet- and plate-glass processes. As of 2015, more than 400 float plants are operated worldwide, units being up to about 500 m long (Figure 7). With a typical size of about 25×60 m, melting tanks are bigger than Olympic swimming pools to produce 600 metric tons (and even up to 1300 tons in the biggest plants) of flat glass per day with an investment cost ranging from 70 to 200 million dollars or euros, depending on actual size, location, and product complexity. As for the inflation-adjusted production cost (cf. Chapter 9.6), it has been almost continuously decreasing by a factor of 4 from 1965 to reach today a range of 200–300 dollars or euros per ton (Chapter 9.6), raw materials and energy accounting both for about 20% of it.

When a molten glass is poured onto a clean molten metal bath, it floats, thanks to its much lower density, spreads out, and thins to the point where the gravitational forces and the surface tensions among the glass, molten metal, and atmosphere are in equilibrium to reach the so-called equilibrium thickness. The lower and especially the upper surfaces of the molten glass are fire-polished, perfectly flat, and parallel except at the edges. The float process is based on this principle. Among metals or alloys

that are liquid between 600 and 1050 °C, the relevant temperature range for glass forming, pure tin was the obvious choice because of its low melting temperature of 232 °C, high density of about 6.5 g/cm^3 at 1000 °C, low vapor pressure of about 10^{-7} atm at 1000 °C, high boiling point of 2602 °C, low reactivity with silicates in the metallic state, and not too high cost (about 20 dollars/kg as of 2015).

The aforementioned equilibrium thickness T_e is given by

$$T_e^2 = 2\rho_t(S_{ga} + S_{gt} - S_{ta}) / [g\rho_g(\rho_t - \rho_g)], \quad (1)$$

where S_{ga} , S_{gt} , and S_{ta} are the surface tensions at the glass–atmosphere, glass–molten tin, and tin–atmosphere interfaces, respectively, g is the gravitational constant and ρ_t and ρ_g are the density of the molten tin and glass, respectively (Table 2). For soda-lime silicate glass floating on clean molten tin under a nitrogen-hydrogen atmosphere, T_e is 6.9 mm (Figure 8), a thickness that is actually insensitive to small changes in the chemical compositions of the atmosphere, metal bath, or glass [1, 3–9].

5.2 Float Bath

The float bath contains several metric tons of molten glass. It is a large unit with a length of up to more than 50 m enclosed by a steel shell that is lined with thick insulating and nonreactive refractory materials and holds a pool of molten tin whose depth is 50–100 mm and total amount is up to more than 200 metric tons kept at temperatures decreasing from about 1000 to 600 °C from the

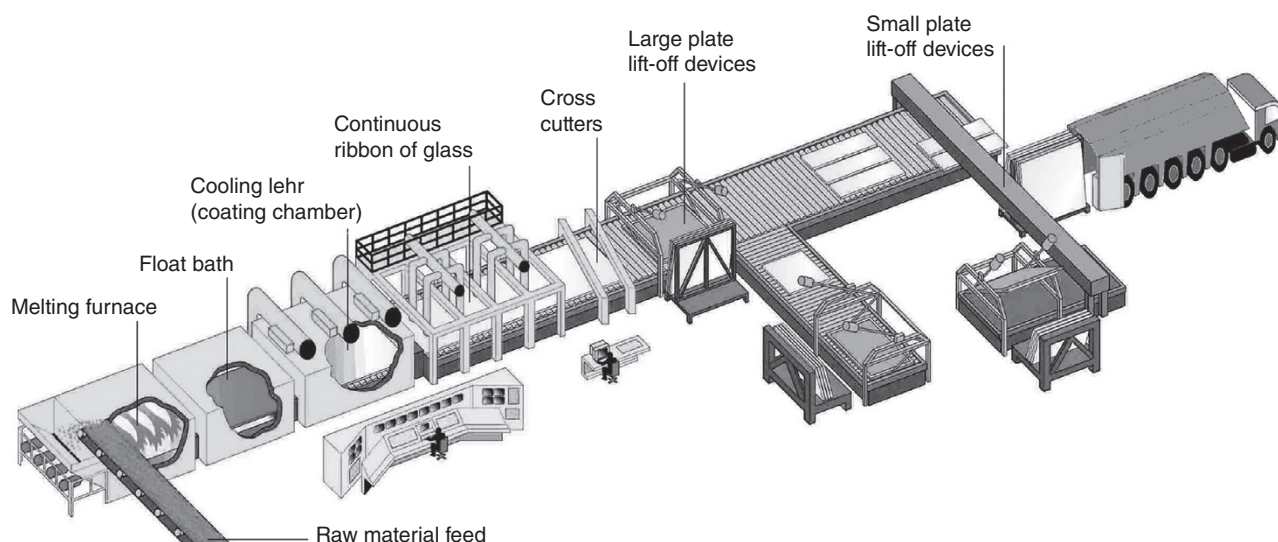
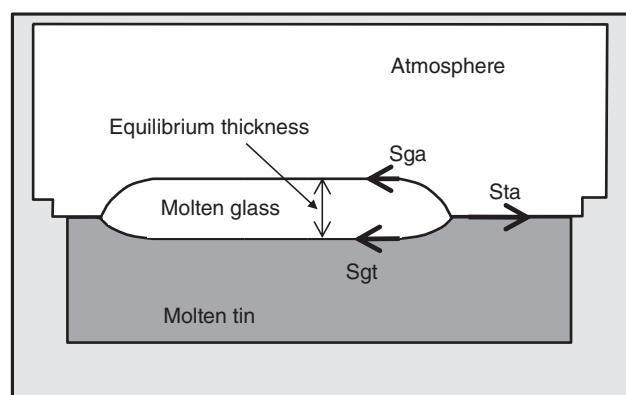


Figure 7 Overview of a float-glass plant (scale not right: size of the right-hand side, for instance, much exaggerated) <http://www.glassforeurope.com/en/industry/float-process.php>

Table 2 List of symbols regarding equilibrium thickness mechanism.

Symbol	Denotation
T_e	Equilibrium thickness
ρ_t	Density of molten tin
ρ_g	Density of molten glass
S_{ga}	Surface tension at glass–atmosphere interface
S_{gt}	Surface tension at glass–molten tin interface
S_{ta}	Surface tension at tin–atmosphere interface
g	Gravitational constant

**Figure 8** Equilibrium thickness of floating glass on the molten tin when the gravitational forces and surface tensions are balanced [3].

hot to the cold end (Figure 9). A reducing gas mixture made up of 2–8% hydrogen and 98–92% nitrogen is supplied at a high rate of the order of $10^3 \text{ m}^3/\text{h}$ from above to the bath to prevent oxidation of the molten tin and to maintain a positive pressure difference with the atmosphere at the bath exit where leakages are highest. The heaters, coolers, and other devices are installed and inserted in the bath. The molten glass is continuously supplied from the furnace conditioner via a canal where its flow rate is precisely controlled by an adjustable gate called a tweeel. It arrives to a ceramic spout lip, which is an inlet of the float bath, through which it falls freely onto the molten tin. After many years of struggle at Pilkington Brothers to achieve excellent quality, the design and engineering of the inlet area were an outstanding invention to force the contaminated molten glass in contact with the refractory lip to flow outwardly so as to be brought forward at the outer edges of the ribbon [9].

Once poured onto the tin bath with a thickness of about 50 mm, the glass spreads out and thins to its equilibrium thickness in the upstream area in the float bath. As formed to the required thickness and width in the forming area (see Section 5.3), the glass ribbon is taken

out from the bath either to receive appropriate reflective, low-emissivity, solar-control, self-cleaning, or other specific coatings (Chapters 6.7 and 6.8) or to enter directly the annealing lehr at the temperature at which the viscosity is about $10^{10} \text{ Pa}\cdot\text{s}$ (i.e. about 600°C for soda-lime silicate). At the end of the lehr, whose length can reach 120 m, the ribbon is finally cooled down to room temperature and brought into the cutting area. Whereas both edges are cut out (to be recycled as cullet) because of the imprint left by the top rolls, the ribbon itself is cut either according to customers' specifications or as standard sheets, for instance, $6.0 \times 3.21 \text{ m}$ in Europe where tools used in the flat-glass transportation industry have been fitted to this size (which, by the way, is too large to allow flat glass to be shipped in containers).

5.3 Thinner (Top-Roll Process) and Thicker (Fender Process) Glass Ribbons

For forming thin sheets, the molten glass with its initial equilibrium thickness in the upstream area in the bath is subjected at the same time to longitudinal and lateral forces. The former are exerted by conveyor rolls that stretch the ribbon from the annealing lehr and pull it at a typical speed of up to 25 m per minute. The latter are exerted outwardly on the ribbon edges by pairs of top rolls, which are water-cooled rotating gears, to reduce the narrowing of the glass ribbon because the imposed longitudinal stretching reduces not only its thickness but also its width (Figure 10a). In parallel, the glass ribbon is cooled down to prevent it from returning to its equilibrium thickness until its width is constant at the end of the forming area. In view of the fundamental influence of viscosity within the glass ribbon upon stretching and thinning, the temperature distribution and the top-roll operations must be controlled very tightly to ensure a good forming quality. Besides, keeping the glass ribbon as wide as possible is important to maximize productivity.

For producing float glass thicker than the equilibrium thickness, a pair of water-cooled carbon fenders serves as slipping guides to the flowing glass in the bath (Figure 10b). The glass thus proceeds with a restricted width and a large thickness. As it passes down the fender area, the effects of gravitational forces and surface tensions make both its upper and lower surfaces flat and thickness uniform. The glass is then cooled to an appropriate temperature in the downstream area of the fender where its viscosity is high enough not to allow width changes. In contrast to what is taking place in the top-roll process, stretching is not significant at all and there is no drive to return to the equilibrium thickness because there is no glass–tin–atmosphere interface in the fender area.

Figure 9 Sketch of the tin bath part of the float process: (a) on vertical plane along centerline; (b) on horizontal plane. A reducing nitrogen–hydrogen gas mixture is supplied from above. Heaters and coolers are installed [10].

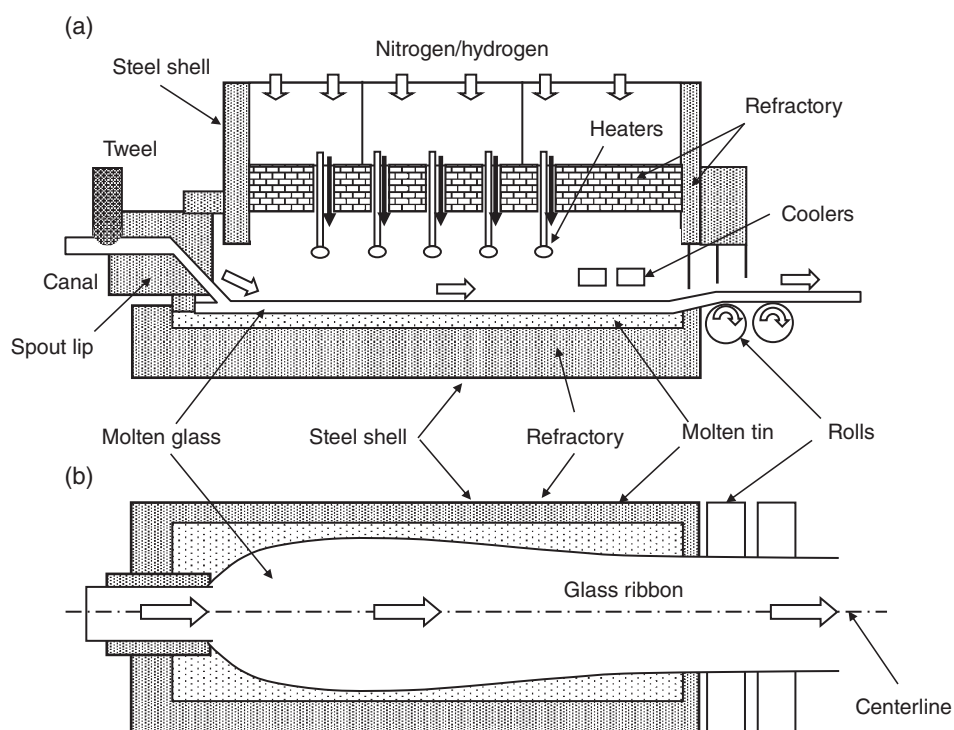
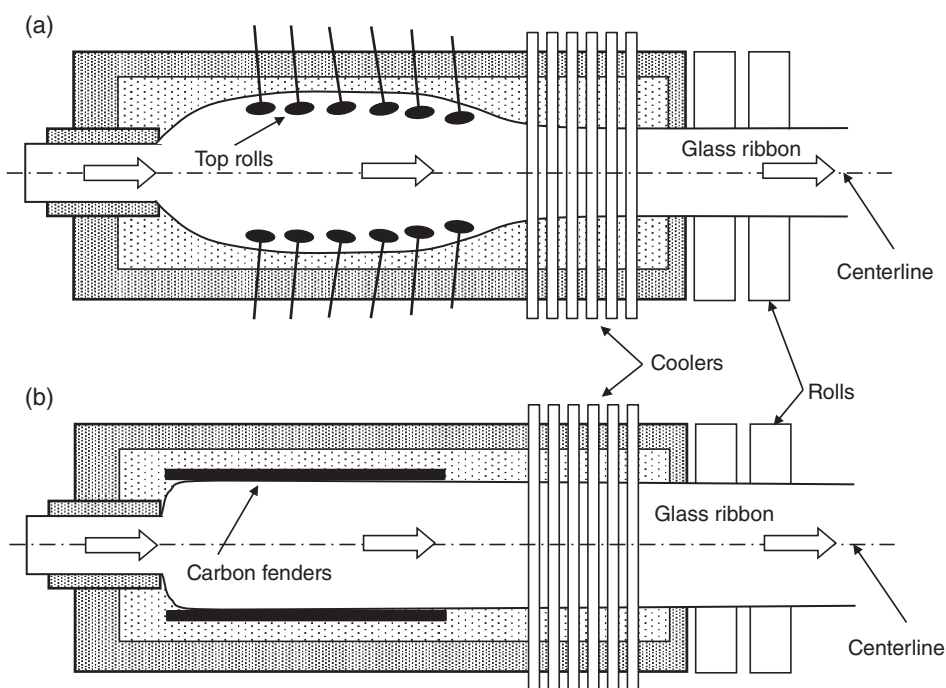


Figure 10 Sketch of the float process: (a) for sheets thinner than the equilibrium thickness, where the glass is stretched, from its edges by top rolls and from its downstream part by conveyor rolls; (b) for sheets thicker than the equilibrium thickness, where water-cooled carbon fenders serve as slipping guides to glass flowing [7].



5.4 A Complex Industrial Problem

In spite of the simplicity of its principles, the float process is not readily implemented because flow in both tin and glass and heat transfer among tin, glass, and the radiative field are really complex processes. Glass

forming is mainly determined by parameters such as the glass flow rate, conveyor speed, rotating speed and angle of top rolls, and by the viscosity distribution within the glass ribbon. It goes without saying that the viscosity of the glass strongly depends on temperature, but the temperature distribution in the bath is itself influenced

by radiative heat transfer, the flow of molten tin, and the glass forming conditions. Radiative heat transfer is predominant in the bath at temperatures higher than 600°C , but the flowing molten tin also contributes markedly to heat transfer as a result of its high heat capacity, high thermal conductivity (about 50 times higher than that of the glass), and low kinematic viscosity (about 8 times lower than that of water), whereas the glass flow carries a large amount of convective heat. On the other hand, molten tin flows by traction from the glass ribbon (i.e. velocity distribution) and buoyancy convection (i.e. temperature distribution in the bath). In order to understand forming conditions, one thus needs to understand the whole set of processes taking place in the bath since glass forming, heat transfer in the bath, and flow of molten tin affect one another in a very complex manner.

As summarized by C.K. Edge [4], the float bath thus is “a remarkable entity which, although first envisioned as a finisher of glass surfaces, also functions as a container, a conveyor, a forming unit, a chemical reactor and a heat exchanger.” In view of this complexity, valuable information has been drawn from mathematical simulations not only of the glass forming mechanisms, but also of the temperature field and the mutually related dynamics of the molten tin and glass ribbon. As examples, calculations with finite-element methods of the thickness contour over the glass ribbon and of the lateral thickness distribution of the ribbon at the bath exit are shown in Figures 11 and 12 [10]. The rather good agreement of such model values with the temperatures, thicknesses, or ribbon shapes that can be measured on line illustrates how simulations can be used to optimize the operating conditions, to design new facilities, and to check new ideas for process improvement and development.

From a chemical standpoint, potentially annoying impurities are oxygen from leaks or the $\text{N}_2\text{--H}_2$ gas mix, and sulfur originating from the molten glass. Both deteriorate productivity and glass quality if they induce alteration on the bottom surface of the glass caused by reactions with tin, and contamination adhesion on top and bottom surfaces (Chapter 5.6). In the so-called oxygen and sulfur cycles (Figure 13), SnO and SnS vapors form, condense, and precipitate, the former as SnO_2 and the latter as SnS (which is ultimately reduced to Sn particles). Thanks to extensive research, however, these impurities are now carefully managed through monitoring, sealing, cleaning, atmosphere controlling on flow and pressure, etc.

5.5 Trends in Float Production

The float process is advantageous because it yields excellent flatness, high flexibility with regard to thickness and

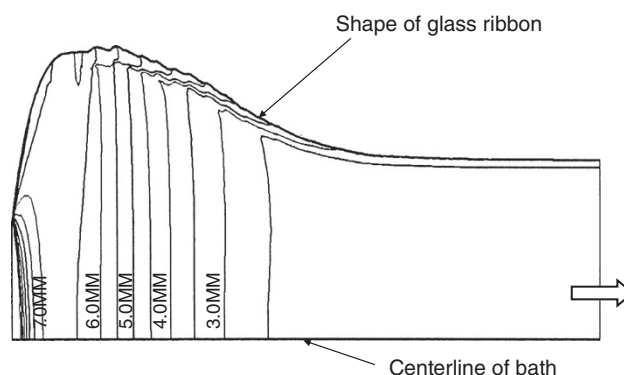


Figure 11 Shape and thickness distribution of a 2 mm thick float-glass ribbon calculated with an integrated glass-forming model [10]. Forming (i.e. shape, thickness, and velocity distributions of the glass ribbon) and the flow of molten tin are first calculated for a given temperature distribution of the glass ribbon. Heat transfer (i.e. the temperature distribution) in the float bath then is simulated, and the whole calculation is iteratively repeated until convergence is reached for the three interrelated mechanisms.

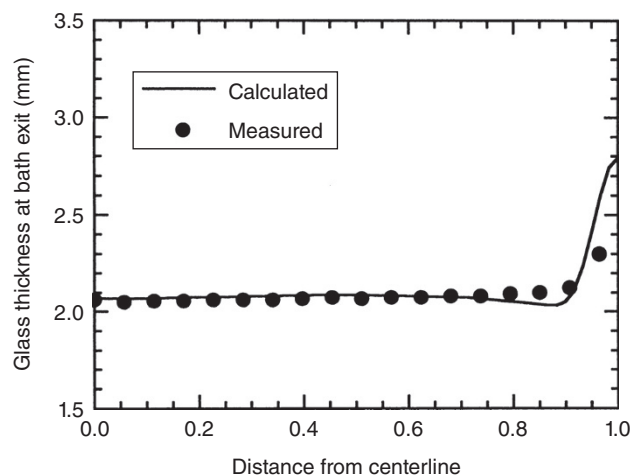


Figure 12 Simulated thickness distribution at the exit of the bath for 2 mm thick glass ribbon. The lateral distance is normalized [10].

width, and high productivity owing to completely continuous operation during the whole lifetime of the melting furnace, which can now reach up to two decades. Ever since its conception, plenty of technological improvements have been conducted for achieving higher throughput, larger width, and higher still quality, the thickness currently extending down to less than 0.4 mm and up to around 25 mm.

Originally the float process was designed to produce glass sheets for architectural window and mirrors. Since the 1970s, the technology has evolved to meet other demands, especially that emerging from automotive

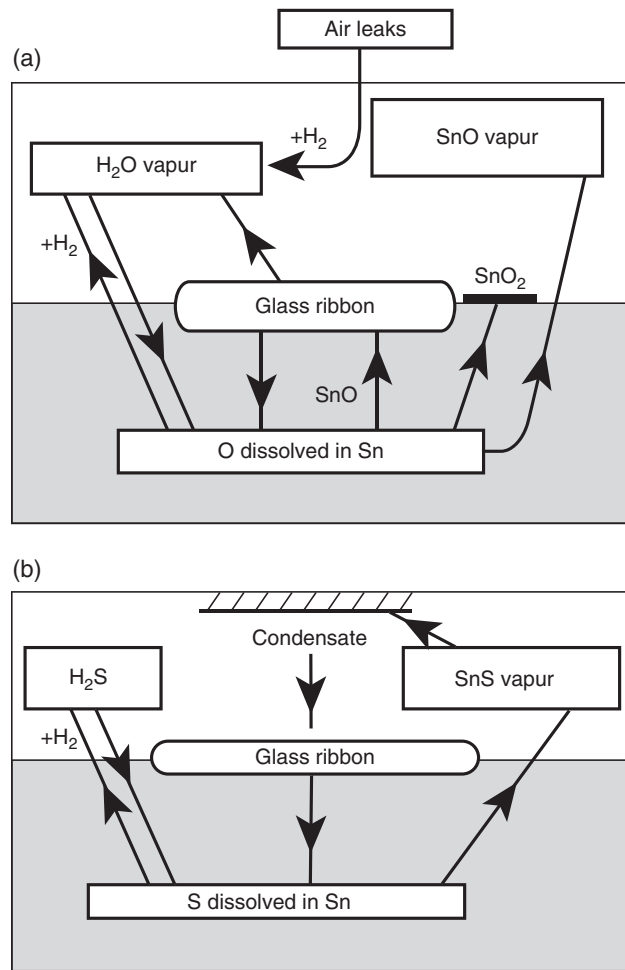


Figure 13 The complex interactions of impurities with the atmosphere, tin bath, and glass ribbon in the float process: (a) oxygen cycle; (b) sulfur cycle. Source: After Pilkington [9].

market for higher optical quality and thinner sheets along with higher throughput to keep production costs reasonable. In addition, the float process has contributed to the growing solar generation market with products such as mirrors for solar power systems and cover glasses for photovoltaics.

In the early 1980s, the float process achieved production of ultrathin glass of less than 1.1 mm for twisted nematic (TN)/super TN (STN) liquid crystal display (LCD) substrates, touch panels, and other electronics products with a remarkably high quality for flatness, thickness constancy, defect level, etc. Beginning in the 1990s, the float process has been producing flat glass of various kinds of compositions other than the traditional soda-lime silicate. Examples are alkali-free glass for thin film transistor (TFT) LCD substrate, high strain-point glass for plasma display panel (PDP) and solar panel substrates, specialty glasses for heat-resistant products, hard

disk drive (HDD) substrates, and other products such as touch panels and display covers that are then chemically strengthened.

