# 10.11. A History of glass science

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## Abstract

In terms of both products and processes, glassmaking has been a highly successful but purely empirical activity for more than three millennia. Natural philosophers did pay attention to glass in Antiquity, but their emphasis on its kinship with metals did not lead to any better fundamental understanding of its properties. Likewise, alchemy did not result in any advance  despite the dual importance it attached to glass as a material and as an illustration of the deep transformations of matter that man could effect. In the 17th century, it was at the time of the Scientific Revolution that new concepts appeared. When van Helmont experimented with glass dissolution, Descartes gave the first description of vitrification at a microscopic scale while the possibility of achieving outstanding mechanical properties was announced by Prince Rupert's drops. From the late 18th century, the chemical revolution then lead to the modern notion of chemical composition and to the discovery of the elements that make up glass (silicon, alkali and alkaline earth elements, etc.). Studies of glass crystallization and crystal melting gave a clearer picture of the mutual relationships of the two kinds of phases and, in particular, demonstrated the kinetic nature of the vitrification process. Following the discovery of a great many new elements, investigations were made from the mid 19th century to determine their glass-forming abilities and their effects on physical properties of practical interest. Particularly noteworthy outcomes of this work were the considerable diversification of optical glasses and the invention of the commercially important borosilicates. Systematic investigations of physical properties then began to be made as a function of composition and temperature. Whereas phase diagrams gave a sounder basis to glassmaking, tempered glass and Griffith's theory of rupture were important mechanical achievements. Surprisingly, however, the specificity of glass as a material was not understood until the 1920s when the existence of a glass transition was at last recognized through calorimetric measurements. The issues of relaxation and viscoelasticity were then raised, benefitting much from the theoretical framework set earlier for mechanical systems displaying delayed responses. In the

**meantime, the random network model of glass structure had been formulated and the new technique of X-ray diffraction had been used for the first structural determinations, quickly followed by Raman spectroscopy. Glasses are now made in a variety of chemical systems and by other methods than melt quenching. Some of them are unstable at high temperatures before undergoing a glass transition. Although these features make a general statement difficult, one can define glass as a macroscopically homogeneous amorphous solid whose properties (physical, chemical, or structural) vary with its preparation conditions.**

## 1. Introduction

What is glass? And what is peculiar to this form of matter to justify the existence of a specific Glass science? In a glass history that began about three millennia and a half ago, both questions have been making sense only in the last century. Whether glass would have been defined in terms of structure or of properties, experimental and theoretical means were of course lacking to arrive earlier at anything resembling modern standpoints. As a material, however, glass did not escape reflections from savants throughout the ages even though its making was remaining an empirical practice. The present contribution will try to make it clear for the five broad, overlapping periods that have been distinguished with the part of arbitrariness and lack of comprehensiveness inherent to short historical accounts. It will thus complement to the chapters devoted to early technology (Ch. 10.9) and to the scientific advances made possible by glass (Ch. 10.10).

Beginning in Antiquity, the first period lasted until the Middle Ages. The most obvious features of glass were its transparency or its vivid colors, which made it akin to gems, and its production from a melt, like that of metals. From the Near East to the Latin West, this dual kinship with precious stones and metals thus remained of particular concern during about two millennia. In the early modern period, glass became the subject of a different kind of rational enquiry. Experiments were made to understand some fundamental properties of matter at a time when the dramatic advances in the exploration of the universe made possible by glass lenses (Ch. 10.10) led to the first speculations on the microscopic constitution of glass-forming liquids.

From the late 18th century, a few decades then heralded the entry into a scientific age in the modern sense of the term. This change was felt by the glassmakers of the period as illustrated in 1791 by the Essay on the Art of Glassmaking where the chemist Pierre Loysel (1751-1813) stated that

> "Glassmaking is, among all the arts, the one that can be rigorously submitted to the principles determined by physics, the one that, therefore, can reach the greatest precision, but it requested an observer who would be as familiar with all its processes as

instructed in physics" [1].