6 Downdraw Processes

6.1 Slot Downdraw

It was for forming thin glass sheets that the slot down-draw process was developed in the 1940s. As driven by pairs of rolls, the molten glass is pulled downward through an accurately dimensioned narrow slot, made of platinum, which is fixed at the bottom of the fore-hearth. The glass sheet pulled from the slot is then gripped on its edges to prevent narrowing (Figure 14). The suitability of this process for making thin glass stems from the fact that a viscous molten glass can be pulled downward with a higher speed than if it were just subjected to free fall [3, 7, 11].

6.2 Fusion Downdraw

The slot downdraw process has disadvantages in terms of imperfect flatness and other defects caused by slot deformation and foreign contamination on the inside of the slot. It was to overcome them that the fusion downdraw process was developed by Corning [3, 5, 7, 11]. As sketched in Figure 15, the well-stirred molten glass is delivered through a conduit tube to one end of a rectangular trough that is the upper part of a fusion pipe. The molten glass flows over the weirs uniformly along the full length of the trough and then runs down on both sides of the fusion pipe. Two glass streams join and merge together at the “root,” which is a bottom apex of the fusion pipe. A pair of rolls grips the edges of the glass sheet just below the root to prevent the sheet from becoming narrower as it is stretched downward. The glass sheet is then cooled down while its edges are still held by pulling rolls as it proceeds through a vertical annealing lehr, and is finally conveyed to the cutoff station. The distinguishing advantage of the fusion downdraw process thus is that the glass is formed without touching anything except air so that one obtains a smooth and defect-free fire-polished surface. To be achieved, however, this result requires a highly homogeneous molten glass and a minute control of the distribution of glass temperature and flow.

Since the 1960s, the fusion downdraw process has produced photochromic glass, heat-resistant glass, and glass for chemically strengthening. It provides ultrathin specialty glass of less than 1.1 mm thickness used for electrical capacitors, microscope slides, optical filters, touch panels, micro electronic mechanical systems (MEMS),

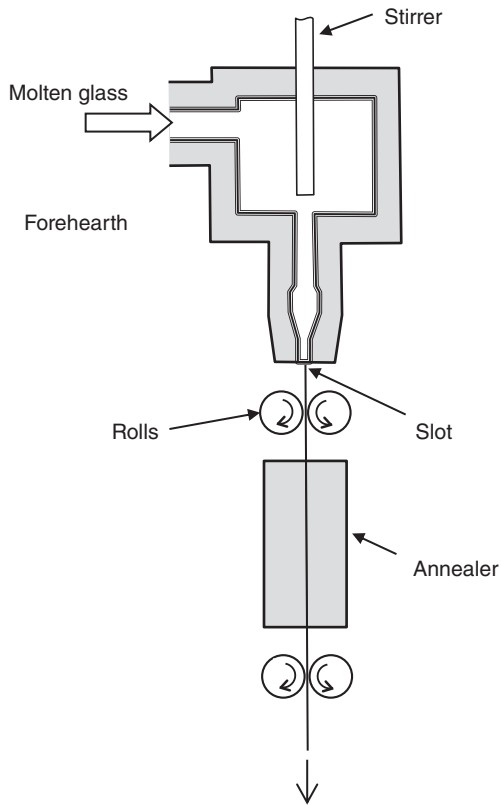


Figure 14 Sketch of slot downdraw process in cross section. The molten glass is pulled downward through a narrow slot driven by rolls [7].

substrates of TN LCD, and thin film solar cells. Besides, production of alkali-free glass for TFT LCD substrate was started in 1984 by Corning. Although the specifications are in this case much more severe, the fusion glass can also be used for TFT LCD substrate without polishing,

thanks to its excellent surface quality. To meet the market demand for larger size substrates, the width has been extended up to around 3 m. In addition, the downdraw process is applied to specialty glass for emerging chemically strengthened products such as touch panels and display covers.

7 Perspectives

Over the years the demand for flat glass has paralleled the growth of the global economy. In addition to architectural applications, the automotive, solar energy, and electronics especially flat panel display (FPD) application markets have all been at the same time growing and an important source of new, value-added products (Chapter 6.10). Recently, glass sheets for chemically strengthened components such as cover glass for displays and ultrathin glass for touch panels have emerged as important products driven by the explosive diffusion of mobile phones and tablets with touch sensors [12]. These trends are supposed to continue and affect markets such as appliance, transportation, interior architecture, and many others. The important role of flat glass keeps increasing in these domains as well as in the field of information and communication, optics, healthcare, and so forth. Further improvements will thus be made to meet new specifications and respond to various market demands. From an industrial perspective, however, not only the cost and quality of the glass itself but also controllability, investment size, yield, delivery time, versatility, cost of post-processing, and other factors of the manufacturing process have to be taken into consideration for each application. Therefore, an overall and comprehensive understanding of the forming process remains a key issue.

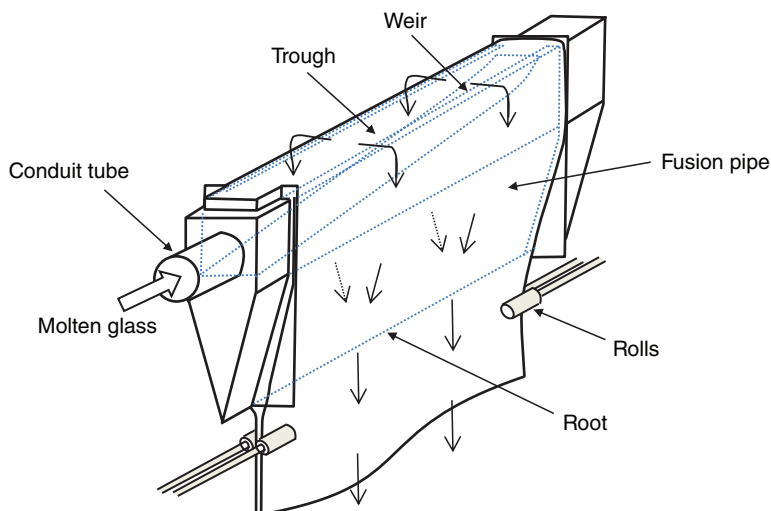


Figure 15 Sketch of fusion downdraw process in a bird's-eye perspective. Molten glass flows over weirs and run down on both sides of fusion pipe. Two glass streams join and merge together at the root and are stretched downward [3].

For new applications, work is in particular being conducted on ultrathin flexible glass (0.2 mm–30 μm) and on rolled glass for flexible display, OLED lighting, and organic thin-film solar cell to take advantage of unique features of glass such as bendability, impermeability to gas, transparency, surface quality, chemical and thermal durability, and so on [13]. Such products are not yet on the mass market because the fundamental technologies are not mature, but flexible and rolled glasses are nonetheless expected to come out in the near future. The applications to the field of health care, electrical and optical packaging, MEMS, and so forth are anticipated to become more popular as well [14]. The relevant information can be found on the websites of glass manufacturers.

Two directions for development of the forming process can be followed. One is to improve further currently existing processes in terms of flatness, thickness, width, productivity, controllability, cost, versatility, facility life-time, etc. The other direction is to add values through online introduction of other features such as coating and surface treatment (cf. Chapters 6.7 and 6.8). A closer match and harmonization between forming process and glass composition and properties might be also attractive.

As for forming commodity glass, invention of a novel process surpassing float with regard to energy consumption and investment costs would be desirable. For specialty glasses, innovative processes with higher quality and lower cost will of course also be sought after. Advances in basic science, simulation methods, sensing procedures, and information technology are presumed to become still more important either in operation and engineering or in development and innovation. Moreover, newly developed materials could make other innovative progress possible. In this respect, could unprecedented innovations based on novel mechanism make the processes described in this chapter obsolete in a near future? Their advantages should be considerable to write off the capital invested in current production plants all over the world. But would those innovations give rise to new applications and create new markets? A never ending challenge will change the world [15, 16].

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1.5

Fabrication of Glass Containers

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1 Introduction

At the beginning of the twentieth century, glass-container manufacturing still was a strenuous business, involving much manual labor and sweat. In 1903, Michael J. Owens developed in Ohio the world's first fully automatic glass-forming machine (Chapter 10.9). The concept consisted of a rotating machine that sucked glass from a pool of melt into forming molds. A preform of the final container (the so-called “parison”) was first produced, and then transferred into a second mold where the parison was blown to its final shape to form the container itself. This truly revolutionary concept gave major advantages over semiautomatic methods since it cut labor costs by 80% and also led to the end of child labor in glass-manufacturing companies. But this concept still had its drawbacks because the machine itself was expensive and cumbersome and a true monster of tons of rotated, lowered, and lifted metal.

In 1915, Karl E. Peiler and F. Goodwin Smith established a fully automatic press-and-blow rotary machine, which was fed with glass from above by an automatic paddle-needle gob-feeder (Chapter 10.9). Although this design resulted in a much less complex forming cycle, the machine was still a rotating system that involved again much mechanics and moving metal. And, most importantly, as soon as one section of a rotating machine experienced any problem, the machine as a whole had to be stopped. Hence, yield was significantly decreased when the complete machine had to be paused because only one section was experiencing problems.

With gob-feeding getting more and more sophisticated, a search began for a more efficient forming process. In 1924, F. Goodwin Smith and Henry W. Ingle developed a totally new concept for automated glass-container forming: the IS-machine, where “IS” stands for *Individual Section*. The machine sections were no longer arranged in a circle but in a row. This meant that each section of the forming machine operated independently from the others. Hence, if failure occurred in one section, just this section and not the complete machine had to be stopped and fixed. This made production much more efficient and flexible. Production speed and container quality also were greatly increased.

With 4 individual sections in the first IS-machine, the concept was soon improved and enhanced from initially 4 single gob sections (in total, therefore, 4 containers in one complete machine cycle) to nowadays 12 section-systems with multi-gob delivery to each section. In the most recent form, IS-machines can consist of 12 sections, with 4 forming molds per section (quad-gob system), summing up to 48 containers produced in one machine cycle.

Looking at a modern IS-machine, however, one should nonetheless recognize the basic features that were designed when the concept was first developed. As shown in Figure 1, one section is made of the following zones, which will be explained more in detail later in this chapter:

- 1) Delivery equipment, consisting of scoop, trough, and deflector.
- 2) Blank-side with plunger, neck-ring, guide-ring, mold-halves, and baffle.
- 3) Invert with invert-arm holding neck-ring and guide-ring.
- 4) Blow-side with bottom-plate, blow-head, and mold-halves.
- 5) Take-out with tongs, dead-plate, and pusher to conveyor belt.

Reviewers: A.J. Faber, Celsian Glass & Solar, Eindhoven, The Netherlands
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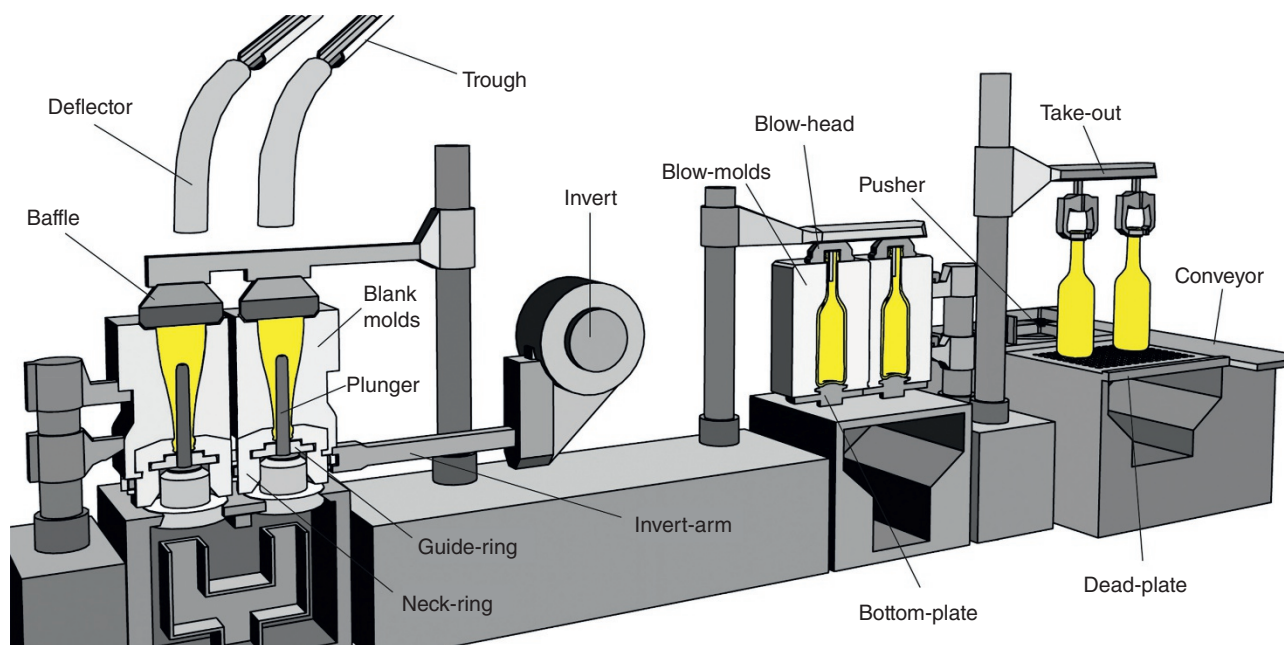


Figure 1 Schematic overview of one section of an Individual-section machine (here Narrow-Neck Press & Blow process, double-gob set-up).

Several major improvements have been implemented in the forming process since its beginnings. We will, for instance, describe how, following the *Press & blow* (PB) and *Blow & blow* (BB) processes, the *Narrow-neck press & blow* (NNPB) process has recently met with much success because of its more efficient forming. And it should also be stressed that the original pneumatic control of IS-machines has given way to servo-electric devices with which higher precision and reliability has been achieved.

2 Principles of Glass-Container Forming

Before a glass can be formed, it usually has to be melted out of the respective raw materials. The melting of container glass bears some peculiarities such as a high usage of foreign (external) recycled cullet or auxiliary devices such as batch and cullet preheaters. Because these features and the basics of the melting of container glass are described elsewhere in Chapter 1.3, we will focus solely on forming.

Glass containers for mass-market are formed with the aid of molds in which the molten glass is blown or pressed. The forming process consists of two steps. First a “parison” is made in cast-iron “blank-molds.” Then, in the second step, this parison is formed into the final container in “blow-molds” that are made of either cast iron or aluminum bronze.

2.1 Heat Management in Glass-Container Forming

A basic feature of the forming process is that it is highly non-isothermal. On the one hand, temperature differences over the dimensions of the glass component are present and on the other, the glass experiences a great change in temperature and thus in glass properties. As a result, the forming process has of course to be designed to cope with these changes, which are the largest for viscosity.

When the gob enters the mold in the first forming step, it has a bulk temperature of about 1050°C . The mold itself has a temperature of $450\text{--}520^{\circ}\text{C}$ at the end of the parison forming cycle, depending on forming conditions and container type. The glass–metal interface temperature T_C , which is a very important parameter for the forming, is almost constant (Figure 2) because of the short contact time t of only a few seconds between the gob and mold material. It depends on the temperature of the glass T_1 , on that of the contact material (mold) T_2 , and on the thermal conductivity λ , heat capacity C_p , and density ρ of both the glass and the mold material [1–3].

For soda-lime-silica glass, at the relevant temperatures these values can be taken as $\lambda \approx 10 \text{ W/m}\cdot\text{K}$, $C_p \approx 870 \text{ J/kg}\cdot\text{K}$, and $\rho \approx 2500 \text{ kg/m}^3$. For laminar cast iron, appropriate parameters are $\lambda \approx 55 \text{ W/m}\cdot\text{K}$, $C_p \approx 500 \text{ J/kg}\cdot\text{K}$, and $\rho \approx 7300 \text{ kg/m}^3$. From these values, one can estimate T_C with:

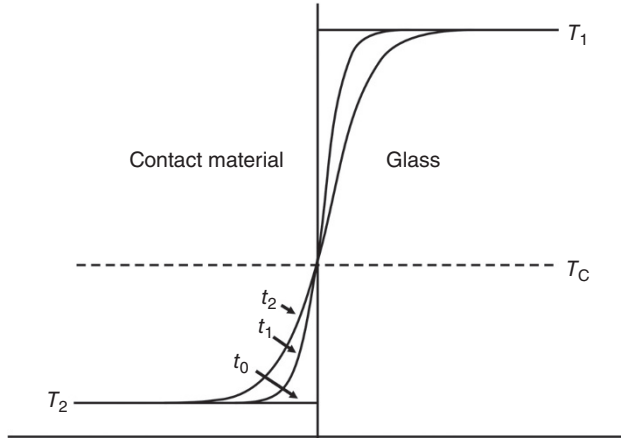


Figure 2 Temperature gradients and interface temperature between contact-material and glass over time.

$$\frac{T_1 - T_C}{T_C - T_2} = \frac{\sqrt{(\lambda \cdot c_p \cdot \rho)_{\text{mold}}}}{\sqrt{(\lambda \cdot c_p \cdot \rho)_{\text{glass}}}} \quad (1)$$

One finds in this way that temperatures of 1050°C for the gob and 470°C for the blank mold yield an interface temperature of ca. 614°C if no oxide layer resulting from corrosion of the mold is present and if the heat balance of the blank mold is correctly managed.

A certain cooling of the glass during the forming process is mandatory to achieve a stable enough product that does not lose shape in subsequent processes (handling, coating, etc.). If cooling is not applied correctly, too low a viscosity will prevent the parison from maintaining its shape and, thus, correct dimensions from being achieved and the final container from conforming to its specifications. In glass-container forming, this stabilization is realized, thanks to the surface layer of the parison that cools down through contact with the mold. Heat transfer thus is, in general, an important aspect in the forming of container glass. Not only large amounts of heat need to be removed from the glass, but heat transfer must be controlled locally to avoid internal tension that would build up if the shrinking rate were variable throughout the glass. The average heat transfer Q_{0-t} during the short contact period t between the glass and mold can be calculated according to

$$Q_{0-t} = \frac{\lambda_g \cdot \lambda_m}{\lambda_g \sqrt{\lambda_m / (c_p \cdot \rho)_m} + \lambda_m \sqrt{\lambda_g / (c_p \cdot \rho)_g}} \cdot \frac{2(T_1 - T_2)}{\sqrt{\pi \cdot t}} \quad (2)$$

where m designates the mold and g denotes glass properties. With the aforementioned parameters, one, for instance, finds a very large average heat transfer of 647 kW/m² for a typical forming cycle for which $t = 6$ seconds.

2.2 Interface Interactions in Glass-Container Forming

Whenever a glass container is formed through contact with a solid material, such as a mold or roller, the interface between the two bodies is a crucial point. From the preceding presentation, it appears that problematic situations occur when the interface temperature is either too high or too low.

If cooling of the mold is not rapid enough in relation to the gob temperature, the interface temperature between the gob and mold increases and at a certain point the glass begins to stick to the mold. The sticking temperature has a lower bound at which the glass still can be separated from the mold without significant damage. Nevertheless, reaching this lower bound leads to process failure because sticking of the glass causes a bad loading and an inhomogeneous temperature distribution, which themselves give rise to defects in the final container. At the upper sticking temperature, removing the glass from the contact material inevitably leads to damages of the glass, like checks or torn-out pieces.

The glass sticking temperature is widely independent of the type of the contact material. It is basically a function of the interface temperature T_C , but surface conditioning of the contact material may play a role as well. Sticking appears when the viscosity of the glass at the interface becomes lower than 10^{8.8} Pa·s [4, 5]. For an average container-glass composition that means sticking begins to take place when the interface temperature T_C between the gob and mold becomes higher than ~ 645°C.

The interface temperature of about 614°C calculated above is lower than the sticking temperature. However, it can easily happen in production that this temperature increases locally such that sticking of the glass does occur. This may happen because of changed cooling conditions, cooling failure, or the growth of an oxide layer on the molds, which significantly decreases thermal conductivity.

The friction coefficient μ between the glass and contact material plays a crucial role during forming. A low dynamic friction between the contact material and the glass favors a good gob-loading and glass-forming. Often the molds and the finish equipment are coated with a lubricant that decreases the friction. This so-called swabbing process is widely used in glass-container manufacturing. The swabbing lubricant mainly consists of graphite with various additives. Periodically, the molds are swabbed automatically by robot or by human hand to allow precise and stable forming. The swabbing intervals depend on the respective machine setup and container produced and can range between 15 minutes and several hours. The effect of swabbing on the friction coefficient is a temporary decrease in friction as well as a change in the heat-transfer characteristics between the glass and mold.

There are also different permanent and nonpermanent coatings available that can be applied to the mold and forming equipment to extend or even avoid the swabbing. Important physical aspects of gob-loading, including models of the mechanics of gob/blank-mold interaction and of dynamical friction, have been extensively discussed in papers to which we refer for further details [e.g. 6, 7].

2.3 Deformation Rates in Glass-Container Forming

As already pointed out, in container-glass manufacturing, the gob is first formed into the parison, and then the parison into the final container. The (de-)formation of both the gob and parison depends on the actual viscosity of the glass. A low forming- or interface-temperature leads to a high viscosity at the glass surface. Hence the glass surface starts to get “brittle.” If such a glass is then subjected to high deformation rates, as it happens not only upon pressing and blowing but also earlier in the process upon gob-cutting, it can experience too high tensile or shear stresses. The critical tensile stress σ_c (in MPa) that a hot soda-lime-silica glass can sustain at a given temperature T may be estimated from an empirically derived correlation [8]:

$$\sigma_c = \frac{4.8 \cdot 10^3}{\sqrt{T}} \quad (3)$$

Hot fracture occurs if the tensile stresses exceed this critical value. The maximum velocity $v_{\max}$ at which a glass container with a thickness d can be formed at viscosity η without experiencing hot fracture can be approximated by:

$$v_{\max} = \frac{\sigma_c \cdot d}{4\eta} \quad (4)$$

One thus concludes that at temperatures of about 1000°C, deformation velocities of ca. 500 m/s are, for instance, possible without hot fracture for a 2 cm-thick soda-lime-silica glass layer. At 900°C, the maximum allowed velocity is already down to 100 m/s and is lower than 10 m/s at 800°C. Below 700°C the risk of defects caused by hot fracture becomes significant. Because usually such defects cannot be inverted (“healed”) in later forming steps, care must be taken to prevent them from appearing.

3 Glass-Container Forming Processes

3.1 Glass Composition

For cost reasons, glass containers are made out of soda-lime-silica glass whenever special constraints do not

apply. An exception is, for instance, laboratory ware for which borosilicate glass is used instead (Chapter 7.7). Even though the forming process needs to be adapted to account for the specific properties of each glass type, the principles at work are similar for given kinds of containers. Three different forming processes are applied, namely BB, PB, and NNPB. Their main differences concern blank-side forming where the parison is made, the subsequent forming steps to make the final container being identical. As a matter of fact, many containers can be produced with more than one process so that there is much overlap between them in terms of product range.