In fact, it was not so much physics than chemistry that was about to influence glassmaking most as exemplified in 1810 by the Attempt to Establish the Art of Glassmaking on Scientific Principles authored by Aldolph Ferdinand Gehlen (1775-1815) who explained how Glauber's salt [sodium sulfate] could be used as a new source of soda [2,3]. Until then a glass could be basically characterized only by its density and index of refraction. Hence, the great novelty was the concept of chemical composition that resulted itself from the notion of oxides, which replaced that of earths, and the discovery of the relevant chemical elements. In parallel, a new attention was paid to the relationship of glasses with crystals, which made kinetics entering the picture of both glass formation and crystallization.

Following the first systematic measurements of physical properties, a specific glass science was finally born in the 1920s when consistent evidence pointed to the existence of a glass transition and experimental means became available to study disordered atomic structures. Since then, glass science has grown tremendously as is obvious to any reader of the Encyclopedia and summarized in an extensive bibliographic study [4]. Hence, this fifth and last period will not extend beyond the mid 20th century to avoid unnecessary overlap with other chapters. Owing to an apparent lack of any in-depth historical study of Glass science in the literature, this chapter will nonetheless be longer than others and its bibliography more detailed, as it must be in any such account. In preamble, however, it may be useful to review briefly how the definition of glass has evolved in response to the advances made in the understanding of this material, which is now termed structural glass to distinguish it from the newer spin, orientational or vortex glasses.

## 2. Glass: an impossible definition?

Traditionally glass was defined by the manner in which it was made. It "is a more or less transparent material, coloured or colourless, shiny, fragile, smooth in its fracture, & which is produced by the fusion of vitrifiable stones or earths from saline, alkaline & metallic lime substances" [5], asserted in 1774 Antoine Baumé (1728-1808), best known for his work on thermometer intercalibration and the invention of the areometer for measuring the densities of liquids. Half a century later, the chemist Louis Jacques Thénard (1777-1857) stated more simply in an influential treatise that "Glass is a product one obtains by exposing a mixture of silica and different substances, most of the time very fusible, to the action of a violent and sufficiently continuous fire" [6].

These definitions could have already been given in Antiquity. Perhaps the most detailed one was that of Theophrastus (~371 - 287), Aristotle's friend and successor as head of his school, the Lyceum. After having noted in his treatise devoted to stones that

"earth indeed may undergo processes of melting, softening and hardening again", Theophrastus added: "if, as some maintain, glass is made from vitreous earth, so too it is firing that causes this earth to become glass" [7]. As made by Jean-Baptiste Dumas (1800-1884) for sugar, sulfur and arsenic oxide, however, other kinds of substances were already regarded in the 19th century as vitreous not from their chemical composition and mode of synthesis, but from their luster, translucency, shapability or conchoidal fracture [8]. But chemistry was playing other tricks. From silica, silicon was first prepared in the form of a brownish powder by Thénard himself and Joseph Louis Gay-Lussac (1778-1850) through reaction of siliceous hydrofluoric acid [silicon tetrafluoride] on potassium [9]. But the two friends did not realize that they had isolated a new element and still less that it was in an amorphous state.

Considering such a new substance as vitreous would have thus led to abandon any convenient macroscopic criteria to characterize a glass. Selenium, which was discovered in 1818 by Jacob Berzelius (1779-1848) [10], was especially interesting in this respect because it existed as both an amorphous powder and a vitreous form, which were rapidly shown to be identical [11]. In addition, selenium had the original property observed in 1851 by Johann Wilhelm Hittorf (1824-1914) to "melt" without any heat effect [12], and was found in 1871 to be highly refractive and dispersive with an index of refraction varying from 2.65

to 2.98 [13], which illustrated considerable differences in physical properties with the traditional silicate glasses.

Alternatively, the need of annealing might have looked typical of glass. As explained by Baumé,

"When the glass cools quickly, the two inner and outer surfaces of the pieces first take on all their strength, and then retreat: but the middle of its thickness is still red and soft; it is in a state of compression; it forms a spring that remains in a state of tension, and is always ready to break the obstacle that hampers it; this is what happens to all glass vessels that are a little thick, and have been badly annealed" [5].