3.2 Blow & Blow Process

The BB process is the oldest and remains still widely used in manufacturing of large and heavy containers such as wine or sparkling wine bottles. The gob is loaded into the blank mold, often via a funnel (Figure 3a). After loading, the mold is closed with a baffle and a settle-blow is applied from above through the baffle (Figure 3b). The settle-blow presses the glass gob deeper into the mold and down to the finish equipment, which basically consists of a neck-ring, a guide-ring, and a short plunger. On loading, the plunger is in upper position. In this very first step, the opening, sealing surface, and thread (if present) are thus formed before the bulk of the container itself, which represents an important difference with respect to the other forming processes.

In the current IS-machines, the loading speed of the gob is often so high that the finish is already formed at the gob-loading step, which would make the settle-blow unnecessary for the finish forming. This step is nonetheless maintained in the process to guarantee a constant heat transfer between the glass and the blank, from cycle to cycle, before counter-blow. During settle-blow, a vacuum can be applied through cavities in the molds to support the parison and finish forming. Some modern BB IS-machines work without a funnel. They control the switch between settle-blow and counter-blow by a valve in the baffle to exhaust the compressed air that is used for settle-blow.

After settle-blow, the baffle is quickly lifted, the funnel is removed, and the baffle settles again and closes the blank-mold completely. A counter-blow is applied from the down side through the formed finish, blowing the glass fully into the mold shape and forming the parison (Figure 3c).

This two-step blowing process with settle-blow and counter-blow on the blank-side causes an inhomogeneity in the container because of different contact times between the glass and the mold above and below the loading line. Such an inhomogeneity can be seen as a horizontal, optical streak in the body of the containers. It is called

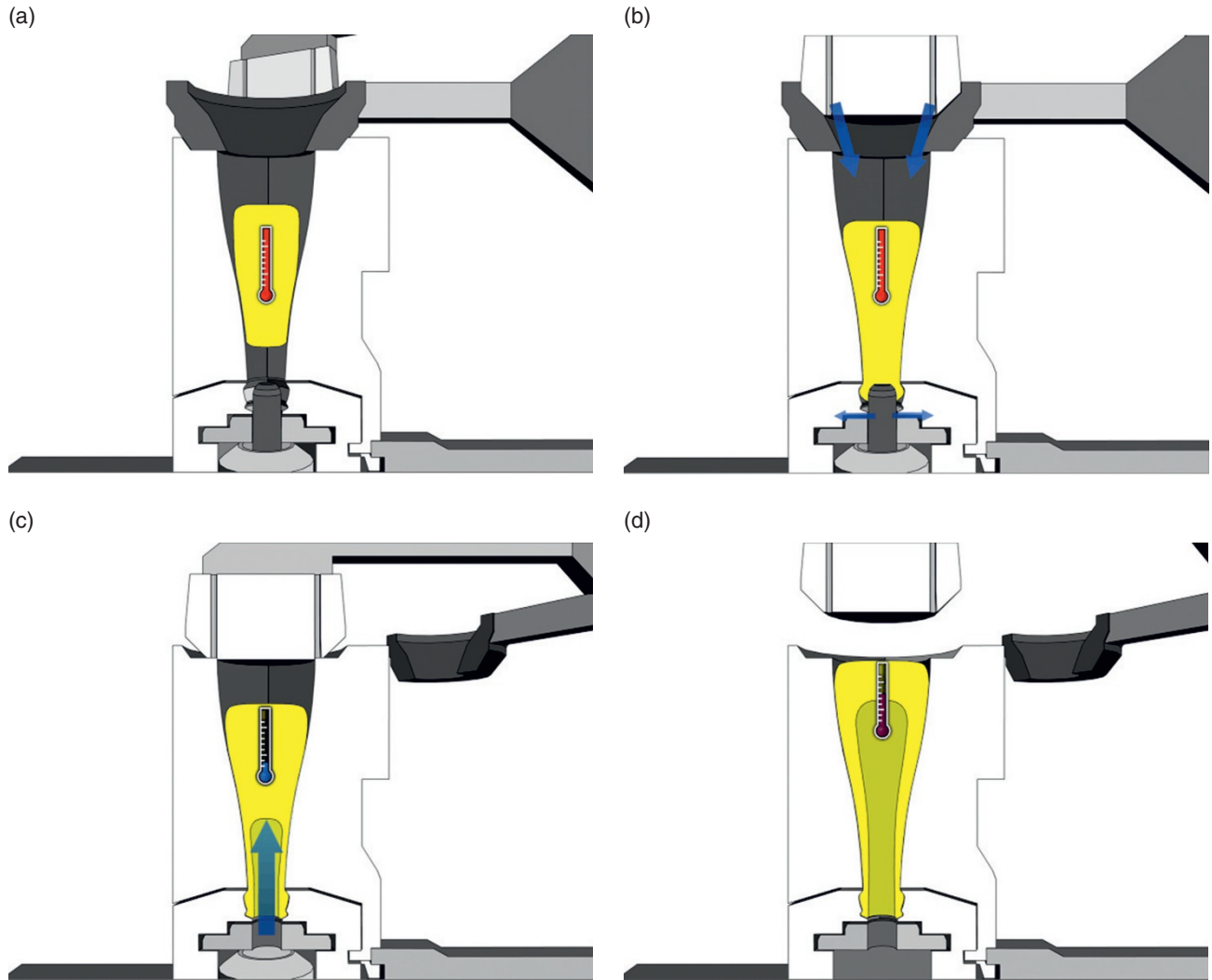


Figure 3 (a–d) Blow & blow process, blank-side.

settle- or feeder-wave and can be reduced in several ways, but not fully avoided. When looking at a final container, the existence or nonexistence of a settle-wave thus indicates whether or not the container has been produced with the BB process.

After the parison has been formed, the baffle is removed (Figure 3d), the mold opens, and the parison is transferred via the invert mechanism to the blow-side.

The final forming of the container is in principle the same for all three forming processes. The following description will thus apply to all of them. When transfer to the blow-side is over, the parison lengthens into the blow-mold as determined by its viscosity and the machine parameters. This causes the outside of the parison to be reheated by the heat stored in the hot inside and temperature to homogenize within the parison (Figure 4a). This reheat is essential to ensure that the container is to be precisely formed to its intended shape. The blow-mold is

then closed, leaving the finish outside. The invert-tongs open and the container is released from the invert. Directly after releasing, the blow-head with a blowing-tube is placed on top of the finish (Figure 4b). Through this blow-head, the final-blow is applied, giving the parison the final shape of the container (Figure 4c). Strictly speaking, the reheat ends when the final-blow is triggered.

After the container has been released by the blow-mold, a take-out grips it by its finish (Figure 4d) and places it over a dead-plate through which air is blown from below to cool it further. Finally the container is transferred via a pusher onto a conveyor belt.

3.3 Press & Blow Process

The PB process is used for wide-mouth containers of all weights, such as jars and baby-food containers. It differs



Figure 4 (a–d) Forming of the final container at the blow-side (same for all processes).

significantly from the BB process at the blank-side. After loading the gob (Figure 5), the blank-mold is closed fully by the baffle and a plunger presses in an upward movement the glass from below into the mold (Figure 5b). The plungers usually are made out of tungsten carbide (WC) or another hard metal to ensure a long lifetime. In contrast to BB-forming, the process causes the finish to be formed at the end of the blank-mold process (Figure 5c) and no disturbance such as settle-wave is introduced into the parison because it is formed by a single (smooth) motion at the blank-side. As in BB, the baffle is removed after the parison has been formed, the mold opens (Figure 5d), and the parison is transferred to the blow-side to get its final shape as described above.

3.4 Narrow-Neck & Blow Process

The NNPB process is mainly used for lighter containers such as beer bottles, small water and juice containers, and other lightweight containers. It is the most advanced forming process because it yields not only the highest machine speeds but also a homogeneous glass distribution in the final container. It is similar to the PB process in that the gob is not blown into the parison but pressed via a plunger. After loading the gob (Figure 6), the mold is closed fully by the baffle and a plunger smaller in diameter than in PB presses in an upward movement the glass into the mold (Figure 6b). The plungers are also made out of tungsten-carbide. As with PB, the finish is formed at the end of the blank-mold process (Figure 6c). Again, the baffle is removed after the parison has been formed,

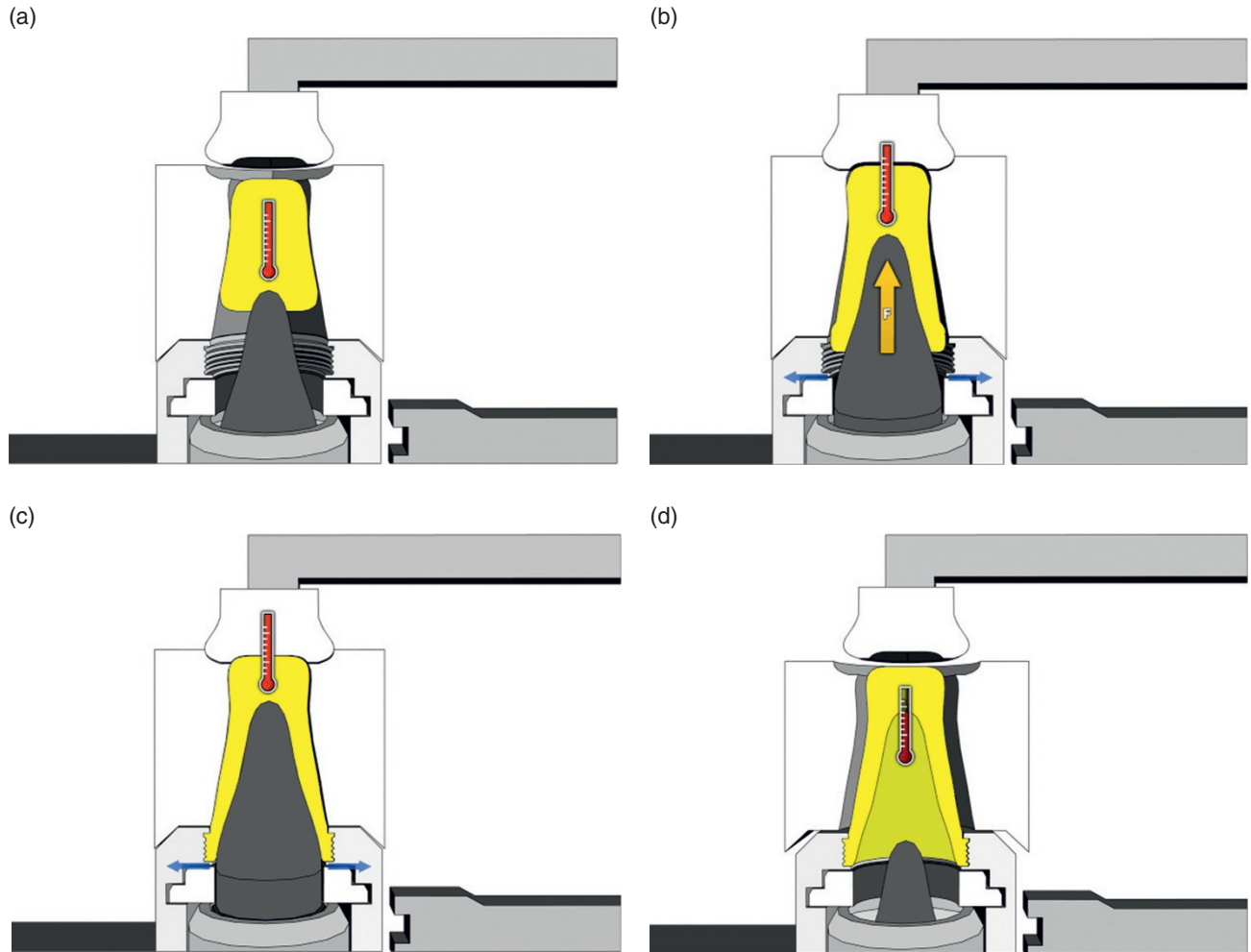


Figure 5 (a–d) Press & blow process, blank-side.

the mold opens (Figure 6d), and the parison is transferred to the blow-side.

Restrictions in usage of the NNPB process are due to the plunger dimensions and finish openings and the corresponding cavities pressed into the parison. The parisons are usually shorter for NNPB than for BB if the same final container shape is to be produced (e.g. a 0.33 l beverage bottle). Another significant difference between NNPB and BB is that the required gob temperature is from around 20 to 50°C higher in NNPB because of difficult pressing conditions. This difference in consequence leads to different thermal requirements during the process in terms of mold-cooling and reheat-timing.

4 Making of the Gob: Forehearth, Feeder, and Shears

Most forming processes take place at a viscosity of 10^2 – 10^4 Pa·s. Hence, for soda-lime-silica containers, the glass

needs to be cooled from melting and fining at ca. 1500°C and a viscosity of 10 Pa·s down to ca. 1050°C and a viscosity of 10^3 Pa·s. This quite demanding task is accomplished in the forehearth. The forehearth is directly connected to the working-end and ensures the required homogeneity of the glass while bringing it to the desired temperature and viscosity.

After the forehearth, a feeder enables glass-portioning and gob pre-shaping (Figure 7). It consists of a refractory tube and one or more plunger(s) that are moving periodically up and down. The tube is rotating to homogenize the melt in this final stage. With each upward stroke of the plunger, the glass stream is released from the shear blades in order to cut a gob without having a glass stream loaded on top of these shears. For a single-, double-, triple-, or quad-gob setup, the respective number of plungers operates simultaneously in the feeder, hence as many openings in the orifice ring are required. The final gob shape is influenced by the sizes of the orifice ring and plunger, and by the shape, height, and motion profile of the plunger.

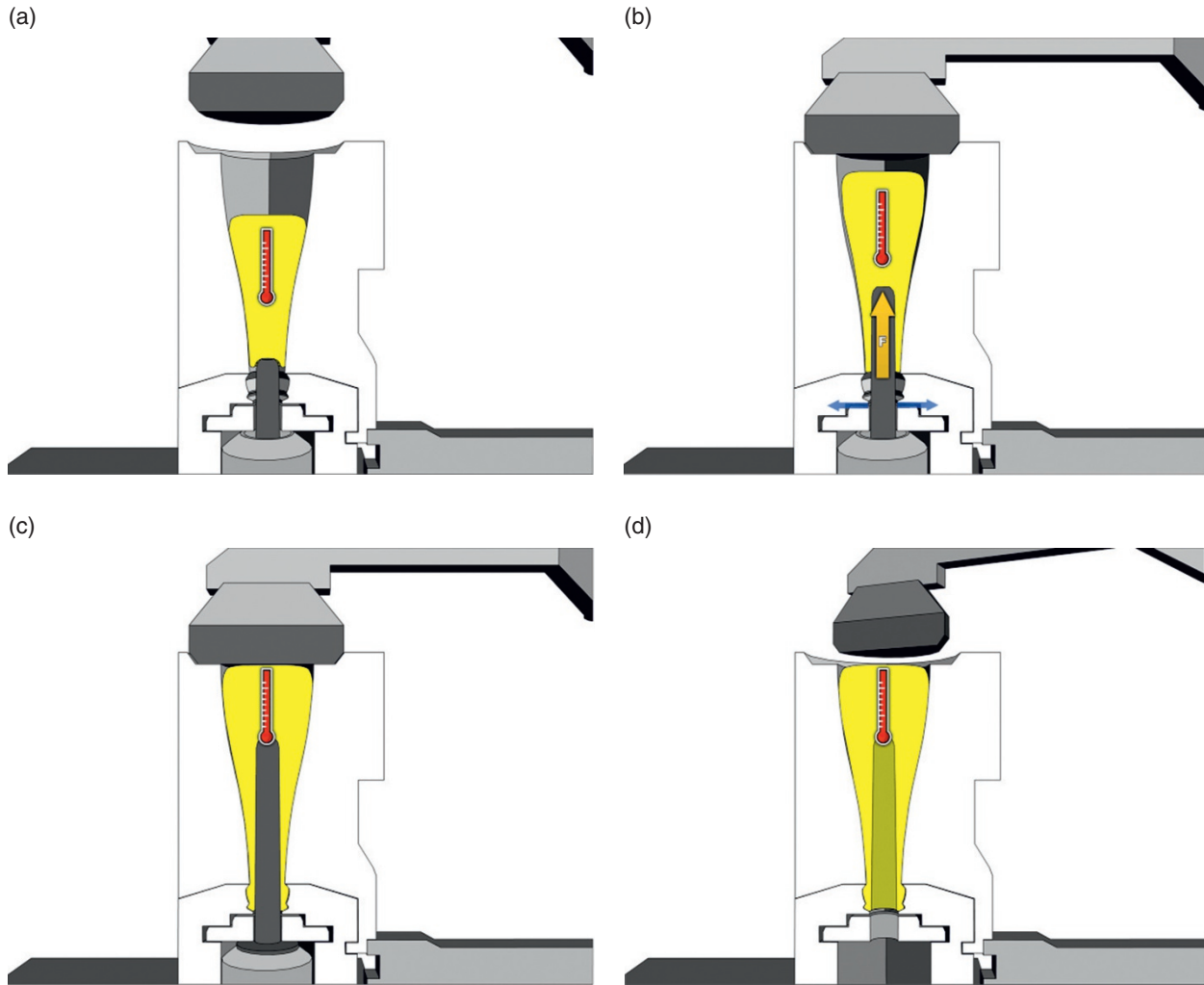


Figure 6 (a–d) Narrow-neck press & blow process, blank-side.

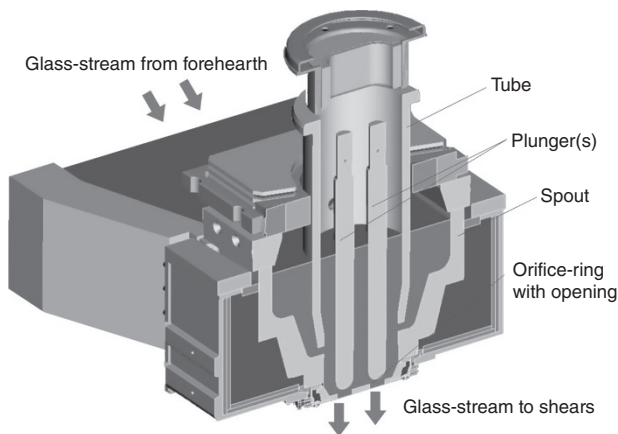


Figure 7 Cross section of a modern feeder (double-gob setup).
Source: Courtesy Bucher Emhart Glass.

The originally continuous glass stream is cut by the shears right after it has been “pre-shaped” by the feeder and plunger and has passed through the openings of the

orifice ring. The gob needs to be completely separated from the glass stream by the shears to prevent any glass fibers from being attached to it. Any misaligned or poorly operating shear will result in shear marks and, consequently, in defects in the final container. For shears, the materials most commonly used are steel (cheap, but short-lived) and hard alloys such as WC (more expensive, but long-lived). In all cases, the shears are cooled by a shear-spray, a mixture of water and cooling fluids.

5 IS-Forming Machine

5.1 General Principles

Rotational forming machines are nowadays used only in some rare cases. The principles of glass-container forming will thus be described for IS-machines, with which almost glass containers are made. Derivatives of the IS-machine such as the Emhart RIS and Heye H 1–2

machines have been developed in the past but are hardly in use any longer [9]. They work with two molds on the blow-side forming, which are loaded alternately. This approach is advantageous in terms of longer reheat and more homogeneous glass thickness distribution but is much more complicated, expensive, and prone to jamming.

In a narrow sense, IS-machines consist of a gob-distributor and delivery equipment, blank-side forming, invert, blow-side forming, and take-out and have several identical sections aligned in a row (Figure 1). The only differences between sections are the individual delivery (as different distances from gob-cut to mold need to be overcome) and the distance of the section to the annealing lehr. The differences in delivery distances cause different gob speeds and different gob arrival-times at loading and thus require different section-timings. The differences in distance to the annealing lehr may cause different containers temperatures at the hot-end coating and at lehr entrance. When entering the lehr, there is, for example, a difference of 50 K or more in surface temperature between containers from section 1 and from section 12, which are the farthest from the annealing zone.

The IS-machines in principle can be adapted to all three forming processes that have been mentioned earlier. To a certain extent the machines can be converted between a triple-gob setup to a quad-gob setup or, given another machine construction, from a triple-gob setup into a double-gob setup. How widely a machine can be adapted depends on different parameters, especially on the inner-section distance, which describes the possible center distances of the molds to each other within one section. The type of setup to be used depends on different parameters such as the size and weight of the container to be produced, desired machine speed, and portfolio of the respective glass-manufacturing plant.

5.2 The IS-Machine Families

The IS-machines can be separated into three groups:

- 1) Pneumatic-controlled IS-machines with angular mold-opening.
- 2) Pneumatic-controlled IS-machines with parallel mold-opening.
- 3) Servo-electric-controlled IS-machines with parallel mold-opening.

In the earliest types of IS-machines, all movements are controlled by pneumatic valves. The mold opening and closing is in an angular motion, which means that in a multi-gob setup at the blank-mold-side, the inner blanks are more widely opened than the outer blanks, causing difference in radiation between the glass and the open

blanks. At the blow-side, the inner molds are not opened as wide as the outer molds, which may lead to difficulties in machine accuracy and forming.

A significant step forward, therefore, was the introduction of pneumatic-controlled IS-machines with parallel mold-opening and closing. Here the mold-halves from the inner, middle, and outer cavity open in a parallel motion to each other. This leads to more comparable conditions between the molds of a given section. Furthermore, the parallel closing and opening is more precise, leading to a more reliable forming. In the color section of this Encyclopedia, a picture of a modern pneumatic-controlled IS-machine is shown.

The next logical improvement was to exchange the pneumatic-controlled movement for a servo-electric-controlled motion to take advantage of the enhanced stability, reliability, and precision of servo-electric drives. In this way, motions are much more easily cushioned and are gentler for the hinges, molds, and also for the glass itself. In the latest generation of IS-machines, mold opening and closing, plunger motion, invert, blow-head, take-out, pusher, and other parts are thus servo controlled.

The machine speed is a general parameter to describe the production performance for a given container. It is expressed as the cavity rate (C), namely the number of containers produced per minute (cpm) for each cavity considering the total numbers of cavities (N_S) of the IS-machine:

$$C = \frac{\text{cpm}}{N_S} \quad (5)$$

For a 12-section machine with a triple-gob setup and container output of 324 containers per minute, the cavity rate C is, for instance, $324/12 \times 3 = 9$. Hence, a 12-section IS-machine with a triple-gob setup producing 240 containers per minute is running a lower cavity rate than a 10-section IS-machine with the same triple-gob setup producing the same number of containers per minute. Highly efficient IS-machines can go up to cavity rates of 25 for small container sizes. This rate translates to production speeds of more than 700 containers per minute. In general, one can state that the higher the gob weight and the larger the container size, the lower is the corresponding cavity rate.

As illustrated in Figure 8 for 0.3-l beverage bottles, the performance of IS forming machines has steadily improved since their inception in the 1920s. In 90 years, one forming line has been producing 26 times more containers per minute. And in the same period the weight of such containers could be decreased from more than 300 to less than 170 g. These figures show vividly the very strong potential that this forming process had when it was invented.

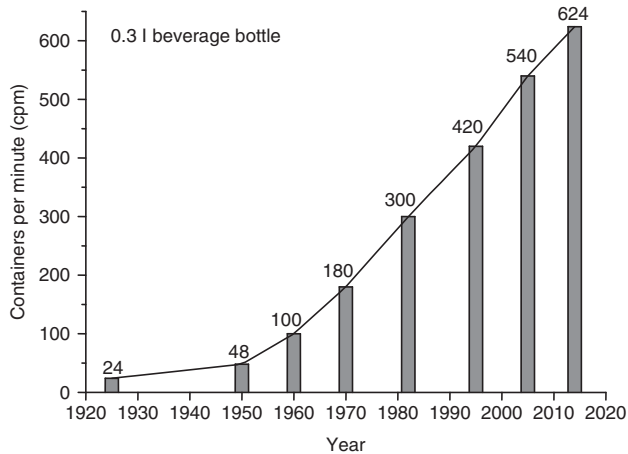


Figure 8 Performance increase of IS forming machines over the years in containers per minute.

5.3 Delivery Equipment

The delivery equipment consists of the gob-distributor (also called scoop), the trough, and the deflector. After the gob has been cut, it falls into the scoop which distributes the gobs to the different sections in the forming machine. The gobs slide through the respective troughs and then are redirected by the deflectors into the blank-molds. Although the delivery section looks like a simple part of the IS-machine, it bears considerable neuralgic points. The gob temperature decreases during the delivery but the upward side of the gob loses less heat than the side in contact with the metal delivery, which in some cases is in addition cooled and lubricated. Forming problems can thus happen if the gob acquires a non-uniform temperature profile.

The speed of the gob when it leaves the deflector is also an important parameter. When leaving the deflector, the gob is loaded into the mold. The higher the speed of the gob, the more beneficial it is for a good loading. Too slow a gob speed may lead to incorrect loading and hence to problems in the forming process or defects in the final container. In extreme cases, the gob is not fully loaded into the mold and the upper end of the gob is caught by the baffle. This leads to immediate failure of the respective section. The average gob speed at loading is between 6.5 and 7.5 m/s.

5.4 Blank-Side Forming

At the blank-side the three different forming processes come to play as explained in Section 3. Molds at the blank-side are usually made of laminar cast-iron. The glass gob is loaded into these molds and is formed into the parison. Because of process-sequence, the parison is formed upside down, the finish facing downward and

the bottom of the container upward before the invert leads to the proper upright formed final container. Upon forming of the parison, the mold is always cooled by air to allow fast heat extraction from the glass. As already explained, this is necessary to have a stable parison with a high enough viscosity after the mold has opened. If the parison is too hot and hence has a too low viscosity, it may collapse after opening the mold, causing section failure.

Different mold-cooling techniques are available. Most dominant are inside-mold cooling systems, where air is lead through channels in the mold either from below or from above and an older technique called stack-cooling. Here, fins are attached to the outside of the mold and the mold is streamed by air. This version is less efficient than inside mold cooling so that it usually leads to lower machine speeds.

5.5 Invert and Reheat

After forming of the parison, the blank-mold opens and the parison is transferred via an invert to the blow-side. The invert consists of an invert-arm in which the finish equipment with neck-ring and guide-ring is fixed. As soon as the blank-mold opens and invert takes place, the so-called reheat starts. During the blank-side process, the glass-surface has been cooled down, especially through the contact with the molds and blowing air. The glass viscosity rises in this way, which is necessary to give the parison a certain rigidity to move it without deformation. After having been released from the blank-mold, the outer parts of the parison get reheated from the hotter inner part through thermal conduction, which is in fact needed to lower again surface viscosity before the last forming step that will give the container its final shape.

5.6 Blow-Mold Forming

The forming of the final container in the blow-mold is from a mechanical point of view identical for all three forming processes (BB, PB, and NNPB) as explained in Section 3.

As with parison forming at the blank-side, final blowing at the blow-side can also be aided by vacuum. A main task for the blow-mold is to extract as much heat from the container as fast as possible to increase its viscosity, stabilize its shape, and avoid deformations during take-out and transport of the container after it has been released from the blow-molds. Because of this need to extract large amounts of heat in a short time, blow-molds often are made out of aluminum-bronze, which has much higher heat conductivity than cast-iron, hence allowing faster heat removal from the container.

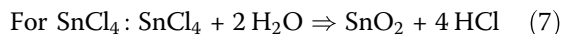
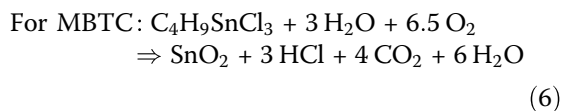
A picture of a triple-gob setup in the color-section of this Encyclopedia shows the parisons just having arrived at the blow-side and the final containers just having been removed from the blow-mold and placed over the dead-plate by the take-out.

6 Hot-End Handling, Hot-End Coating, and Annealing

The conveyor belt transports the container to the annealing lehr for stress-relaxation. Once the container has left the IS-machine, a first inspection often takes place with cameras that record the infrared images of the hot containers. From these images, defects can be identified and immediate corrections of the process can be initiated. This is very beneficial as the feedback between defects and applied corrections is direct and without the time delay that would occur if the container were first annealed and then inspected.

Before entering the annealing lehr, the outside body (not the finish) of the containers receives a hot-end coating of a 5–15 nm thickness. Even so thin, the hot-end coating serves different important functions. It first saturates the highly reactive surface bonds that are present at the surface of the new glass container. It also provides a surface suitable for good adhesion of the cold-end coating, which is applied later. Furthermore, it may slightly increase the strength of the container by disabling surface flaws that have been introduced during the forming process.

As precursor for hot-end coating most frequently used is monobutyltin-trichloride, $C_4H_9SnCl_3$ (MBTC) or tin-tetrachloride, which both gives rise to a SnO_2 coating on the container. The process is chemical vapor deposition under air at atmospheric pressure (atmospheric CVD) and is supported by the moisture of the air. The reactions that take place are:



Other precursors based on titanium or titanium-silicium are also in development to yield a TiO_2 or TiO_2 - SiO_2 coating. As explained, after forming and hot-end transport, the containers from different sections experience different cooling whereas the surfaces of a given container cool faster than its bulk, the rate being higher for the outer than for the inner surface. These differences create tensile stresses in

the container, which can lead to spontaneous breakage. Containers are thus reheated in the glass transition range in a continuous-annealing lehr long enough to ensure complete stress relaxation. The annealing times depend on the size of the containers, but are typically between 45 and 60 minutes. The containers can then cool down to room temperature homogeneously.

7 Cold-End Handling and Inspection

When they leave the annealing lehr, containers have a temperature between 80 and 120°C. They are coated a second time in a spray process. The main purpose of this cold-end coating is to protect the container against scratches upon further handling and later at the filling line. Usually a polyethylene wax is used to decrease surface friction, hence making the containers less susceptible to scratches when being handled or touching one another. The cold-end coating also serves to provide a surface suitable for good adhesion of the label, which is usually fixed at the filler.

After application of the cold-end coating, another inspection takes place in a highly automated way such that additional inspection by human eye is applied only in rare cases. Most inspection systems are based on various sophisticated optical systems, each checking for a certain type or group of potential defects that include flaws, scratches, cracks, blisters, seeds, loose or stuck glass particles, or dimensional errors of the container. Because special attention is paid to the finish of the container, mechanical inspection systems are, for instance, applied for testing that it is free of obstacles. Finally, random checks are made offline, e.g. to check that the strength exceeds definite values that depend on the kind of container. For impact strength, usually a minimum lot-size of 30 containers is tested on a shift, daily or some other regular basis, depending on the container made and plant procedures. The container is hit by a pendulum of a certain weight – depending on the chosen specification and domain of the container – in a well-defined matter until it breaks. As for the burst pressure strength, which is especially relevant for carbonated liquids such as sparkling wine, water, and champagne, the container is filled with water and its pressure is increased until breakage. Also here, due to the Weibull-characteristics of brittle materials, a minimum of at least 30 containers should be tested. After inspection, the containers are pelletized, wrapped, and prepared for shipment.

8 Perspectives

With the introduction of PET and other plastic containers, the glass industry has experienced a severe loss in market share for certain types of products such as juice, water, and milk. After years now the market seems balanced and the container-glass industry could maintain a quite stable production level of ca. 65 million tons worldwide, which amounts to ca. 200 billion containers in 2012.

Recently, however, disadvantages of plastic containers have been recognized. Because of the leaching of endocrine-active substances, phthalates and other substances into the container content [10, 11] and the dispersion of plastic waste on land and especially in the oceans [12], glass might even be able to gain more acceptance from the consumer. Here, glass can play out its strengths as, among other positive aspects, it is fully inert and can be 100% recycled. Furthermore, glass in a landfill does not pose any threat to the environment as it degrades to the components it was made of.

Nevertheless, glass has also its well-known drawbacks and a positive future of container glass strongly depends on the capabilities to overcome them. First, there is the fact that glass containers are energy-intensive to produce. Emission control, CO₂-trading, rising energy costs, and other environmental regulation force the glass-industry to push limits farther (Chapter 9.7). As processes are already highly optimized, there are no more “low-hanging fruits.” Although the effort that has to be made financially and risk-wise increases exponentially with the possible benefit that can be gained, the container-glass industry is aware of the need of innovations. The increasing number of batch and cullet preheaters or the latest concepts to

allow heat recovery for oxy-fuel fired furnaces illustrate the kind of efforts made to keep shifting the limits.

Other weak points are the fact that glass containers are brittle and mostly regarded as heavy. In specific instances, however, weight is considered a positive aspect of glass packaging. For example, think of the smooth texture, the reassuring heft, and the feel of value when lifting a glass bottle of wine or perfume. Nevertheless, many investigations have been carried out to decrease the weight of glass containers while increasing their strength. Coatings based on silica-sol-gels (Chapter 8.2) can, for instance, increase the strength of glass containers by 20% or more.

Besides, most impressive are current developments which aim at thermal strengthening of containers. After forming, the containers are reheated and then cooled from both inside and outside much faster and in a much more controlled way than in an annealing lehr. In this manner, compressive stresses at the inner and outer surface are introduced, which significantly increase the strength of the glass so that containers can be lightweighted further or be reused. The key to this development is to control the cooling very precisely and to adjust the balance between compressive stresses at the surface and tensile stresses in the bulk of the container (Chapters 3.7 and 3.12).

Innovations are also targeted in the field of glass-contact materials. Coatings for enabling a full non-swabbing production of all types of containers are investigated, but this task is still unsolved. Furthermore, it is highly desirable to avoid all lubricants that are currently used in shear-, trough-, and mold-lubrication. This would allow a full “dry-gob” delivery that would give considerable advantages over current process.

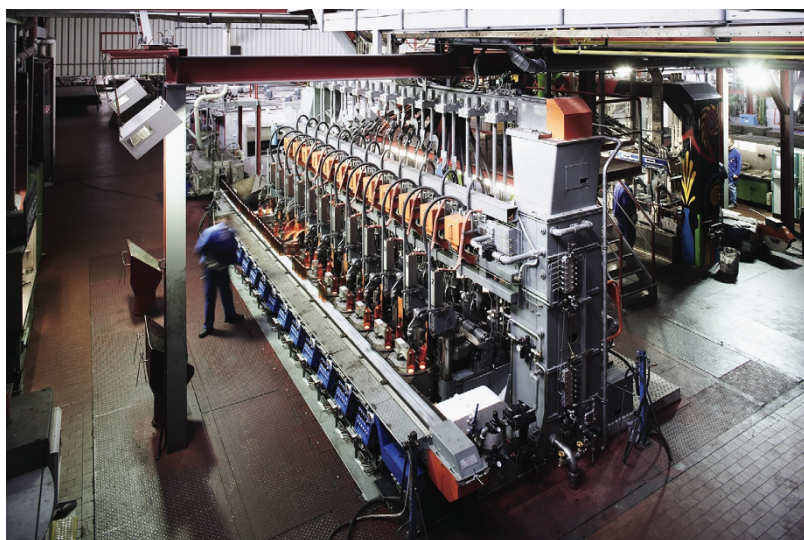


Figure 9 A modern pneumatic-controlled 12-section double-gob individual-section machine; on the left, the conveyor belt evacuating the newly blown bottles (courtesy Bucher Emhart Glass).



Figure 10 Parison just before blow-mold closing and final container on the blow-mold-side. Source: Courtesy Bucher Emhart Glass.

Concerning the IS-machine itself (Figures 9 and 10), a significant improvement would be to ensure a more precise and controlled forming process and, hence, a more homogeneous wall-thickness distribution in the final container. This could, for instance, be achieved by a direct gob-loading without the need of a delivery or by a forming process, which would allow a more precise reheat to have a more homogeneous final container forming. Because cost competition with alternative packaging is one of the biggest drivers and deciders for innovations, however, all the aforementioned approaches and concepts will have to distinguish themselves not only by their technical feasibility but also by their economic efficiency.

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1.6

Continuous Glass Fibers for Reinforcement

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1 Introduction

Numerous examples of the use of glass drawn as fibers can be found throughout history. The early Egyptians wrapped glass fibers over clay vessels and then fused them to form glass vessels. Venetian glass blowers in the sixteenth and seventeenth centuries used glass fibers to decorate elaborate glass articles. Glass fibers were even used as fabric elements in fashion garments in the late nineteenth century. It was in the mid-1930s, however, that two key developments created the means for glass fibers to become the base for a new industry based on composites—organic polymers reinforced with glass fibers, more commonly known as glass reinforced plastics, or GRP. The first was improvements in the process of manufacturing glass fibers at the Owens-Illinois Glass Company so that commercial fibers could be made in a multifilament strand form that met basic material handling requirements for downstream processing into composite structures [1]. The second was the development of polymeric resin systems by DuPont and others that could be combined readily with glass fibers. These glass-fiber reinforced polymer–matrix composites offered key material advantages over conventional metallic materials, including light weight, stiffness, and strength, and resistance to corrosion and fatigue.

Today, glass fibers have become the most widely used and cost-effective reinforcing fibers in the arena of commercial polymer–matrix composites. Early melt spun processes producing discontinuous fibers have evolved to today's large-scale direct melt continuous fiber-forming operations. One of the first needs for continuous fibers was for insulation of electrical wires for high-temperature applications, leading to the development

of a new glass composition based on a $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ system that met the electrical requirements and subsequently became known as E-glass. Because these fibers also exhibited excellent mechanical properties and could be made in relatively high-volume manufacturing operations, the original E-glass compositions rapidly spread into many composite applications. Today, the glass fiber reinforcement spectrum has grown to include an increasing array of specialty glass compositions that are targeted for key expanding markets in electronics, transportation, corrosion, construction, and in energy management.

Prior to 2000, most major glass fibers manufacturers were concentrated in North America and Western Europe. Today, fiberglass production facilities are flourishing in China and beginning to spread to other regions of the world to satisfy a constantly growing demand of GRP. It is the intent of this overview to provide insight into the technology that is associated with the continuing success of glass as a reinforcing fiber. Fiberglass technology associated with both material characteristics and manufacturing processes are described at a high level.

2 Commercial Glass Fibers

2.1 History of Fiberglass Development and Glass Chemistry

2.1.1 Fiber Types

Reinforcement glass fibers can be broadly divided into two categories – general-purpose and premium special-purpose fibers. The former are known as E-glass and subject to specific compositional ranges as defined by recognized standards such as ASTM D578 [2]. Historically, E-glass fibers have been predominant in the commercial production of fiberglass products for use as

Reviewers: R. Conradt, RWTH University of Aachen, Aachen, Germany
J. Thomason, The University of Strathclyde, Glasgow, Scotland, UK

reinforcements in various industrial polymer–matrix composites applications. Other types of fibers that have been used in special purpose and low-volume applications include S-glass, R-glass, D-glass, ultrapure silica fibers, and hollow fibers [3].

Continuous glass fibers for composite reinforcement have been categorized by the specific properties required for end-use applications (Figure 1). An overview of the historical timeline of the development and commercial use of these major glass types is represented on the horizontal axis. Further detail on the typical oxides and oxide ranges, physical and mechanical properties, and processing-related properties that are characteristic of the major glass types used in glass fibers are listed in Tables 1 and 2, respectively. More specific examples of recent developments in the areas of D-, S-, and R-glasses are also included.

2.1.2 E-Glass

First commercialized in the late 1930s [1], E-glass fiber remains the most widely used class of fiberglass for GRP materials [3, 4]. Its composition primarily lies within the ternary $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system with B_2O_3 and F_2 contents that vary from 0 to 10 wt % and 0 to 2 wt %, respectively. For much of its history, E-glass fiber production incorporated B_2O_3 in commercial compositions at levels of 7–8 wt %, which provided an optimal balance of melting and fiber-forming characteristics, mechanical properties, and electrical properties. Over time, however, increasingly restrictive environmental emissions requirements for particulates have been driving costs up for emission control systems. Countries such as Canada and Norway were leaders in the push to improve environmental conditions, leading to the introduction of the first boron-free commercial glass fibers. These glasses had in addition excellent corrosion resistance under strongly acidic conditions [7]. They have been designated as E-corrosion resistant (E-CR) glass fibers in the late

1970s. Over time, optimizations of minor oxide components such as TiO_2 , ZnO , and MgO served to improve their cost and manufacturing efficiencies while also providing proprietary regions in the compositional space as their use was growing rapidly.

In key areas outside of the corrosion markets, however, there was resistance to move to low-boron compositions. The electronics industry, dominated by E-glass fabrics used in printed wiring boards (PWB), relied on the unique value set of electrical consistency, dimensional stability, processing predictability, and low cost provided by conventional E-glass over many years and resisted any change in the E-glass standards. The aerospace industry also resisted the change, based on a well-defined history of performance of conventional E-glass and a desire to minimize any risk, however small, which might be incurred by what was perceived as a significant material change.

As a consequence of these developments, commercial E-glass fibers today fall into two major categories: low or zero B_2O_3 levels for general reinforcements, and higher B_2O_3 levels (>5%) for electronic and aerospace applications. The distinction between these categories is clearly defined in ASTM D578 [2].

2.1.3 C-Glass

Other reinforcement fibers containing B_2O_3 were developed in the early 1940s as C-glass, which has limited use as discontinuous fiber products for roofing materials. Continuous boron-free variants of C-glass fibers with improved chemical resistance to acids came to market in the mid-1960s. The composition is primarily composed of Na_2O , CaO , Al_2O_3 , and SiO_2 . The absence of boron resulted in improved acid resistance; the mechanical performance (strength and modulus) of C-glass fiber is inferior to those of both E-glass and E-CR glass, however, so that applications of this glass in the reinforcements industry have been limited to nonstructural uses

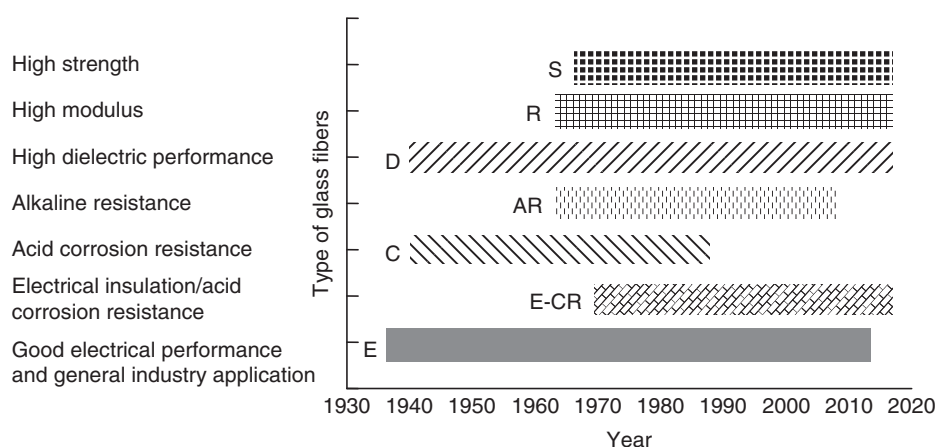


Figure 1 History of commercial continuous fiberglass development (most active period in development shown and beyond 2015 most intensive research areas projected are S, R, and D glass fibers) and standard nomenclature/classification based on their key properties used in commercial applications [4].

Table 1 Composition of glass fibers found in literature and/or commercial market [2–6].

Fiberglass	SiO ₂ (wt %)	Al ₂ O ₃ (wt %)	MgO (wt %)	CaO (wt %)	SrO (wt %)	BaO (wt %)	B ₂ O ₃ (wt %)	R ₂ O (wt %)	F ₂ (wt %)	ZrO ₂ (wt %)
E including E-CR	52–62	12–16	0–5	16–25	—	—	0–10	0–2	0–2	—
C (China) ^a	67.0	6.2	4.2	9.5	—	—	0	12	<1	—
C (Europe)	53–65	3.8–16	2.4–3.8	14–16	—	—	3–6	7–9	0.3	—
A ^b	72–72.5	1–1.5	2.5–3.8	9–10	0	0	0	13–14	0	0
AR ^c	61–71	0–3	—	<5	—	—	0	<18	—	16–22
D	72–76	0–1	—	<1	—	—	20–25	<4	—	—
D (derivative I)	52–60	10–18	0	4–8	—	—	20–30	Trace	0–2	—
D (derivative II)	50–60	10–18	1–6	2–5	1–9	1–5	14–20	<1	0–2	—
D (derivative III)	60–77	9–15	5–15	0–11	—	—	5–13	0–4	0–2	—
R	58–60	23–26	5–6	9–11	—	—	0	—	—	—
R (derivative)	56–65	12–20	6–12	8–16	—	—	0–2	0–2	—	0–2
S	64–66	24–25	9.5–10	<0.2	—	—	0	<0.3	—	—
S (derivative)	55–65	23–26	9–15	—	—	—	0–4	<1	—	—

^a C-Glass (China) is specified by Chinese Standard JC583-1995.

^b A-glass fiber (close to window glass composition) has low hydrolytic resistance, sensitive to moisture attack at room temperature, and, hence, is inappropriate for GRP composite applications.

^c ZrO₂ in AR-glass is specified by ASTM C1666/C1666M-08.

such as nonwoven fabrics for corrosion liners, building insulation materials, sewage pipes, etc. For many years, C-glass served as the primary form of glass fiber for low-cost regions of the world in emerging markets, at present less than 10% in volume relative to E-glass fibers produced each year in China. The balance of mineral components with no need for a boron source provided a glass fiber based on widely available raw materials that could be easily manufactured in low-technology operations. Hence, these properties led to the broad commercialization of C-glass as a low-cost substitute for E-glass fibers in regions where modern fiberglass furnace technology was not commonly available. Many early fiber producers in China used C-glass. The trend today, however, is to move away from C-glass fibers to the production of E-glass and other high-performance fibers. Little development has occurred since the mid-1980s, and C-glass fibers represent less than 5% of fibers used in glass fiber reinforced composites today.