Regardless of this particular interpretation, an "annealing" criterion to define glass would have been irrelevant anyway to amorphous substances not prepared in large pieces whereas the need of slow cooling was not unique to glass. It was also required for many ceramics as a result of the volume change at the ⟩ transition of quartz, which would be discovered only at the end of the 19th century by Henry Le Chatelier (1850-1936).

In a closely related modern variant, glass has been defined as a substance whose second-order thermodynamic properties [heat capacity, thermal expansion coefficient, compressibility] vary abruptly in a narrow temperature interval upon heating. But this criterion is not generally valid since solid phases akin to glasses produced vapor deposition (Ch. 3.14), pres-

sure-induced amorphization of crystals (Ch. 3.10), or sol-gel reactions between starting organic liquids (Ch. 8.2) may crystallize or decompose before undergoing a glass transition. As a matter of fact, even some silicate glasses quenchable at not extreme rates (e.g., $Na_2SiO_3$) crystallize rapidly hundreds of degrees below their estimated glass transition ranges. Alternatively, glass has been defined in terms of structural disorder at the atomic scale, which is making sense in view of the tight connection between this disorder and typical macroscopic features of glass such as unlimited shapability, lack of grain boundaries, mechanical strength or extent of solid solutions. From a purely material standpoint, glass thus is commonly said to be a substance deprived of the long-range order of crystals. Because a good definition must be positive and not negative, however, one is then faced with the problem of stating the kind of order existing in glasses, which is known to lack a universal solution.

There nonetheless seems a possibility to conclude this discussion positively. Glasses are solids, i.e., substances whose atoms occupy essentially fixed positions. At any scale, they are a-morphous in the original sense of the term, which means that they are deprived of any characteristic shape. Compared with crystalline solids, they have in addition an original feature first reported for a variety of silicate glasses in 1845 by Eugène Chevandier (1810-1878) and Guillaume Wertheim (1815-1861), in the case of density

and elasticity, which is that their properties differ depending on whether they are quenched or annealed [14,15]. It is thus tempting to define very simply a glass as a macroscopically homogeneous amorphous solid whose properties (physical, chemical, or structural) vary with its preparation conditions.

## 3. The origins

### 3.1. The Middle-Eastern beginnings

Genuine glass pieces appear in the archeological record in the 16th century BC, i.e., in the Late Bronze age (Ch. 10.2). Regardless of the place (s) where bulk glass was initially made and the sequence of events that led to its production, it is obvious that ancient craftsmen were good observers otherwise ceramics, metallurgy and glassmaking would not have developed as they did over the centuries. Either in a fortuitous way or by trial and error, much experimentation took place to identify the raw materials with which definite goals would be achieved.

Siliceous sand and plant ashes were easily recognizable sources for glassmaking but how trona [$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$], the mineral improperly called natron [actually $Na_2CO_3 \cdot 10H_2O$], came to be used and was mined is not known [16]. In glasses, its earliest chemical signatures date back to the beginning of the first millennia BC [17]. Natron had already long been used for glazes, however, and from Sumerian times it also served a great many purposes in the urban settings of Mesopotamia, as condiment, soap or

product for the embalming of mummies [18], so that a fortuitous reaction with sand in the way described by 19 (Ch. 10.0) might have been possible.

The selection of the all-important coloring agents was more tricky because of the differing hues of the raw materials and finished products. The mastery achieved in this respect is nonetheless revealed by the variety of colors yielded by metals such as copper [red and blue-red], iron [black, brown and green], antimony [yellow], cobalt [blue] or tin [white] ([20], Ch. 10.2, 10.3)]. As for instance noted by Theophrastus, "A most peculiar earth is that which is mixed with copper, for it not merely melts and mingles with the metal, but also has the remarkable power of enhancing the beauty of its colour" [7]. By observing that small changes in raw materials could result in marked color differences, ancient glassmakers unknowingly discovered how a given property of a material could be varied almost at will in a continuous solid solution. In this way, Mesopotamian glassmakers replicated obsidians, which were thus distinguished depending on whether they were "genuine" or "from the kiln" [20]. In addition, they produced synthetic basalt by firing local silt without apparently recognizing its kinship with the real rock, which was extensively brought from the Zagros and High-Mesopotamia mountains to make steles and statues in Assyria and Babylonia [21].