2.1.4 AR-Glass

As named for its alkali-resistant properties, AR-glass fiber was invented in the mid-1960s and first commercialized by Pilkington Brothers in the United Kingdom in the early 1970s under the trade name Cem-Fil®. It was presented as a glass fiber option for reinforcing concrete structures. The glass chemistry was actually developed by a chemist at the Building Research Establishment and licensed to

Pilkington by the National Research and Development Corporation, leading to its initial commercial application. The glass chemistry is primarily comprised of Na₂O, CaO, ZrO₂, and SiO₂ with a small amount of Al₂O₃. The higher Al₂O₃ found in most commercial glass fibers results in lower ZrO₂ solubility. Unlike E-CR fibers, AR-glass fiber offers high resistance to alkaline corrosion as well as to acid corrosion. This resistance is attributed to the formation of a protective layer rich in ZrO₂ on the fiber surface in corrosive media. Because of the relatively high Na₂O and low Al₂O₃ levels, the fiber modulus and tensile strength are lower than for E-glass fibers despite the high concentration of ZrO₂. The overall higher production and material cost of AR-glass limits its utility to challenging fiber applications in cement reinforcement. Current developments are focused on increasing ZrO₂ solubility to improve further corrosion resistance and to improve melting and fiber-forming costs.

2.1.5 D-Glass

An optimum combination of dielectric constant (D_k) and dissipation factor (D_f) over a frequency range of 1 MHz to 40 GHz is provided by pure SiO₂ glass. This property set is of particular utility in the field of PWB and electronic chips and circuitry, driven by the dramatic growth of computers and consumer electronics. It is to allow production of glass fibers approaching the performance of SiO₂ glass in a reasonable commercial process that

Table 2 Typical properties of fiberglass found in literature and/or commercial market [3, 4, 6, 7].

Fiberglass	Fiber density ρ (g/cm ³)	Pristine strength σ_f (GPa)	Sonic modulus E (GPa)	Dielectric constant D_k (1 GHz)	Coefficient thermal expansion CTE (10 ⁻⁶ /°C)	Softening temperature T_{soft} (°C)	Liquidus temperature T_{liq} (°C)	Forming temperature T_F (°C)	Melting temperature T_M (°C)
E (including E-CR)	2.60–2.65	2.8–3.5	70–85	6.6–7.1	5.4–5.9	846–920	1080–1220	1180–1282	1345–1460
C (China)	2.53	2.6	65	7.5	8.4	—	1095	1217	1469
C (Europe)	2.52	3.3	69	—	—	750	1127	1157	1400
A	2.46	3.0	62	10.6	9.0	704	996	1185	1443
AR	2.68–2.78	3.2–3.7	73–77	—	—	820–847	1049–1192	1237–1247	1430–1467
D	2.11–2.14	2.4–2.5	52–55	3.8–4.0	3.1	771	953	1410	>1600
D (derivative I)	2.30	—	55–59	4.7–5.0	3.3–3.5	850	997–1270	1314–1382	>1550
D (derivative II)	2.30	2.5–3.1	57–64	5.4–5.8	4.0–4.9	830–875	1000–1054	1174–1298	1384–1502
D (derivative III)	2.34–2.42	3.3–4.1	73–82	4.8–5.6	4.1	944	1083–1287	1244–1388	1465–1641
R	2.55	4.1–4.5	85–87	6.4	3.3	952–975	1330	1410	—
R (derivative)	2.55–2.62	3.7–4.5	85–90	6.5	4.5–5.0	920–980	1170–1238	1265–1300	1468–1550
S	2.45–2.49	4.7–5.0	87–88	5.4	1.6–2.8	1030–1056	1439–1471	1424–1448	1620–1640
S (derivative)	2.53–2.56	4.2–4.8	86–95	—	2.8	920–968	1320–1450	1283–1450	—

Note: CTE values correspond to temperature range from room temperature to 300 °C; T_{soft} corresponds to glass viscosity of 10^{7.6} Pa·s as typically used in fiber glass production; T_F is defined by melt viscosity of 10² Pa·s as a reference temperature for drawing fibers; T_M is defined by melt viscosity of 10 Pa·s as a reference fining temperature to be reached in the industrial melting process.

D-glass has been designed. The earliest D-glass fiber composition was essentially a binary mixture of SiO_2 and B_2O_3 . Although D-glass fiber has significantly lower processing temperatures than pure SiO_2 , these temperatures are still substantially higher than those of E-glass fibers for PWB yarns. Melting temperatures are greater than 1600°C and fiber drawing temperatures greater than 1400°C . Recent developments have widened the D-glass fiber composition space by introducing Al_2O_3 , alkaline earth oxides (MgO , CaO , BaO , and SrO), and/or small amounts of Li_2O (Table 1) [5]. These composition modifications significantly lowered glass melting and fiber drawing temperatures, providing more favorable production costs and improved commercial viability. The drawback is a modest increase in D_k and D_f relative to the original D-glass composition. To achieve target product electrical properties, PWB laminators can use different resins with lower D_k and D_f . It is also possible to change the PWB layer stack and layout to meet target electrical performance for high-end PWB substrates. Another development is to lower the coefficient of thermal expansion of the glass fiber to improve PWB substrate thermal stability. This reduces thermal fatigue susceptibility and leads to a reduction in thermally induced cracking on chips. Continuing improvements in D-glass compositions keeps glass fiber at the forefront as a key element of choice in smaller, faster, lighter, and more electrically dense electronic components.

2.1.6 S-Glass

Known as S-glass, fibers primarily composed of MgO , Al_2O_3 , and SiO_2 were first developed in the late 1960s for high-temperature and high-strength applications and further expanded into military ballistic protection applications in the 1970s [6]. Because of high liquidus temperature (1470°C), fibers must be drawn at temperatures significantly greater than 1500°C to avoid fiber breakage caused by crystallization as the fibers are formed. This property attribute means that S-glass fibers must be drawn in a much lower viscosity range than that of typical commercial fibers (Section 3.2). The challenges of this severe process limit the number of product forms and result in very high costs that have limited the commercial utility of S-glass fibers to high-performance markets such as aerospace and military applications where strength and weight combined can justify a premium over other materials. There are no large-scale commercial production platforms in the S-glass family. Derivatives of S-glass have been investigated through introduction of small amounts of B_2O_3 and other oxides (Li_2O , CeO_2) to improve glass melting and fiber-forming performance. To date no large commercial-scale production has materialized.

2.1.7 R-Glass

For military applications, R-glass was first developed in the mid-1960s within the quaternary $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ system. In its original chemistry, its production, like that of S-glass, was limited because of the requirements imposed by its high melting temperature. The addition of CaO to the S-glass ternary system improved the processing conditions required to make glass fibers while still providing a high level of strength, but conditions were still more challenging than E-glass. Developments centered around the R-glass compositional range increased in the mid-00s, driven by the needs of wind-turbine blade producers who required longer blades with higher-modulus glass fibers to reduce the unit cost of electricity generation. Most of the improved technology made is based on reducing glass melting temperature while increasing fiber modulus, which has been realized by optimization of mixed alkaline earth oxides (MgO/CaO). As a result, large-scale furnaces and large direct-draw bushing operations are possible. [4]. These developments have provided a balance of mechanical performance, cost, and large-volume production capability that is in good alignment with the scale of production and cost of energy drivers in the wind-energy composites market. The speed at which these new high modulus fibers have been put on the market is unprecedented in glass-fiber history.

2.1.8 Glass Type Summary

With its derivatives such as ECR glass, E-glass continues to dominate global commercial sales of glass fibers for reinforcement applications. The unique combination of mechanical properties, weight savings, and durability combined with a wide array of available form factors in the form of fiber diameter, strand size, resin compatibility as delivered by sizing chemistry, continuous or chopped forms, and cost-effectiveness make E-glass fibers by far the best value for designing and manufacturing high-performance composites on a large scale. In parallel with ongoing improvements in E-glass performance, technology developments associated with high-performance fibers, i.e. re-engineered or derivatives of S-glass, R-glass, and D-glass will continue to be key focus areas in the future. These technologies serve to expand the growth of glass-fiber reinforcements in transportation, aerospace, both traditional and renewable energy, and safety and security markets. These added technology options in glass fiber address light weight, high strength and high modulus [4, 6], improved durability, and improved electrical performance such as low signal loss and high-speed communication in the PWB industry [5].

In developing new glass fibers, a fundamental understanding of glass network structures and glass properties

for both performance and processing are critical. In boron-containing glasses such as E- and D-glass, speciation of boron in the network, i.e. $\text{BO}_4 \leftrightarrow \text{BO}_3 + \text{NBO}$ (non-bridging oxygen), is affected by both melting temperature and glass composition [8]; in turn, melt viscosity and glass dielectric property are affected. Besides the speciation of silicate network affected by modifying oxides [9], all commercial silicate glass fibers contain alkaline earth oxides and alumina; an in-depth understanding of composition effect (particularly high field strength metal oxides, MO_x) on speciation of aluminum, i.e. $\text{MO}_x + \text{AlO}_y \leftrightarrow \text{MO}_{x-1} + \text{AlO}_{y+1}$ ($x = 7, 8$ and $y = 4, 5, 6$) [9–11], can assist in glass design for achieving better glass mechanical properties and facilitating melting and fiber-forming processes.

2.2 Major Fiberglass Producers

Worldwide production of E-glass fibers reached about 7.3 million metric tons ($7.3 \cdot 10^{12}$ kg) in 2018 and is projected to grow continuously. The expansion of E-glass fiber production capacity is expected to occur in parallel. Fiberglass companies can be ranked by total annual sales in volume whereas total production capacity of each company is much more difficult to find in the public domain. The current top 10 fiberglass producers globally based on sales in past 5 years are listed in Table 3. The largest rate of expansion has taken place in China, where newly built furnaces in recent years ranged from annual capacity of 30 000 metric tons to 120 000 metric tons per furnace.

3 Manufacturing of Glass Fibers

3.1 Primary and Secondary Processes

The production of glass fibers encompasses a wide range of processes, from raw-material sourcing, batch weighing and mixing, batch-to-glass melting and fining, fiber drawing with the application of a water-based organic sizing, to finally drying. Much of today's glass-fiber production for reinforcements incorporates direct processing wherein the finished product, whether wound into a continuous spool of fiberglass strand or chopped directly after the fibers are formed and coated with sizing, is produced in one step as a part of the forming operation. Secondary downstream processes are still in use for some applications and may include twisted yarn on bobbins, roving packages made by assembling collections of smaller strands into larger strands, fibrous mats made from chopped or continuous strands bound together by mechanical or chemical binders, and chopped products for some specialty applications. The general process is sketched in Figure 2. For E-glass fiber production, combustion technology is moving from natural gas–air or oil–air to natural gas–oxygen to achieve better energy transmission efficiency. Where C-glass fiber is still in production, the use of syngas remains prevalent for furnace and combustion systems because of lower capital costs. For both types of fibers, electric boost technology has increased in utilization for energy efficiency and for lowering top firing and hence lowering the crown temperature of the furnace to prolong its life. The following sections briefly discuss some of the key areas of glass melting/fining, fiber drawing, and sizing chemistry design.

Table 3 Top 10 fiberglass producers (2008 – 2013).

Name	Headquarter	Sales ranking	Major market	History
Owens Corning (OC)	US	1	Construction/Transportation	Since 1938
China Fiberglass Co., Ltd. (Jushi)	China	2	Construction/Infrastructure	Since 1993
PPG Industries, Inc. (PPG) ^a	US	3	Transportation/Renewable energy/Electronics	Since 1945
Chongqing Polycomp International Corporation (CPIC)	China	4	Transportation/Renewable energy	Since 1986
Johns Manville (JM)	US	5	Construction	Since 1958
Taishan Fiberglass Inc.	China	6	Renewable energy/Construction	Since 1983
Nippon Electronic Glass (NEG) ^a	Japan	7	Transportation	Since 1976
3B – Binani (3B)	India	8	Automotive	Since 1996
Sichuan Weibo	China	9	Transportation/Infrastructure	Since 1996
Taiwan Glass Group (TGG)	Taiwan	10	Construction	Since 1990

^a PPG sold its Fiber Glass business to NEG in 2017, which makes NEG's rank No. 3.

Source: Fiber glass market study, PPG, 2014.

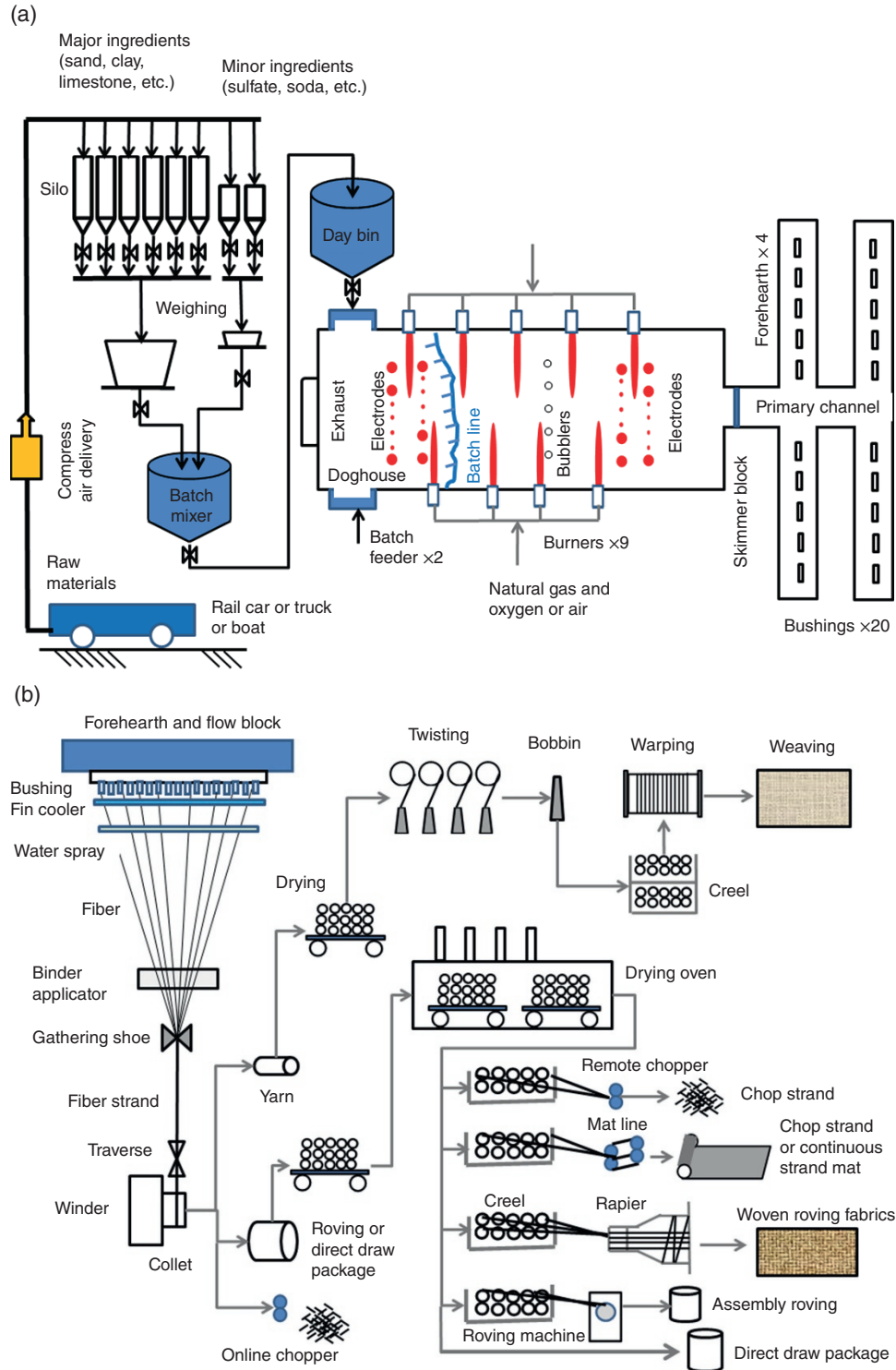


Figure 2 Schematic illustrations of continuous fiberglass manufacturing processes: (a) batch operation, batch melting/glass fining, and glass delivery to bushing positions, common burner locations used in the primary canal and forehearth (not shown) and (b) steps in fiber drawing and downstream processes. Source: Fiber glass market study, PPG, 2014.

3.2 Glass Melting and Fining

Commonly used raw materials for E-glass fiber include sand (SiO_2) as the primary silicon source, kaolin or china clay consisting of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) as the primary source of aluminum, limestone (CaCO_3) or quicklime (burnt lime, CaO) as that calcium, and boric acid (H_3BO_3) as that of boron. More complex minerals are often used in place of or in combination with these major components to manage cost, improve melting performance, or utilize locally sourced ingredients. Some examples of commonly used complex minerals include pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), colemanite ($\text{Ca}_2\text{B}_6\text{O}_8(\text{OH})_6 \cdot 2\text{H}_2\text{O}$), ulexite ($\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$), borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 8\text{H}_2\text{O}$), fluor spar (CaF_2), dolomite [$\text{Mg, Ca}(\text{CO}_3)_2$], spodumene ($\text{LiAl}(\text{SiO}_3)_2$), and soda ash (Na_2CO_3). For C-glass fiber, albite ($\text{NaAlSi}_3\text{O}_8$) is commonly used to reduce the need for soda ash. For simplicity, primary phases of the above natural raw materials are used; all of them can contain other mineral phases and/or impurities, for example, iron from ore and grinding process.

Batch reaction chemistry and kinetics in glass melting have been widely studied with various experimental techniques, including differential thermal analysis (DTA), differential scanning calorimetry (DSC), X-ray diffraction, electrical resistance and temperature distributions from molten glass to the batch pile, for laboratory batch sizes from as little as 0.1 g up to 10 kg in mass [12–14]. Models have also been developed from a thermodynamic approach [15].

As illustrated in Figure 3, the batch-to-melt conversion process of representative E-glass and ECR-glass batches can be characterized in the following steps:

- i) De-hydroxylation of batch ingredients, i.e. removal of both moisture water (120–150 °C) and crystalline

water in the minerals, (colemanite, 350–450 °C; kaolinite or pyrophyllite, 500–600 °C).

- ii) Decarbonization, i.e. removal of carbonates (limestone, 700–800 °C).
- iii) Formation of intermediate crystalline phases (~1000 °C).
- iv) Liquid phase formation (1000–1400 °C).
- v) Final dissolution of residual phases (sand, 1250 °C) [12].

The majority of the batch reactions are endothermic, the energy consumption of these steps constituting a significant portion of the total energy spent in the glass melting process. Finally, the glass fining step, which varies as a function of furnace throughput, consumes even more energy. The fiberglass industry is continuously searching for new raw materials to lower the energy consumption in batch melting [12] and improved technology to increase the furnace throughput without sacrificing glass quality. This in turn reduces the unit energy consumption of glass melted and glass fiber produced. In practical terms, successful implementation of these approaches can provide savings of up to 20% compared to typical E-glass melting energy demands of 7000–8000 kJ/kg of glass [12].

One generally carries out glass melting and fining by controlling the melt temperature of the furnace hot spot near or higher than T_M at which the melt viscosity is 10 Pa-s (Figure 4), which will ensure sufficient fluidity of the molten glass to promote both mixing of the batch components and removal of seeds (or bubbles). The latter is also aided by the use of fining agents such as sodium sulfate (Na_2SO_4), which is commonly used in making E-glass fibers. However, because much higher melting temperatures are often required for specialty glass fibers, other fining agents such as manganese dioxide (MnO_2) or cerium dioxide (CeO_2) are also used with or without

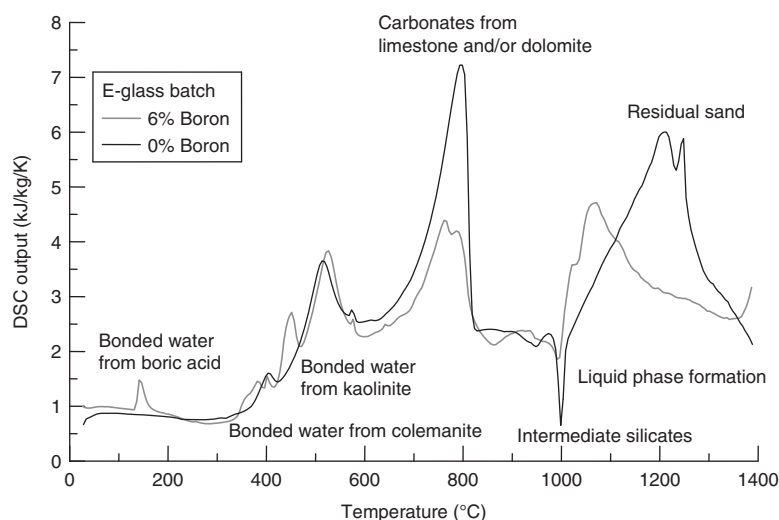
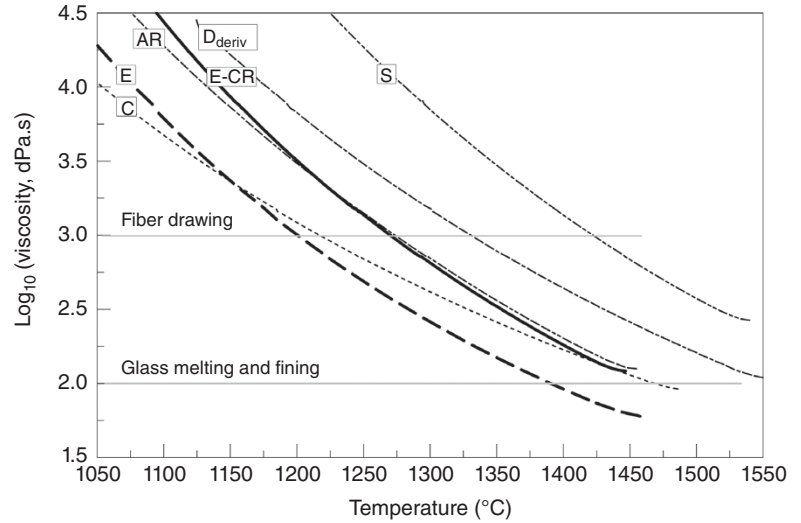


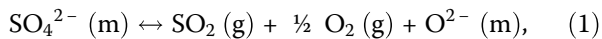
Figure 3 Differential scanning calorimetry output of E-glass batches with and without boron from room temperature to 1400 °C (10 K/min heating rate), illustrating both endothermic and exothermic reaction events as batches are converted into glass through initial steps of dehydration and decarbonation. The intermediate silicates formed are anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and/or wollastonite (CaSiO_3). Source: PPG, 2014.

Figure 4 Viscosity curves of E-glass, E-CR-glass, AR-glass, D-glass (derivate), S-glass, and C-glass, illustrating composition effects on reference temperatures of glass melting/fining and fiber drawing. Source: PPG, 2014.

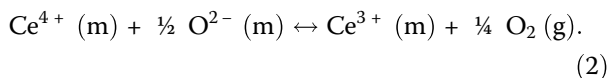


added sodium sulfate. Fining agents may also serve as oxidizing agents to control the iron oxidation states for both glass melting and fiber drawing process as will be discussed in more detail in a later section.