Because the first glassmakers were by definition entering an uncharted territory, the uses they found for the new material developed along with their understanding of its properties and, especially, of its shapability, which distinguished it clearly from metals and ceramics (Ch. 10.5). It was a well-established Mesopotamian tradition to keep written records of all activities so that the technical nature of some tablets was not particularly remarkable in itself. The fundamental importance of what we term viscosity was thus recorded in cuneiform tablets from the 14th or 12th century B.C. from Nineveh, found in the library of the Assyrian King Ashurbanipal (r. 668-~628), advising the glassmaker to observe how droplets of glass were sticking to the tip of the rake used to stir the melt.

Mesopotamian glassmakers were thus familiar with stirring [to achieve chemical homogeneity] as well as with grinding and sintering, a process already long familiar to ceramists. They were aware of the deleterious effects of fumes [through vapor-melt interactions] and thus kept recommending "You keep a good and smokeless fire burning". They used bellows to achieve sufficiently high temperatures and also knew that the color obtained [through redox reactions] depended on whether their pots were covered or not and the door of their kilns open or closed.

Glassmakers also mastered quenching procedures by dipping or immersing glass pots in water, and annealed their pieces to prevent them from breaking spontaneously on cooling.

As would still be exemplified by the venturina pro-

duction in 17th-century Venice (Ch. 10.7), glassmaking operations were nonetheless tricky and not necessarily reproducible. To ensure success through the protection of gods, specific rites were practiced as documented by 7th-century B.C. tablets in which procedures for building kilns are reported. The craftsman was for instance instructed:

"When you set up the foundation of a kiln to [make] glass, you [first] search in a favorable month for a propitious day, and [then only] you set up the foundation of the kiln. As soon as you have completely finished […] no outsider or stranger should [thereafter] enter [the building], an unclean person must not [even] pass in front of [ritual Kùbu-images]. You regularly perform libations offerings before them. On the day when you plan to make the metal in the kiln, you make a sheep sacrifice before the Kùbu-images, you place juniper incense on the censer and [then only] you make a fire in the hearth of the kiln and place the metal in the kiln" [20].

### 3.2. The Graeco-Roman world

The use of the term metal to designate glass in Assyrian tablets was not accidental. Not only had glassmakers shared many things with metallurgists in their transformations of earthy materials, but fusibility was another reason for considering glass akin to metals, and not to rocks, which could not be melted at the highest temperatures reached in furnaces. Galen (129-~216), the most famous physician of Antiquity, defended himself the analogy between glass, gold, silver and even iron. [22] As a matter of fact, the Greek and Latin terms metallon and metallum did not refer to any property of the substances but to a common origin in the ground from where they were extracted [23]: in this respect, sand was for glass the analog of ores for the other metals. In this way glass became part of the grand correspondences established in the Graeco-Roman world between the seven mobile celestial bodies (the two luminaries and the five known planets) and the seven metals more or less well identified at that time: the Sun was of course associated with gold, the Moon with silver but sometimes with glass, Mars with iron, Venus with tin or copper, and Saturn, Mercury and Jupiter with copper, tin, electrum [natural Ag-Au alloys] or with glass [23].

In Egypt, their close association with the imitation of precious stones led the glassmakers to be called makers of lapis lazuli. It was also in Egypt that glass began its long and tight association with alchemy (Ch. 10.4, [24]). The dramatic transformations clearly undergone by the raw materials in glassmaking raised the issue of the kinship between man-made and natural materials and sustained the idea that man could even go farther than nature in his own operations (Ch. 10.4).