Fining action from the decomposition of Na_2SO_4 dissolved in the melt is created as the molten glass stream moves toward the higher temperature fining zone, or hot spot, of the furnace. The melt with dissolved sulfate becomes oversaturated at higher temperatures ($>1350^\circ\text{C}$) and sulfate decomposition and bubble formation begins to occur. The onset temperature of sulfate decomposition depends on many factors – water vapor pressure in the furnace combustion space, water dissolved in the glass, organic species in the batch materials, any addition of carbon to the batch, partial pressure of oxygen above the melt, and others [16]. Driven by buoyancy action, bubbles containing SO_2 and O_2 travel to the melt surface; along the way the sulfate bubbles expand, stripping smaller bubbles of CO_2 (primarily from decomposition of carbonates) and air (primarily N_2) trapped in the melt. The sulfate fining process can be described by the reaction



where O^{2-} is the free oxygen, which depends on glass composition. With other fining agents, for example CeO_2 , oxygen fining gas is generated according to the reaction



Adequate use of fining agents is critical. The quantity needs to be optimized based on the furnace firing setup, types of fuel and air or oxygen used, glass composition,

and types of fiber products to be made. Excessive use of fining agents can result in uncontrolled melt foaming. The foam layer reduces energy transfer from the combustion space to the glass melt beneath the foam blanket, resulting in energy waste because of excessive firing required to maintain the underglass temperature and in poor glass quality caused by inhomogeneous melting. Excessive foam can also lead to potential overheating of the furnace crown, shortening the furnace service life.

3.3 Fiber Forming

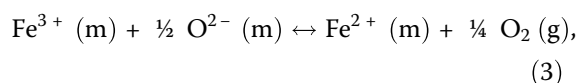
The *bushing* is the device that controls the fiber-drawing process. It is the interface between the glass melting and fiber formation processes. Bushings are made of precious metal alloys of platinum (Pt) and rhodium (Rh), typically in alloys of 90Pt/10Rh or 80Pt/20Rh. The tip plate of the bushing contains an appropriate number of tips or nozzles, typically ranging in number from 100 up to 8000 and in diameter from 0.75 to 2.00 mm. Proper selection of these parameters then enables production of the desired number and diameter of glass fiber filaments in a strand of fiberglass (Figure 2b). The bushing is electrically heated to provide very precise control of the temperature and, thus, of the viscosity of the glass flowing through the nozzle. The combination of tip size and glass viscosity coupled with the controlled speed of the take up winder allows for very good control of finished-product filament diameters and linear-strand density.

The rate of melt flow (F) through the bushing nozzle or bushing tip follows Poiseuille's relationship, i.e. flow is proportional to $r^4 h / l \eta$ where r is the fiber radius, h is the depth of molten glass above the bushing tip plate, l is the length of nozzle, and η is the melt viscosity at the tip plate [3]. In practice, the actual interior geometry of

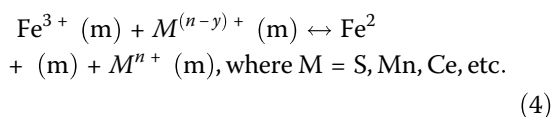
the nozzle may be varied, which affects the melt flow rate for a given winder speed; modified Poiseuille equations can be found in the literature [3].

The fiber attenuation process is usually completed in less than a second, during which the diameter of the melt stream through the tip changes by three orders of magnitude from millimeters at the tip to micrometers in the finished filament. At a fiber attenuation speed between $3 \cdot 10^4$ and $3 \cdot 10^5$ m/s, depending on bushing type and specified fiber product, the estimated fiber cooling rate is approximately $0.5 \cdot 10^6$ K/s for a typical commercial fiber-forming process. Stable drawing processes require adequate control of the fiber cooling rate, which is managed through a combination of process controls, including appropriate bushing design, cooling manifolds (commonly known as fin coolers), cooling air flow, and water spray. In addition, one optimizes the fiber drawing and cooling rates by tuning the oxidation state of iron (either from raw material impurities or intentionally added) in the glass, specifically the concentration of ferrous ion (Fe^{2+}).

The oxidation–reduction of iron in the melt is affected by glass chemistry and oxygen partial pressure ([16, 17], Chapter 5.6)



and by the presence of other multivalent species either from additives or impurities,



In general, drawing processes for making finer or smaller diameter fibers (and typically smaller bushings also) require glasses with a relatively lower concentration of Fe^{2+} (hence, slower cooling rate) than coarse fibers made from larger bushings (hence, higher cooling rate). The control of the iron oxidation state (or ferrous ion concentration in glass) is directly related to the amount of fining agent in the batch and the total iron in the batch, both of which are adjustable variables to maintain process stability. The ferrous ion concentration in glass is routinely monitored in production with a colorimetric method through acid digestion of a glass powder sample or with a calibrated UV-VIS spectroscopic method on an optically polished glass disk.

In commercial production, glass fibers are drawn at a temperature T_F where melt viscosity is near 100 Pa·s (Figure 4). Stable melt viscosity at the tip plate is critical for an efficient fiber-forming process. If melt viscosity at the tip plate is too low (i.e. too high temperature at the tip plate), spreading of the glass melt across multiple tips on the tip plate results in flooding and disruption. If melt

viscosity is too high (i.e. too low temperature at the tip plate), fiber drawing tension increases and the stable forming cone at the tip exit begins to fail, causing fiber breakage [3]. In addition, the actual forming temperature must be greater than the glass liquidus temperature, T_{liq} , by at least 50 °C to reduce the risk of devitrification. Microcrystals formed in colder spots along a primary canal or forehearth (Figure 2a), no matter how small, can lead to significant fiber breakage in the drawing process and hence, adversely impact productivity.

In making commercial glass fiber products for reinforcements, various processes are used to provide the desired end form. Direct draw or single end winding, direct chopped fibers, and numerous downstream secondary processes may be employed. Depending on the product needs, the types of bushings vary in dimension, number of tips, and tip diameters. In addition to the glass and process elements necessary to produce commercial glass fibers, the surface of the fiber must be treated to provide optimum compatibility of the inorganic glass fiber with the organic resins used in the reinforcements industry. This leads naturally into a discussion on the role of sizing chemistry.

3.4 The Role of Sizing/Binder in Glass Fiber Products

The long history of growth in both volume and breadth of glass-fiber commercial successes has been driven by unique combinations of strength, stiffness, weight, and cost attributes that can be achieved through glass chemistry. However, to realize fully the value of the glass fiber in a reinforced composite, a means must be provided to facilitate the effective interactions between the inorganic fiber and the organic polymer that together make up a reinforced composite material. One maximizes this interaction by designing an interface that synergistically combines the material properties of each element. A design that provides for effective load transfer between the constituents transforms an inherently heterogeneous material into one that behaves as a homogeneous structure.

In fiber-glass composites, the system that delivers the optimum interfacial properties is the *sizing* or binder that is applied to the surface of the fiberglass. The sizing is generally applied as a continuous coating just after the fibers are formed and before the individual glass filaments are gathered into a strand below the bushing. The most common sizing formulations comprise a water-based mixture of molecular species such as adhesion promoters, film formers, lubricants, and other processing aids as summarized in Table 4. It is the role of the sizing chemist, working in conjunction with the glass scientists and the process engineers, to deliver a sizing formulation that appropriately enables efficient production rates of the

Table 4 Classification and functionality of ingredients in fiber sizing/binder formulations.

Classification	Functionality
Coupling agents	Adhesion promoters that bond or couple the glass surface with specific matrix resin systems; may also provide excellent filament protection and increased dry breaking strength.
Film formers	Hold filaments together and provide protection to the fiberglass strand.
Film modifiers	Modify the film formation to increase strength, flexibility, and tackiness.
External lubricants	Provide resistance to abrasion damage at external contact points such as strand guides in downstream processes.
Internal lubricants	Reduce the filament-to-filament abrasion within the fiberglass strand.
Emulsifiers/ Surfactants	Form stable suspensions or emulsions of immiscible ingredients, generally in water-based systems.
Other process aids	May be used as required to control foam, wetting, static behavior, biological activity, and any other special requirements by a particular end-use or internal processing need.

fiberglass while also providing maximum compatibility with the targeted composite polymer matrix and the end-use performance requirements.

Good sizing design begins with a selection of the appropriate adhesion promoter that will provide good bonding between the inorganic glass surface and the reactive sites in the targeted polymer system. The most widely used class of chemicals for this function are organosilanes. These species can be designed to promote reaction between the silanol sites on the glass surface and on the organosilane molecule, leading to an Si–O–Si bond at the glass/polymer interface. The silanes as supplied are hydrolyzed in the final sizing formulation to provide Si–OH groups that can then condense with the Si–OH groups on the glass surface to provide strong interfacial bonds. The organic functionality of the silane is then chosen to maximize compatibility with the target polymer in the final composite. Common examples are shown in Table 5. Other classes of chemicals that have seen more limited utility as adhesion promoters include organotitanates and organo-chromium complexes.

It is important to note that characterization of the quality of the sizing as well as the glass fiber in the finished composite is critical to confirming technical success of a fiberglass product. Good adhesion at the interface implies the formation of an interphase that makes the materials compatible through covalent bonding, and provides a discrete pathway for stress transfer between the materials. Many standardized tests related to interfacial adhesion, interfacial shear stress, tensile stress, modulus, and hydrolytic stability have been developed over the years and are widely available in international standard testing organizations such as ASTM and ISO. Many academic laboratories have also developed more sophisticated tests. One example is the measurement of composite critical fiber length [18]. As defined by Eq. (5), the critical fiber length (l_c) is the minimum fiber

length at which fibers with given diameter d reach their ultimate tensile strength σ_{fu} and the matrix/fiber interface experiences a maximum interfacial shear stress τ_y , [18]. When $l > l_c$, an increase in interfacial adhesion will result in a decrease in critical fiber length and may lead to improvements in other properties such as impact strength in certain resin systems. However, the sizing may also act to protect the fiber from surface damage and defects in addition to providing improved adhesion. In that case, reduction of fiber surface damage would lead to an increase in the critical fiber length by increasing σ_{fu} . Interestingly enough when $l > l_c$ and the composite is stressed to failure, then the fiber will break at regular intervals of l_c within the composite. This result can be used to estimate the interfacial shear stress:

$$l_c = \frac{\sigma_{fu}}{2\tau_y} d \quad (5)$$

This example also serves to illustrate that broader conclusions from micromechanical experiments should consider that different outcomes may result depending upon material selection. The most common material options include chopped or short fibers vs. continuous fibers and thermoset vs. thermoplastic resin systems, which of course complicates the task of the sizing chemist in product development.

It remains for the sizing chemist to complete the establishment of the final formulation from a virtually limitless palette of film formers, process aids, and modifiers to deliver the desired performance of the fiberglass as a commercial product. Commercially, the resultant amount of sizing on the fiberglass surface is typically in the range of 0.3–1.5 wt % of the dry fiberglass.

An excellent in-depth review of the complexity of this field from the sizing chemists' point of view can be found in Thomason's book, *Glass Fibre Sizings: A Review of the Scientific Literature* [19].

Table 5 Common organosilanes.

Chemical name	Structure	Class
γ -Aminopropyl trialkoxy silane	$(\text{RO})_3\text{Si}-(\text{CH}_2)_3-\text{NH}_2$	Amine
γ -Methacryloxypropyl trialkoxy silane	$(\text{RO})_3\text{Si}-(\text{CH}_2)_3-\text{OOC}(\text{CH}_3)\text{C}=\text{CH}_2$	Methacryl
γ -Glycidyloxypropyl trialkoxy silane	$(\text{RO})_3\text{Si}-(\text{CH}_2)_3-\text{O}-\text{CH}_2\text{CHCH}_2\text{O}$	Epoxy
Vinyl trialkoxy silane	$(\text{RO})_3\text{Si}-\text{CH}=\text{CH}_2$	Vinyl
	$\text{R} = \text{CH}_3\text{CH}_2- \text{ or } \text{CH}_3-$	

4 Markets and Applications

4.1 Global Glass Fiber Reinforced Polymeric Composite Markets

The glass fiber reinforced polymeric composites market will grow from about \$18 000 million in 2010 to an estimated \$30 000 million in annual shipment value by 2017 according to a recent survey. These composites find many applications in commercial markets globally. A breakdown by major regions of the world is shown in Figure 5 for the Americas, EMEA (Europe, Middle East, and Africa), and Asia Pacific.

Construction and transportation dominate the Americas market place for GRP composites, with construction taking the largest share. Other segments are more or less equally distributed among industrial, oil and gas, and wind-turbine blade applications, along with numerous smaller segments. In the EMEA region, construction and transportation are also the largest markets, but here the leading industry is transportation. The wind-turbine blade segment is much higher in Europe, and the other segments hold similar shares as seen in America. In the Asia Pacific region, once again transportation and construction combined are the largest segments. In this region, however, electronics and industrial markets are more prominent, combined with a large “other” segment driven by the large variety of needs and applications in the region. The electronic segment is particularly strong, reflecting the strong position of the PWB industry and its supply chain of E-glass fiber, fabric, and laminators in the Asia Pacific region.

Generally, GRP composite materials are classified into two categories: thermoplastic and thermoset. Thermoplastic GRP products most commonly use resins based on polypropylene, polyamides (nylon 6 and 6,6), polyesters (polybutylene terephthalate, polyethylene terephthalate), and many other specialized thermoplastic polymers. Thermoset GRP products commonly use resins based on epoxies, unsaturated polyesters, and vinyl esters, with smaller but growing applications use phenolic and urethane-based resin systems as well as other

specialty resins. Thermoplastic resins generally exhibit higher ductility and impact resistance, while thermoset resins offer better strength and modulus and higher thermal stability. There are many new developments underway in both processing and resin chemistry that often blur the traditional divisions between thermoplastic and thermoset-based glass fiber composites. The glass fiber industry will continue to be at the forefront in supplying reinforcement solutions for these new developments.

Thermoplastic automotive applications include window frames, automobile body components, dashboard sections, and bumper beams. Typical processes for combining fiber forms with thermoplastics resins as intermediates for molding of final parts include extrusion compounding of short fibers, glass-mat thermoplastic sheet, and long-fiber thermoplastic compounding.

Major thermoset products include composite pipes for oil and gas, marine, and industrial applications; wind-turbine blades; flue-gas desulfurization tanks and towers; PWB; boats; construction beams and structures; composite leaf springs; and numerous sporting-goods applications. Other components are countless and limited only by the imagination. Typical conversion processes for thermoset composites include filament winding, pultrusion, resin transfer molding, hand lay-up, spray deposition, continuous laminating, centrifugal molding, sheet molding compounds, and bulk molding compounds.

Glass fibers can also be used as a reinforcement for cement structures, in many cases with AR-glass fibers as already noted. Like E-glass, it also finds utility in some of these applications where short-term strength is the major requirement. Some geotextile reinforcements also use E-glass as a base in a coarse mesh form. Chopped glass fibers are the predominant reinforcement for asphalt roofing shingles, primarily in North American markets (*Source*: fiber glass market study, PPG, 2014).

4.2 Emerging GRP Composite Markets

Traditional E-glass still dominates total glass fiber volume produced around the world, with a well-established

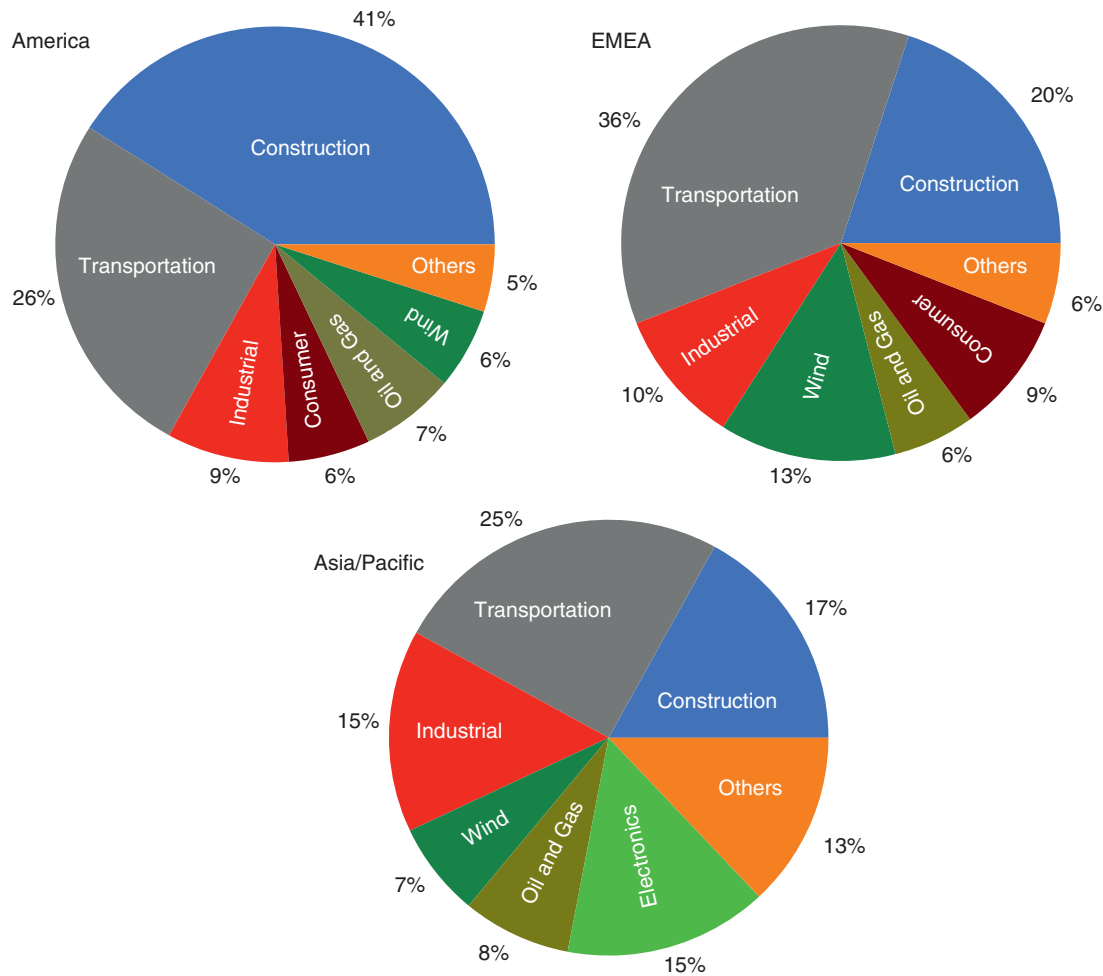


Figure 5 Global GRP composite market shares in America, EMEA, and Asia Pacific regions. Source: Fiber glass market study, PPG, 2014.

history of delivering value in many markets for more than 70 years. This trend is expected to continue because of the E-glass value in use and the maturity of the manufacturing technology. Along with its variants, E-glass will continue to be the material of choice in most applications. Fiber manufacturers will continue to move toward more environmentally compliant variants, and product development scientists will continue to tailor the glass composition, form factor, and surface chemistry to maximize synergy with developing resin chemistries and process technologies. A good example of this evolution is E-CR glass and its performance in strongly acidic environments. This adequacy has resulted in the specification of E-CR glass as a requirement in applications such as waste water pipe systems, desulfurization towers in power plants, and filtration bags in power plant or cement productions (Figure 6a).

Specialized fibers, including redesigned and more manufacturing friendly versions of S-glass, R-glass,

and D-glass for high-strength, high-modulus, and premium electrical properties, respectively, continue to be in demand where limits are being pushed to the extreme for traditional E-glass. Some examples include aerospace, driven by weight and fuel economies; wind energy, driven by the need for increased stiffness at a fair value cost in order to achieve lower energy costs; transportation, driven by fuel economy and energy management in crashes; better electrical properties, driven by increased bandwidth, faster computing speeds, and miniaturization; and energy storage, driven by higher strength for hydrogen storage tanks and other components. A specific example of the role of improved glass design is related to the design of ultra-long wind-turbine blade. Newly designed high modulus and low-density glass fibers will likely replace E-glass fibers (Figure 6b) in the future, helping to drive the unit cost of electricity generation to a more competitive level.

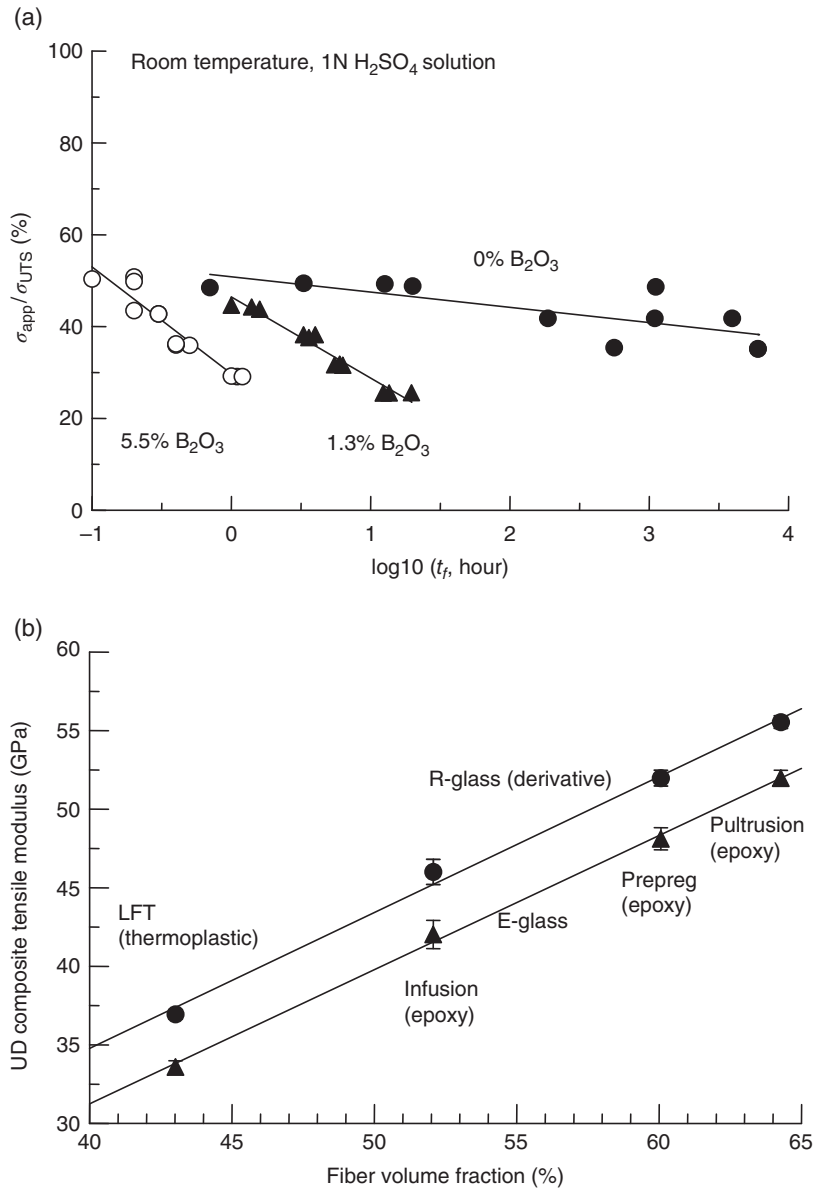


Figure 6 Improvement in fiber properties through compositional changes. (a) Effects of boron reduction on acid stress corrosion performance as shown by a comparison of boron-free ECR and E-glass fibers [7]. (b) Improvement of composite unidirectional tensile modulus with newly designed R-glass fibers for various potential applications for both thermoplastic and thermoset composites [4] (σ_{app} – applied tensile stress on rod samples, σ_{UTS} – ultimate tensile strength of as-received rod samples, unidirectional nonwoven fabric reinforcement – UD composite panel, long fiber thermoplastics – LFT).