Such reflections on glasses considered as molten gems were pursued in Greece where elementary cons-

tituents or qualities were invoked to account for vitrification (Ch. 10.4). But little was said or claimed about real physical properties. When discussing liquids in On Generation and Corruption, Aristotle (384-322) emphasized that their "readily adaptable" shape conferred by their "small particles" made their mutual combinations easy, but mentioned "viscous liquids" only to state that they "produce no effect except to increase the bulk", without alluding to any glass-forming ability [25]. Likewise, Aristotle did not mention at all glass when he adumbrated the notion of viscoelasticity in his Meteorology:

"A thing is viscous when, being moist or soft, it is tractile. Bodies owe this property to the interlocking of their parts when they are composed like chains, for then they can be drawn out to a great length and contracted again" [26].

The viscous liquids cited by Aristotle were "pitch and birdlime", not glass, perhaps because of a more fundamental kinship with metals that was briefly evoked by the statement that "Gold, then, and silver and copper and noted tin and lead and glass and many nameless stone are of water: for they are all melted by heat" [26].

A similar theoretical framework was at the basis of Theophrastus' reflections in his short treatise On Stones. To account for the formation of slags (Ch. 7.4) during smelting operations, Theophrastus thus stated that

"When silver and copper and iron become fluid, the stone from them becomes fluid at the same time, possibly owing to the moist character of its constituents or possibly indeed trough the agency of the metals."

Theophrastus also paid attention to actual glassmaking. Because the kinship of obsidian and man-made glasses was early recognized, of special interest are his remarks about melting experiments made on the well-known obsidian from Lipari island (Southern Italy): "The Lipara stone, which before burning is black, smooth and dense, is not only rendered porous by combustion, but also assumes the appearance of pumice, so that its colour changes along with its density". Hence, it was obvious that obsidian could not be used in glassmaking. As we now know, the water always present at a few tenths of wt % in obsidian exsolves as bubbles upon heating when the viscosity becomes lower than about $10^9$ Pa.s (i.e., at temperatures of the order of 800°C) so that, as described by Theophrastus, one obtains a pumice that either quickly devitrifies or is much too viscous anyway to lend itself to any glass-forming operation. Regarding the fundamental invention of glass blowing made right before the beginning of the Christian era (Ch. 10.3, 10.5), it will suffice here to recall that the process required a strict control of viscosity during the alternating periods of working and reheating before the final annealing. As for the production of transparent glass that became extensive at the same period, it was relying on the addition of substances

now called antimony oxide [$Sb_2O_3$] and especially manganese oxide [pyrolusite, MnO], the famous glassmaker's soap (Ch. 6.2), which had perhaps been an outcome of the making of black glass in Egypt in the 5th century BC [27]. Thermal shock was another physical process put to use to cut a piece at the desired place and also for severing it from the blowpipe. The dramatic impact of such advances in glassmaking and the practical advantages of glass over metals could have given some credit to the famous legend of malleable glass, shapable with a hammer, told by the Latin writer Petronius (1st c. AD) in the Satyricon: when the emperor was told that no one else than its inventor knew how it was made, he ordered him to be beheaded "because if this invention were generally known we should treat gold like dirt" [28]. If the story has some truth in it, then it might have had as a starting point a parison falling on the ground while being blown and at once recovered by the blower to finish the work [27]. But the fact that Pliny ([19], cf. Ch. 10.0) himself did not take the story seriously has not prevented it from enjoying great success throughout the ages.

### 3.3. The western medieval literature

In the West, relatively little is known about glassmaking activities after the fall of the Roman Empire. One rare source is the Etymologies written in Visigothic Spain by the bishop saint Isidore of Seville (~560-636). Noting that obsidian "is counted as a type of glass. Sometimes it is green and sometimes black, and it is translucent", Isidore reported that "the highest esteem is granted to clear glass with its close similarity to crystal", which "used to be made in Italy". As he explained further,

> "Throughout Gaul and Spain the softest white sand would be ground with a mortar and pestle, and then mixed with three parts, by weight or measure, of natron, and after being melted it would be poured into another furnace. This lump would be called ammonitrum. When heated again, it would become pure, clear glass" [29].