5 Perspectives

It is expected that E-glass and its variants will continue to be the predominant form of glass fiber for most reinforcements markets in the near term. However, as larger volume applications grow with increased performance needs, the glass fiber industry will face challenges to develop manufacturing technology platforms capable of making these products at costs acceptable to the markets. Innovation is needed in both glass chemistry and manufacturing technology to grow specialty fiber businesses that usually provide higher profitability than traditional glass fiber

markets. Some examples of manufacturing technologies could include new melting furnace designs, new melting techniques, new fining methods for higher temperatures, and new refractory materials for high-temperature operations. In terms of fiber-glass chemistry, an in-depth fundamental understanding of glass structure–property relationships will aid glass optimization for performance and manufacturing scalability. Most ongoing research, including molecular dynamic modeling, focuses on local structure of both network work formers (primarily Si, B, and conditionally Al) and network modifiers (primarily alkali, alkaline earth, and rare earth).

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1.7

Simulation in Glass Processes

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1 Introduction

Numerical simulations of glass processes are performed in lieu of physical trials, which often involve conditions too harsh to allow measurements, are difficult to control, or are prohibitively expensive. Used as a screening tool, a simulation model can thus allow technologists to avoid several iterations of actual physical trials on an industrial apparatus. Alternatively, simulations can be used to examine phenomena which are too difficult to observe in practice because of the extreme environment of glassmaking. Moreover, numerical simulation allows for fundamental phenomena to be studied, thanks to its capability of identifying and controlling factors that influence the process. Such factors cannot usually be independently modified in the real process, in view of its complexity, and the insights gained from such virtual experiments can be used to guide technology development efforts.

Following the advent of electronic computers in the mid-twentieth century, these methods were pioneered in the 1960s to deal with glassmaking problems elementary enough to be handled with the simplifying assumptions required by the then limited computing power. Much more complex and realistic 3-D problems can of course be tackled now as massive increase in this computing power has dramatically changed engineering analysis in general. Concomitant with hardware advances have been significant developments in software, including both computational algorithms and user interfaces. Several commercial offerings of the relevant software are available for glassmaking. Process engineers are encouraged to utilize such tools. Some of these software packages are general purpose, adaptable to a wide range of situations,

whereas others serve the glass-processing industry specifically.

Both general-purpose and niche-software products will be used in the example simulations presented in this chapter where the focus will be put on the mathematical techniques used to simulate the two major phenomena involved in glassmaking, namely fluid flow and heat transfer. Mathematical models, formulated from the classical laws of physics, are used to calculate relevant field variables, such as temperature, velocity, stress, etc., within a glass manufacturing process. Modeling results are then interpreted with post-processing procedures, which are less abstract than ever before, thanks to modern techniques capable of displaying results in a geometrical context. When applied to fluid flow and heat transfer, these techniques are collectively referred to as *computational fluid dynamics* (CFD).

To review these new methods, we will first summarize the main six steps they successively involve from the definition of the problem of interest to its solution. The various physical phenomena relevant and their mathematical description and computational treatment will then be expounded. Subsequently, a few representative examples of model simulation will be presented to demonstrate the capabilities and the value of modeling to a glass manufacturing enterprise. Finally, a brief section on the importance of managing simulation data will be provided.

2 A Brief Overview

Numerical simulation is a process made up of the six steps summarized in Table 1. These are: (1) identify the objectives of the modeling study, (2) construct a geometrical domain and discretization of the system of interest (i.e. meshing or grid generation), (3) build the simulation

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Table 1 Summary of simulation process steps.

Step	Process	Description
1	Objective	Identify needed results – quantitative summaries – qualitative insights – comparisons.
2	Geometry and mesh	Construct CAD model and discretize into elements or cells.
3	Physical conditions	Assign materials and properties to regions, boundary conditions, sources, and other abstractions to account for physical behavior. (Can affect Step 2)
4	Solve	Select solver options, such as under-relaxation coefficients, gradient estimation methods, convergence criteria, etc., and solve. (Can affect Step 2 or 3)
5	Post-process	Review computed results, prepare contour plots, vector plots, flow pathlines, and other computed values from results.
6	Document and archive	Prepare presentation or report and store all information in appropriate database.

model by selecting physical phenomena and applying various physical data (e.g. material properties, boundary conditions), (4) choose numerical parameters to execute the calculations and effect a solution, (5) post-process the simulation results, and (6) document them and archive the modeling data. Each of these is important, and some are mutually dependent on one another.

The first step of identifying the objective cannot be overemphasized. It will drive the rest of the process and will lead to key assumptions to be applied along the way. The complexity of the model or its level of detail can very much depend on its purpose. Thus, the second step of geometrically defining the computational domain and discretizing it very much relies on the modeling objectives and requires good judgment in order to resolve the details of interest without adding human and computational effort that are not key to the objectives sought. Therefore, it is crucial to determine a good balance between model accuracy and the effort needed to reach a solution.

Generating a mesh is often the main bottleneck in the modeling process, as it is often rendered difficult by geometrical details which have a negligible effect on the results of interest. Meshing software with de-featuring options may be helpful, but good guidance at the outset of the modeling project is very valuable. This point is well illustrated in Figure 1a where are sketched two ways to represent a burner block used in a hearth (i.e. the heated canal lined with refractory material separating the melting furnace from the forming machinery). The geometry shown in Figure 1a more accurately represents the actual shape of the burner block, but it yields highly skewed and undesirable mesh cells. The low-quality mesh is the result of three surfaces, one of which is curved, intersecting at a point, which will either cause divergence of the computational algorithm or lead to spurious results. Extreme grid refinement thus is required to achieve acceptable mesh quality. An alternative that alleviates the meshing problem, without having a significant effect on computed results, is shown in Figure 1b.

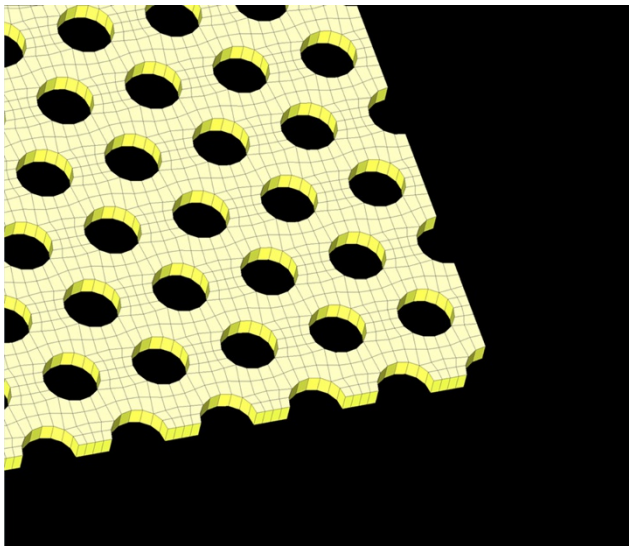
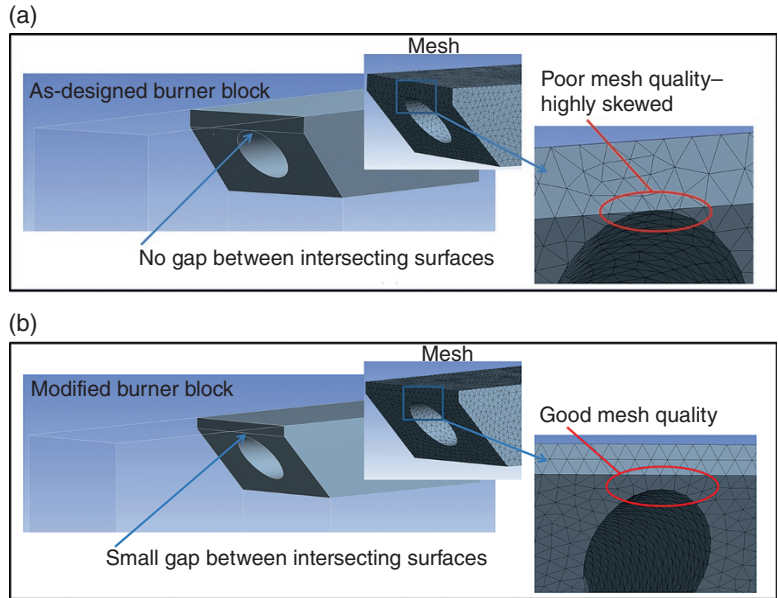
Sound engineering judgment is also needed to build the simulation model, the third step of the simulation process. Many decisions are required. For example, can symmetry be assumed? Another example is linked to the steadiness of the process and whether an assumption of steady state is justified or if transient conditions must be considered. Treating fundamental properties like viscosity (Chapter 4.1) and thermal conductivity (Chapter 4.5) as constant or temperature-dependent represents another decision that must be made by the numerical analyst. Sometimes, it is advantageous to use constant properties to establish an initial solution, followed by another solution attempt with variable properties. This strategy has been used effectively where the initial constant property solution serves as the initial estimate for the more accurate, variable property simulation. It is recommended to begin a simulation project erring on the side of simplicity, and then to add complexity in subsequent simulations.

It is also the case that the physical modeling decisions will affect the geometrical and meshing procedures. For example, a perforated plate through which a fluid flows could require extremely detailed meshing (Figure 2); or the effects of the hole pattern could be accounted for with a much less refined mesh using a more abstract method, in which the screen is characterized by a permeability which relates velocity and pressure drop. The decision on how to proceed will depend on the objectives of the study.

Post-processing (Step 5) is also very important, as it requires the analyst to execute good judgment on the results obtained. Before extracting information and insights from the results, the analyst must scrutinize the calculated field variables, as well as checking for balanced conservation laws; that is, checking for sufficient numerical convergence must be performed. Finally, management of simulation data (i.e. electronic model files) should not be overlooked since it determines the efficiency with which the simulation process is executed.

Figure 1 Examples of burner block geometry.

(a) Accurate representation with poor mesh quality;
 (b) slight modification with improved mesh quality.

**Figure 2** Example of a screen with small-scale features requiring a high mesh density to be resolved.

3 Fundamental Phenomena, Governing Equations, and Simulation Tools

3.1 Glass as a Continuum

The basic principles of engineering science are applied in CFD simulations. These involve fluid mechanics and usually various other phenomena that are typically considered to fall within the category of thermal sciences. A brief overview is provided, but for complete development, interested readers not yet familiar with the details are referred to various textbooks (e.g. [1–3]). Physical

phenomena specific to glass processes must be accounted for within the framework of three fundamental principles and will be reviewed later with respect to a few chosen examples. Readers are also directed to a volume edited by Krause and Loch [4] for a collection of excellent examples of numerical simulations applied to glass processes.

Forming the foundation on which CFD models are constructed, the fundamental principles of classical physics account for conservation of mass, momentum, and energy. Conservation of momentum follows from Newton's three laws of motion, whereas energy conservation is of course the first law of thermodynamics. Contrary to what is done for the very small systems simulated in theoretical studies (Chapters 2.8 and 2.9), it is impractical to account for the motion or energy level of each individual atom or structural entity at the scale relevant to industrial processes. Instead, it is recognized that, for length scales of engineering practicality, substances can be characterized with intensive properties (i.e. per unit volume or mass). Because it describes the mass per unit volume of a particular substance, density is a simple example of such a property that is independent of the size of the system. This abstraction allows substances to be treated as a *continuum* and allows for powerful mathematical models to be constructed.

3.2 Transport by Advection and Diffusion

Referring again to well-recognized texts [1, 2], we will remind that the principle of conservation of mass, applied to an infinitesimally small control volume (CV), is mathematically expressed as

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{V}) = 0, \quad (1)$$

where ρ is the density and $\vec{V}$ is the velocity vector. Equation (1) is often called the continuity equation. A mathematical expression of the conservation of momentum is

$$\frac{\partial (\rho \vec{V})}{\partial t} + \nabla \cdot (\rho \vec{V} \vec{V}) = \nabla \cdot (\vec{\sigma}) + \vec{B}, \quad (2)$$

whose left-hand side represents the time rate of change of momentum (i.e. mass times acceleration), and the right the forces acting upon the fluid by adjacent fluid particles (i.e. the divergence of the stress tensor, $\vec{\sigma}$) and other relevant objects through gravity or electromagnetically generated forces (i.e. a net body force per unit volume, $\vec{B}$). Forces attributable to adjacent fluid particles are collectively represented by *stress*, which is another intensive property quantifying force per unit area.

An important requirement for mathematical modeling of fluid flows is to relate internal fluid stresses to characteristics of the fluid's motion. Such a relationship, which depends on the substance, is termed a *constitutive relationship*. There are many types of material behavior, requiring different constitutive models, but the most commonly used model relates shear stresses to strain rate (i.e. velocity gradient) in a linear manner. Fluids to which this linear relationship applies are known as Newtonian fluids. For example, a shear stress component τ_{xy} for a Newtonian fluid is characterized with

$$\tau_{xy} = \mu \frac{\partial u}{\partial y}, \quad (3)$$

where μ is the dynamic viscosity and u is the x -direction component of the velocity vector. For a Newtonian fluid, viscosity is independent of the strain rate. As long as it is homogeneous, glass is a Newtonian fluid although its viscosity is a very strong function of both composition and temperature (Chapter 4.1).

When the Newtonian constitutive model is substituted into the more general momentum Eq. (2) and the fluid is assumed to be incompressible, the result is the well-known Navier–Stokes equation

$$\frac{\partial (\rho \vec{V})}{\partial t} + \nabla \cdot (\rho \vec{V} \vec{V}) = \nabla \cdot (\mu \nabla \vec{V}) - \nabla P + \vec{B}, \quad (4)$$

where P is the fluid pressure. Not all fluids behave according to Eq. (3). Such non-Newtonian fluids must be mathematically modeled with different constitutive relations substituted into Eq. (2) [5, 6].

Note that Eq. (4) is a vector equation, although it can be decomposed into vector component (scalar) equations, which is often done for the numerical application. In

Cartesian coordinates, these component (scalar) equations are the following:

$$\frac{\partial (\rho u)}{\partial t} + \nabla \cdot (\rho \vec{V} u) = \nabla \cdot (\mu \nabla u) - \frac{\partial P}{\partial x} + B_x, \quad (5)$$

$$\frac{\partial (\rho v)}{\partial t} + \nabla \cdot (\rho \vec{V} v) = \nabla \cdot (\mu \nabla v) - \frac{\partial P}{\partial y} + B_y, \quad (6)$$

$$\frac{\partial (\rho w)}{\partial t} + \nabla \cdot (\rho \vec{V} w) = \nabla \cdot (\mu \nabla w) - \frac{\partial P}{\partial z} + B_z. \quad (7)$$

In fluid mechanics problems, the unknown field variables are the three components of velocity (e.g. u , v , and w) and fluid pressure, requiring four independent equations, which are the three momentum component Eqs. (5)–(7) and the continuity Eq. (1).

The equation for energy conservation is derived in a similar fashion. A common form of the energy equation is

$$\frac{\partial (\rho C_p T)}{\partial t} + \nabla \cdot (\rho C_p \vec{V} T) = \nabla \cdot (k_t \nabla T) + S_T, \quad (8)$$

where C_p and T are the specific heat and temperature, respectively, and k_t the thermal conductivity. In Eq. (8), the transient and advective transport terms are on the left side, whereas the right side has the conduction term and all other energy transfers accounted for as “sources.” An example of a “source” is Joule dissipation; that is, electrical energy converted to thermal energy by an electrical current passing through a resistive material (with an associated drop in electric potential).

In CFD, various transport phenomena are cast in the following general form known as the advection–diffusion equation [7],

$$\frac{\partial (\rho \phi)}{\partial t} + \nabla \cdot (\rho \vec{V} \phi) = \nabla \cdot (\Gamma \nabla \phi) + S_\phi, \quad (9)$$

where ϕ represents a generic field variable related to the property of interest, and Γ a generic diffusion coefficient. For example, temperature is the relevant field variable in the energy Eq. (8). (Likewise, ρC_p is substituted for ρ in the energy equation as it represents its “thermal inertia” per unit volume.) The first member on the left side of Eq. (9) is a transient term, which can be ignored for steady-state problems. The second is the advection term, representing transport by fluid motion. The first member on the right side of Eq. (9) is the diffusion term, representing transport by atomic-scale interactions, and all others are treated as “sources,” often because the model contains mathematical expressions which do not admit to the form of the one of the three standard terms.

Several commonly used mathematical expressions for the advective–diffusive transport of various field variables

Table 2 List of commonly used transport equations in advection–diffusion form.

		ϕ	Transient	+	Advection	=	Diffusion	+	Source
A	Continuity	1	$\frac{\partial \rho}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V}\right)$	=		+	0
B	Momentum (x -direction)	u	$\frac{\partial(\rho u)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} u\right)$	=	$\nabla \cdot (\mu \nabla u)$	+	$-\frac{\partial P}{\partial x} + B_x$
	Momentum (y -direction)	v	$\frac{\partial(\rho v)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} v\right)$	=	$\nabla \cdot (\mu \nabla v)$	+	$-\frac{\partial P}{\partial y} + B_y$
	Momentum (z -direction)	w	$\frac{\partial(\rho w)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} w\right)$	=	$\nabla \cdot (\mu \nabla w)$	+	$-\frac{\partial P}{\partial z} + B_z$
C	Energy	T	$\frac{\partial(\rho C_p T)}{\partial t}$	+	$\nabla \cdot \left(\rho C_p \vec{V} T\right)$	=	$\nabla \cdot (k \nabla T)$	+	S_T
D	Turbulent kinetic energy	k	$\frac{\partial(\rho k)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} k\right)$	=	$\nabla \cdot (\mu_{t,k} \nabla k)$	+	S_k
E	Turbulence dissipation	ε	$\frac{\partial(\rho \varepsilon)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} \varepsilon\right)$	=	$\nabla \cdot (\mu_{t,\varepsilon} \nabla \varepsilon)$	+	S_ε
F	Electric charge/potential	E		+	0	=	$\nabla \cdot (k_e \nabla E)$	+	0
G	Species A	mf_A	$\frac{\partial(\rho mf_A)}{\partial t}$	+	$\nabla \cdot \left(\rho \vec{V} mf_A\right)$	=	$\nabla \cdot (D \nabla mf_A)$	+	S_A

are listed in Table 2. Some are expressions of a fundamental principle, while others are consequences of further abstraction (e.g. turbulent kinetic energy), although still derived from first principles.

In Table 2, the rows D and E show the components of turbulence quantities for turbulent kinetic energy, k , and turbulence dissipation rate, ε . Glass flows are never turbulent, thanks to the stabilizing influence of glass extreme viscosity, in contrast to flows of air, gas, oxygen, combustion fumes, and other fluids that are part of glass processes.

3.3 Turbulence

Turbulence represents an unstable flow condition that is naturally unsteady. Nevertheless, turbulent flows are commonly treated as steady because the velocity field can be well described with time-averaged values, and similarly for other field variables such as temperature. That is, for any given location, a field variable can be decomposed into a time-invariant average, plus a fluctuating component. The time and length scales associated with turbulent fluctuations are small compared with the important features of a glass process, but the effects of these fluctuating quantities are profound and must accounted for in simulation models.

There are many model formulations to account for turbulence, most having variations tuned for specific flow conditions. It is beyond the scope of this chapter to review even a few of them. The so-called k – ε model is the most

prolific, which is why its two equations are mentioned in Table 2. The source terms S_k and S_ε are related to the rate of strain of the average flow.

$$S_k = \mu_t S^2 - \rho \varepsilon \quad (10)$$

and

$$S_\varepsilon = C_{1,\varepsilon} \mu_t \frac{\varepsilon}{k} S^2 - C_{2,\varepsilon} \rho \frac{\varepsilon^2}{k}, \quad (11)$$

where $C_{1,\varepsilon}$ and $C_{2,\varepsilon}$ are model constants, and S represents the modulus of the strain rate tensor determined from the time-averaged velocity field. (The rate of strain tensor is defined as $\dot{E} = \frac{1}{2} \left[\nabla \vec{V} + (\nabla \vec{V})^T \right]$.) Sometimes, these

sources are embellished with additional terms to account for effects such as buoyancy or compressibility.

The purpose of a turbulence model is to account for transport occurring through the turbulent eddies that are not explicitly resolved in the simulation. Such transport occurs through advection as represented by the second term on the left side of the generic transport Eq. (9), averaged over time for steady-state problems. As mentioned above, these eddies are smaller than typical features of interest, but they are much larger than the molecular scale associated with diffusion through the first term on the right side of Eq. (9). The k – ε model accounts for turbulent transport by treating it as a diffusive phenomenon characterized by a “turbulent viscosity,” μ_t ,

$$\mu_t = \rho C_\mu \frac{k^2}{\varepsilon}, \quad (12)$$

where C_μ is another model constant, which adds up to the Newtonian viscosity to yield an effective viscosity, μ_{eff}

$$\mu_{\text{eff}} = \mu + \mu_t. \quad (13)$$

It is usually the case that $\mu_t \gg \mu$ and $\mu_{\text{eff}} \approx \mu_t$. Likewise, similar substitutions are made for the diffusion coefficients of other transport equations.

3.4 Radiative Heat Transfer

Heat transfer by conduction and convection is accounted for by Eq. (8) (or C in Table 2), which is also compatible with radiative heat transfer applied as a boundary condition on an opaque surface. However, glass and other media (e.g. combustion gases) are commonly semitransparent in glass processes, that is, they emit, absorb, and scatter IR radiation volumetrically.

Radiative heat transfer significantly differs from transport by advection and diffusion so that it cannot be mathematically described by an equation of the form of Eq. (9). It is instead governed by an integrodifferential equation, known as the radiative transfer equation (RTE) [3],

$$\begin{aligned} \frac{dI(\vec{r}, \vec{s})}{ds} + (\alpha + \alpha_s)I(\vec{r}, \vec{s}) &= \frac{\alpha n^2}{\pi} \sigma T^4 \\ + \frac{\alpha_s}{4\pi} \int_0^{4\pi} I(\vec{r}, \vec{s}') \Phi(\vec{s}, \vec{s}') d\Omega, \end{aligned} \quad (14)$$

where $I(\vec{r}, \vec{s})$ represents the radiation intensity at a position $\vec{r}$ and in the beam direction $\vec{s}$; α and α_s are absorption and scattering coefficients, respectively; n is the index of refraction; $\Phi(\vec{s}, \vec{s}')$ the scattering phase function quantifying the portion of incident radiation from any direction $\vec{s}'$ redirected into direction $\vec{s}$; and $d\Omega$ is a differential solid angle. The absorption coefficient and index of refraction are material properties, whereas the scattering coefficient and phase function Φ depend on physical conditions (e.g. size of soot particles), as well as on material characteristics. Note that Eq. (14) reduces to a first-order differential equation when scattering is not considered.