This statement was almost a word by word copy of Pliny's Natural History (XXXVI, LXVI, cf. Ch. 10.0) so that its actual significance for Isidore's times is unclear. In the Near East, however, it is known that natron production became insufficient in the 7th to 9th centuries possibly from a combination of too high a demand, unfavorable climatic conditions and political turmoil [17] so that vegetable soda derived from plant ashes had to be used instead as a flux.

Dating back to the 8th-10th centuries, some compilations have transmitted recipes dealing with pigments, inks, varnishes, glues, stones, metals, glasses, etc. The best know are the Compositiones variae [30.], the De Coloribus et artibus romanorum transmitted under the name of the 7th century Byzantine emperor Heraclius (spelled Eraclius [31]) and especially the Mappae clavicula [32] whose content and meaningless Latin title today indicate that it originated in Greek

alchemical manuscripts from the 4th century [33]. Probably this ancient literature found its way to the West through Latin translations made in Italy in the late 8th century. What is clear is that copyists then kept modifying these compilations by additions and deletions of their own and that quite a few recipes do not make sense technically. Along with correct descriptions of glass polishing or of the red and green colors obtained with copper, the Mappae clavicula for instance instructed: "Color thin glass pieces, mix and coat them with dragon's blood, and in this way a reddish color will result". Such technical compilations would be followed by many others: until the 15th century, glass recipes are present in more than 120 of them, generally focusing on softening, coloring and gem counterfeiting [34].

Some compilations incorporated recipes from an Arabic literature that began to be translated in Latin in the 12th century. From Egypt to Mesopotamia, the ancient glassmaking tradition had become part of the new Islamic world after the Arabic conquests of the 7th and 8th centuries. In Islam, too, marked changes in glass chemical composition took place in the 8th-9th century probably as a result of natron shortage [35]. This was the time when alchemy became extensively practiced and when Jabir ibn Hayyân (8th-9th c.) became a semi-legendary character to whom an immense alchemical literature would be attributed [36]. Although the term alkali is the Arabic al qalīy [calcined ashes] and original processes were devised,

new concepts do not seem to have been formulated about glass and its nature. Jabir himself considered it as part of the seven metals and as the best material for making the vessels within which artificial life could be created ([36], cf. Ch. 10.10). Even the great polymath al-Bîrûnî (973-after 1050), who was active in central Asia, devoted more space to poetry than to technical descriptions in the short section devoted to glass in his celebrated Book Most Comprehensive in Knowledge on Precious Stones [37]. His main statement was that glass "is cast from a well-known stone or from sand to which borax has been added. The substance is heated for several days on fire till it accumulates, clarifies and progressively hardens". That said, al-Bîrûnî simply added that "different colours are imparted to glass while it is being melted. These colours persist".

From furnaces to processes, the most reliable ancient review of glassmaking is found in the second book of the 12th-century treatise On Divers Arts of the Benedictine monk Theophilus (Ch. 10.9, [38]). Original views on the constitution and properties of glass are unsurprisingly lacking in this work whose goal was to show how God could be glorified by the practice of the most various crafts. Thanks to its technical descriptions and also to the rich medieval Latin terminology it has transmitted, however, this work has been judged to be "one of the three of four outstanding documents in the written history of mediaeval art-technology", which distinguished itself from the

"random conglomerate" of earlier compilations by the way in which it announced "the rational, ordered, unified composition" of 15th-century treatises [39]. Another book of the same period deserves a special mention by the original fundamental insights it threw on glass. These were presented in On the Elements, a work perhaps written in France toward 1160 by an elusive author named Marius who relied on his own observations to describe how the four elements combined to make up all things from minerals to Man. In his book, Marius was apparently sthe first author to point out the kinship of glass not with metals, but with ceramics and rocks, and explained in addition how mud was transforming into what we now call metamorphic and igneous rocks under increasingly strong action of subterranean heat. As Marius asked his readers,

> "Do you also know that the jar of a potter is a kind of glass? But because it was not cooked long, it is therefore not glass. But if it were cooked for a long time by the fire, it would be turned into clear and glittering glass, like the pot of the goldsmith. Now, therefore, you can observe how stones are created in the body of the earth because of insufficient fire; if the fire were greater, the process would be completed and these stones would be turned into glass. Of this sort are the stones we use for the constructions of houses, and marbles of various colors, and the little white stones which are found on the banks of rivers" [40].