As for the first term on the left side of Eq. (14), it represents the change in beam intensity per unit length in beam direction $\vec{s}$, whereas the second accounts for the decrease in beam intensity caused by the combined actions of absorption and scattering. While absorption has the effect of increasing local temperature, scattering only redirects a portion of the beam without absorbing energy. Finally, on the right side of Eq. (14), the first term accounts for emission, which tends to lower local

temperatures, and the last term for scattering of IR from all directions into the beam path $\vec{s}$.

Radiation is a directional phenomenon and is in addition spectral in nature in that its intensity in principle depends on the wavelength of the IR beam. When spectral variations can be assumed to have negligible effects, Eq. (14) is written for a medium that is said to be *gray*. Extending the RTE to include spectral effects is straightforward [3], but not presented here.

Note that, Eq. (14) only accounts for IR intensity without determining directly temperatures within a material. Integrated over all directions, however, the net effects of absorption and emission are added to the source term S_T in the energy Eq. (8), thereby affecting local temperatures. There are several methods to account for the directional nature of the RTE. Referring to texts on radiation heat transfer for the details of their derivation [3], we will discuss some of them in Section 4.

3.5 Discretization Methods, Solution Algorithms, and Model Specifications

3.5.1 Finite Element and Control Volume Formulations

Several kinds of computational algorithms exist to solve for the field variable in Eq. (9). One category is known as the finite element method (FEM), where the field variable is assumed to have a functional form or shape over discrete portions of the problem domain. In finite element, the governing equations are multiplied by a weight function and then integrated over an element. The weight function can have various forms. As an example, with the Galerkin method, the weight function is the shape function itself. Another category is known as the CV method, where the problem domain is divided instead into a multitude of small volume elements, each characterized by a single, representative value for each relevant field variable. The conservation laws and fluxes are enforced on each CV, where transport or exchange across adjoining boundaries are determined with finite-difference estimates (usually, a truncated Taylor Series expansion based on unknown or estimated adjacent CV values) of the various derivatives in the governing equation. Whereas both of these numerical methods involve discretizing the problem domain into a multitude of elements or volumes that appear to be virtually the same, they are different as explained in detail in [7, 8]. Generally, more mathematics are involved with the FEM whereas the CV method, dealing with fluxes, can easily be associated with representations giving a physical significance to the problem.

3.5.2 Physical and Numerical Specifications

Once geometrical definition and meshing are done, simulation models are set up with various input

specifications (i.e. Steps 3 and 4 in Table 1). Those associated with Step 3 are physical; that is, they describe the physical characteristics of the process, which in turn affect the degree to which field variables at neighboring grid cells (or mesh nodes) influence each other. Essential are material specifications and associated properties, such as viscosity (for fluids), thermal conductivity, density, specific heat, etc. Many software products have material properties defined for commonly used materials, which must be complemented for materials of interest not dealt with in the existing material database. Various boundary conditions such as flow rates, temperatures, and other state parameters at all flow inlets are other physical specifications to be included along with wall boundaries conditions, which could be, for example, a prescribed temperature, heat flux, or temperature-dependent heat flux.

Every portion of the boundary of the simulation domain requires a boundary condition for each transport equation considered. These conditions can be in the form of a prescribed field variable (e.g. temperature T), prescribed flux by definition proportional to the gradient of the field variable (e.g. $q'' = -k_t \frac{\partial T}{\partial n}$), or a mixed condition where the flux depends on the field variable (e.g. $q'' = h(T - T_c)$). Software products generally provide default values for many of these but, for best practice, much care is recommended to review and verify each boundary condition specification with a checklist. Experience has shown that unintended specifications can be the root cause of the frustrating experience of trying to resolve inconsistencies between simulation results and measured data and/or expectations.

In Table 1, model set up specifications for Step 4 are related to the numerical methodologies employed to render a solution. Examples include so-called under-relaxation coefficients (URCs), which are used to stabilize the evolution of iterative calculation procedures required to solve nonlinear problems. These coefficients are very important since many factors cause virtually all glass-process simulations to be nonlinear.

URCs have values between 0 and 1, where 1 represents no under-relaxation and 0 does not allow the estimated field variable to change from one iteration to the next. In general, larger URC values thus allow for more rapid convergence, but divergence will occur instead if a URC is too high. Conversely, small values of URCs tend to be more robust but require many more iterations to satisfy convergence criteria. It remains a bit of an art to specify URCs, especially because optimal values can very much depend on other numerical specifications.

Additional specifications can include the manner in which advection terms are discretized, whether velocity components are solved consecutively as scalar

components or coupled to one another, along with pressure, or if energy and radiation equations are solved in a coupled or uncoupled manner. Choosing these options can depend on the capabilities of the computer used as algorithms that couple equations require larger amounts of memory.

As just noted, prescribing numerical parameters is an art so that experience is required for an analyst to become efficient and develop realistic expectations. Nevertheless, many commercial software providers offer recommended or default values to begin a simulation. Most numerical parameters will not affect the converged solution, but only the time required to obtain the solution. However, some numerical schemes will provide more accurate results for a given mesh than others although their differences should become imperceptible with sufficient grid refinement. For example, a second-order upwind differencing scheme for advection terms will produce less “false diffusion” than a first-order upwind scheme [7].

4 Simulations in Glass Manufacturing Processes: A Few Examples

4.1 Fundamental Studies

As already stated, the importance of a particular phenomenon can be explored by numerical simulations in such a way that the mathematical treatment and/or its numerical implementation can be examined to assess the best way to account for the physical effects of interest. A good example of this approach was the early one-dimensional study of Glicksman [9] of various physical effects on fiber formation. He formulated his model by manipulating the conservation equations (A)–(C) in Table 2, where glass velocity, filament diameter, and temperature were assumed to vary only in the axial direction of the fiber draw. This relatively simple model was very helpful in understanding the relative roles of glass viscosity and surface tension on fiber-forming dynamics, as well as the influences of radiative and convective cooling.

As computational resources grew, more sophisticated models were developed to explore further fiber-forming dynamics from 2-D axisymmetric models with free surface boundary conditions [10, 11]. Both steady-state and transient simulations were performed and revealed the onset of unstable forming conditions, which could lead to poor product quality and/or reduced process efficiency. A view of the deformed finite element mesh, representing fiber attenuation as it is drawn, is shown in Figure 3, whereas the excellent agreement found between numerical and experimental results of the fiber attenuation (Figure 4) illustrated the reliability of the method.

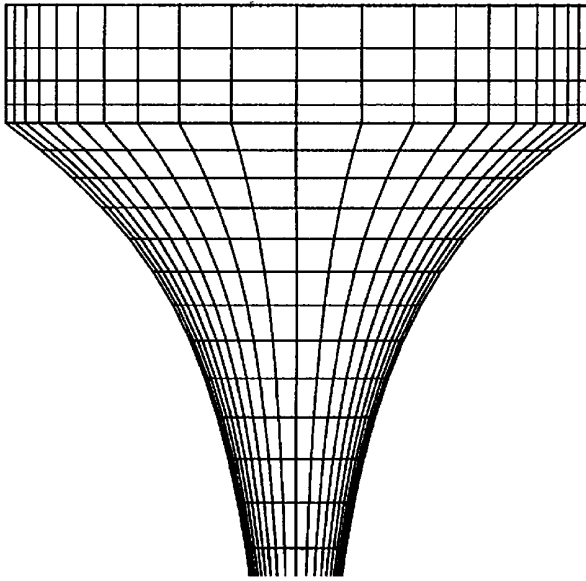


Figure 3 Deformed finite element mesh during a simulation of the drawing of a glass fiber. Source: *International Congress on Glass* [10].

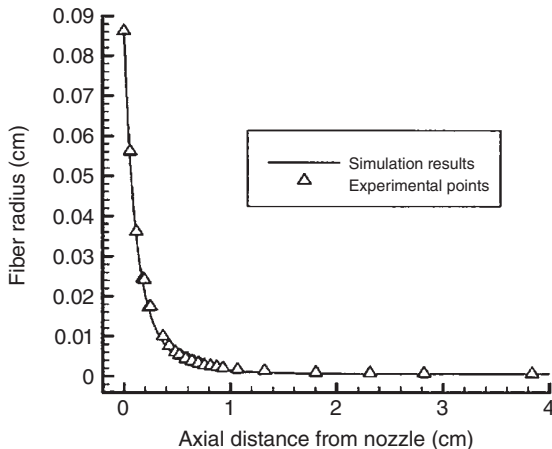


Figure 4 Fiber radius attenuation: comparison of numerical and experimental results for an extension ratio of 19 000. Source: *International Congress on Glass* [10].

Another study examined the manner in which radiation within a semitransparent glass is considered [12, 13]. It was performed in the context of a simplified glass furnace geometry. Because radiative energy is both absorbed and emitted volumetrically, this study examined two methods for accounting the radiative transport with equations (A)–(C) in Table 2. One method is the computationally convenient Rosseland approximation [3], in which one accounts for radiative transport by appropriately adjusting the thermal conductivity of glass; the other employs

the discrete ordinates method (DOM) [3] to solve independently the radiative-transport Eq. (14), the results of which are then coupled to the energy Eq. (8) through source terms. The DOM requires significantly more computational effort and, thus, longer run times. For large models with millions of mesh cells/elements, the difference in run times can be significantly important. For many problems in glass processing, the Rosseland approximation will yield sufficiently accurate results but some situations require a more detailed accounting of the radiative transport. For example, if the refractory-wall temperatures are of interest to assess wear rates, then a DOM might be a better choice. Also, in forming operations, length scales associated with the forming apparatus may be significantly smaller than those for which the Rosseland approximation is valid. A modeling simulation aimed at assessing such fundamental matters is sometimes an appropriate ancillary simulation to perform. Both methods were investigated and compared in [12].

4.2 Glass Melting Furnace

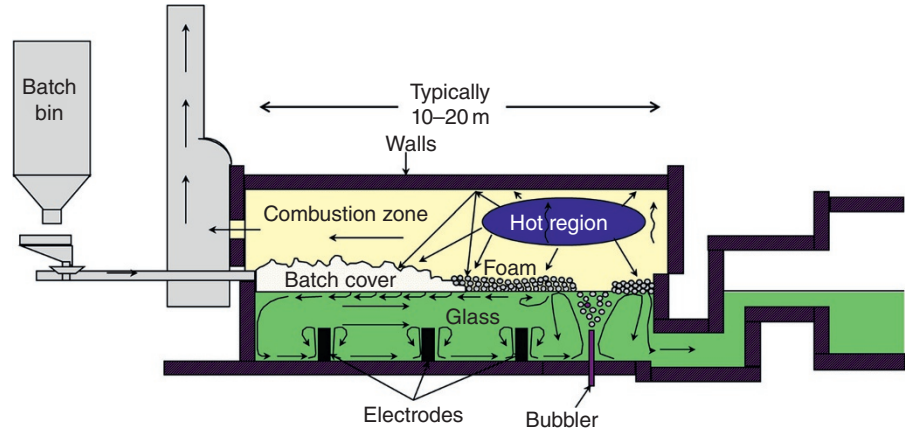
4.2.1 Models

Relatively small simulation models provide a means to understand the behavior of an isolated part or function of a glass process, or to assess numerical treatments. However, many problems require the mutual interactions of several parts or processes to be considered simultaneously. A good example is a glass melting furnace, in which there exist several flow regimes, multimode heat transfer, physical and chemical reactions, and other related phenomena.

Modeling a glass melting tank provides a means to estimate the effects of many things contemplated by a glass maker. Simulations made with a properly constructed model can, for instance, assist in prescribing or changing the profiles of combustion burners, E-boost power zones, or bubbler flow rates. Changes in pull rate, insulation thickness or type, added wind cooling to outside walls, and surface treatments to alter emissivity of crown materials are just a few other examples of what can be considered with a furnace model.

The effects of various changes can be measured in different ways, too. The overall rate of energy consumption is often a key performance index (KPI). Other KPIs relate to the glass quality. For example, the distribution of residence times for material passing through the melting furnace is important to its operators because, with the shortest times, the material is least likely to have been fully conditioned and, thus, is most likely to have some sort of imperfection such as seeds or cords (Chapter 1.2). Other effects of interest include the maximum temperatures of various refractories, the shear stresses and other

Figure 5 Sketch of a glass melting furnace for the production of reinforcement fiber glass.



conditions contributing to wear, the position of the batch line, and the strength of the backflow of glass against the batch layer.

4.2.2 Interacting Zones

Within a complete furnace model (Figure 5), the common zones included are the glass melt, a batch cover and a foam layer both floating on the top surface of the glass, the hot combustion zone above the glass/batch/foam surface, and the wall zones enclosing the glass and combustion zones. Most of these zones are coupled to each other through exchange of mass, momentum, and energy. The governing equations, boundary conditions, and sources applied to each zone depend on the physical phenomena which occur within each of them, as well as the manner in which they are coupled to the others.

Glass flow in the melter is laminar so that Eqs. (1) and (5–7) apply. To account for the exponential dependence of viscosity upon temperature in a manner, the empirical Fulcher law is often used,

$$\mu = 10^{F_1 + \frac{F_2}{(T + F_3)}}, \quad (15)$$

where F_1 , F_2 , and F_3 depend on the specific glass composition (Chapter 4.1).

Glass flow is forced to a certain extent by the introduction and melting of batch as well as by draining through the throat of the furnace. However, additional forces significantly affect flow patterns. Density changes caused by temperature variations give rise to buoyancy forces, which significantly affect flow patterns in the glass melt. These are accounted for through a body force, which is the last term on the right side of each momentum Eqs. (5)–(7). It is convenient and typical for one of the coordinate directions (e.g. the z -direction) to be aligned with the direction of gravity (or at least opposite to it), so that the body force in its respective momentum equation is represented as

$$B_i = \rho(T)g_i, \quad (16)$$

where $\rho(T)$ is the local density evaluated at the local temperature and g_i represents gravitational acceleration in coordinate direction i (e.g. $g_z = -9.806 \text{ m/s}^2$).

Although the glass is heated from above, which usually results in a stable, vertical temperature gradient, freshly melted material from the batch blanket is relatively cool and dense so that it provides a significant driving force for recirculation in the melt. These buoyancy-driven recirculation velocities can be an order of magnitude larger than those resulting from the forward flow of glass associated with the melter pull. Furthermore, lateral temperature gradients along sidewalls and electrodes provide additional density variations that alter the flow structure. Accounting for flow-inducing density variations thus is essential in the glass melt.

Bubblers also induce significant recirculation of glass caused by forced convection. Buoyancy forces acting on the bubbles cause them to rise, and in doing so, they drag glass upward along with them (Chapter 1.3). With sufficient multiphase modeling techniques, it is possible to track explicitly the flow of both glass and bubbles, but one commonly treats the effects of the glass bubbles more abstractly by applying a momentum source to the appropriate component of the momentum equation in the columnar region associated with each bubbler. That is, the source term will be augmented by a calculated force per unit volume based upon either Stokes' law or a modified version of it [14].

Another means of affecting glass flow is with mechanical stirrers. These can be accounted for in several ways including appropriately scaled volumetric-source terms or through basic boundary conditions where the motion of a wetted wall is prescribed.

Other walls, such as the sidewalls, floor, and electrode surfaces, are simply treated as nonslip boundaries where the fluid velocity is zero. Along the top surface, the glass interacts with the batch, foam and possibly the

combustion fumes. Because of extreme density differences, the influences of foam and combustion fumes on the glass velocities are often assumed to be negligible. The interface between the batch and glass, however, represents a greater challenge, because the momentum exchange between these two zones is not considered negligible, and the interface itself can be difficult to define precisely. Moreover, the batch–glass interface is where freshly melted glass enters the glass domain from the batch layer. Commercial codes treat this interface in different ways. Because it is beyond our scope to cover the details, we will just note that this topic is an area of needed, ongoing development.

Equation (8) governs some of the energy transport in the glass and is the basis for which temperature distributions are determined. Sometimes an enthalpy formulation is used in place of Eq. (8) to couple intrinsically the batch and glass zones with a single equation governing energy transport, in which case temperatures are determined from enthalpy through an appropriate thermodynamic equation of state. Energy is also transported into and through the glass by electrical dissipation and thermal radiation. Joule dissipation is determined from the solution of equation (F) in Table 2. The rate of conversion of electrical energy to thermal energy is represented by the following:

$$E_J''' = \nabla E \cdot \vec{J} = k_e \nabla E^2, \quad (17)$$

where ∇E is the gradient in electric potential, $\vec{J}$ is the current flux density, and k_e is the temperature-dependent electrical conductivity of glass. The Joule dissipation calculated in this way is included in the source term, S_T , in the energy Eq. (8).

Thermal radiation is usually accounted for with the aforementioned Rosseland approximation. But a more detailed accounting of thermal radiation transport is possible with methods such as discrete ordinates, which can, for example, be used to resolve spectral characteristics. Other means are available [3].

The combustion zone above the glass is modeled with the same basic governing equations for momentum and energy conservation, but their application is different for a variety of reasons. Furthermore, transport equations for individual species and thermodynamic state relationships must be applied to account for the reaction of fuel and oxidizer and the creation of products of combustion.

Since the combustion zone is turbulent, all diffusion coefficients are replaced with effective values that account for diffusive-like transport. Hence, it is common to include the k and ϵ equations (D and E in Table 2), from which μ_t is determined. Another difference involves radiation for which the assumption of optically thick media required by the Rosseland approximation is not valid.

Use of discrete ordinates in combustion zones is common. The absorption coefficients required of the DOM depend on species concentrations, especially CO_2 and H_2O , which must be determined from a combustion model that accounts for chemical reactions (i.e. the creation and destruction of molecular species) and the transport of the related species.

Through radiative and convective transport, the combustion gases heat virtually all surfaces, including the walls of the superstructure, the top of the batch layer, the foam, and the glass. Furthermore, these surfaces exchange heat through radiation, which is intrinsically included with a discrete ordinates model. Owing to nonlinearities and to the strong coupling between the various zones and between the various transport equations within a zone, a robust, iterative solver is required to converge on a solution. Typically, iterations are performed until conservation laws are satisfied to within 0.1%, whereas adjustments to URCs are sometimes required to improve convergence.

A model of a glass melting furnace must account for transport not only in the glass and combustion zones, but also within the batch, foam, and walls. Whereas all of these zones must obey the same basic laws of physics, their dissimilar material characteristics require different mathematical treatments. Perhaps the easiest to consider are the walls and other solid objects. The energy Eq. (C) (in Table 2) is applied without the advection term since velocities in the walls are zero. Equation (F) is in addition applied to account for electrical current and Joule heating with the assumption that the electric potential is uniform within an electrode, since its electrical conductivity is orders of magnitude larger than that of any other material.

The batch and foam require additional considerations. Considering first the foam, there are many questions to ask. Where does it exist? How thick is it? Does it absorb radiation from the combustion zone and crown, or does it transmit such radiation? What is the gaseous species within the liquid glass membrane? How large are the foam cells? All of these and other factors will affect transport so that choosing a modeling method presents a significant challenge.

One way to deal with foam is to invoke several simplifying assumptions allowing adjustments based on foam conditions, without requiring detailed information regarding its phenomenological behavior. For example, foam can be treated as a layer of material that acts to impede heat transfer between combustion and glass zones, but ignores advection transport within it. A relatively small number of parameters can be used to characterize the thermal behavior of the foam, which can be adjusted, within reason, to render a well-tuned model.

A similar set of questions arises when considering the batch. Whereas the foam is a two-phase mixture of liquid membranes enclosing gas cells, the batch is a multiphase mixture of solid particles, with interstitial gas and liquid, whose proportions depend on temperature. Unlike in the foam, advective energy transport within the batch zone cannot be ignored without large compromises such that, therefore, the velocity field within the batch layer must be computed. A common way to accomplish it is to treat the batch as a pseudo-fluid with a characteristic viscosity that depends on temperature. The batch is assumed to float on top of the glass and to provide an inflow of melt whenever the temperature at its interface with the glass achieves or exceeds a specified temperature where melting occurs. In this way, the batch zone is treated as another fluid zone governed by equations similar to those of the glass. In addition to providing an inlet flow of melt to the glass zone, the batch zone also produces a small amount of gases into the combustion zone because of the chemical reactions that occur upon melting.

The model described in the preceding paragraphs is an example of a powerful tool constructed from well-defined assumptions and mathematical abstractions. It is summarized in Table 3, which indicates for each zone of the furnace the governing equations and interactions with other zones. The required boundary conditions and other physical parameters needed to specify the operating conditions are summarized in Table 4 where a “coupled” condition indicates an internal boundary condition between two zones where the field variable and associated flux are forced to be the same. In addition, many numerical parameters must be specified in such a way as to bring about a converged solution that satisfies the various conservation principles. Modeling procedures and material properties for glass are discussed in greater detail elsewhere [15].

4.2.3 Post-processing Assessments

One gains additional insights by displaying the computed field variables in a graphical form. A common illustration is a temperature-contour plot, sometimes with flow streaks superimposed. A 3-D rendering of a glass melting furnace (Figure 6.), for instance, clearly shows the batch layer that melts at the glass surface and the flame developing from the rear wall, the extent of these zones being important operational characteristics. An alternative to horizontal flames is presented in Figure 7, where the pair of flames from oxy-fuel burners yield the temperature contours and flow streaks shown for a cross-section of the combustion zone. The fuel and oxidizer react as they flow downward from their nozzles mounted in the furnace crown, and the resulting flame directly impinges on the batch and promotes improved melting efficiency. Similar plots can be drawn on different sections or in different orientations within combustion or glass zones. Furthermore, contour plots of electric potential, Joule dissipation, oxygen concentration, or other field variables can be made directly from the computed solution to provide important insights, especially when comparisons are made between plots drawn for differing possible operating conditions.

Other important information can be gleaned from a converged simulation. For example, quantified values of the energy transfers between the zones illustrated in Figure 5 can be extracted from the simulation results. Examining and comparing these values is very insightful, as it can draw the attention to various things such as how the batch is melted and the sources of inefficiency.

Other quantifiable data that can be directly extracted from a model solution include operating currents and potentials of electrodes, average glass temperature, total volume of batch layer, and temperatures at prescribed

Table 3 Interacting zones of a complete glass melting-furnace model.

Zone	Equations (Table 2)	Radiation treatment	Zone couplings				
			Glass	Batch	Foam	Walls	Combustion
Glass	A,B,C,F	Rosseland					
Batch	A,B,C,F	Surface emissivity	Mass, momentum, energy, electric current				
Foam	C	Surface emissivity and transparency	Energy	Energy			
Walls	C,F	Surface emissivity	Energy, electric current	Energy, electric current	Energy		
Combustion	A,B,C,D,E,G	DOM	Energy	Mass, energy	Energy	Energy	
			Glass	Batch	Foam	Walls	Combustion