And Marius concluded that "there are many kinds of these because of the varieties of earth of which there are many kinds — I do not mean earth properly speaking — and because of the variation in the amount of heat they receive [40]." But these ideas received little attention as testified by the single extant manuscript of his book, which had to wait until 1976 to be edited and printed.

While miracles would be soon wrought by transparent glass in the form of spectacles (Ch. 10.10), glass was then about to regain in the colored glazing of churches an importance it had not had since Late Antiquity (Ch. 10.8). Significant innovations (Ch. 10.8) were the production of red glass through complex microstructural effects in the 12th century and yellow staining with silver salts in the early 14th century, followed by the empirical recognition in Venice that purer raw materials were needed to improve quality (Ch. 10.7). Following the use of quartzite pebbles as a source of silica in place of common sand, the complex treatment of soda plant ash made through successive steps of dissolution in boiling water, decantation, filtration and drying of the final sale de cristallo were clearly indicating that a series of well-defined chemical operations was the key to ensure a consistently high quality.

## 4. The early modern period (16th-18th c.)

### 4.1. An alchemical backdrop

Glassmaking progress did not affect the old associa-

tion of glass with alchemy. On the contrary, argued the metallurgist S. Vanoccio Biringuccio (1480-1539) in his Pyrotechny (Ch. 10.9), this art was "born from the speculation of good alchemistic savants, through whose efforts it imitates the metals on the one hand and the transparency and splendour of gems on the other". And although Nature "has produced crystal and all other kinds of gems that are much more beautiful" than glass, Biringuccio added, no way has yet been found for working with these as done with glass" [41].

The beauty of glass was not necessarily lasting, however, as alchemists had long noticed the degradation of their glass vessels after long exposure to heat and chemicals. The attack of glass by soda and potash was thus described in some detail in several books, for example in a text attributed to an enigmatic 15th-century monk named Basilius Valentinius, probably the pen name of a salt manufacturer named Johann Thölde (1565-1614) who was familiar with chemical processes. Likewise, potassium silicate was produced as liquor silicum through reaction of sand with cream of tartar [potassium hydrogen tartrate, $C_4H_5KO_6$] by the chemist Johann Rudolf Glauber (1604-1670) after whom sodium sulfate has been named as Glauber's salt.

This alchemical backdrop would remain clearly present in the reference glass treatises of the 17th century (Ch. 10.9). It is for example clearly apparent in the The Art of Glass Making of Jean Haudicquer de Blancourt (b. ~1650), where one reads: "glass is a perfect metal, since it does not burn more in fire than gold; & that there is only one fire more powerful than that of the common man who can destroy it" [42]. As a reminder of Petronius' famous story of malleable glass, Haudicquer also mentioned "the Elixir of the Philosophers which makes it malleable, & which converts crystals into very fine precious stones" [42]. But the most dramatic experiments made at the same period were those of the physician and alchemist Jan Baptista van Helmont (1579-1644) who reported that the sand incorporated in glass was actually not dissolved in it because it could be entirely recovered by an appropriate chemical treatment. As van Helmont explained in his Dawn of Medicine,

"If one melts a fine powder of glass with a large amount of alkali and exposes it in a humid place, one will presently find that all the glass dissolves into a water. If chrysulca [mainly nitric acid] is poured on in a quantity sufficient to saturate the alkali, one will at once find that the sand sinks to the bottom [of the vessel] in the same weight as it was before it was used in making the glass" [43].

In fact, van Helmont precipitated alkali nitrates and silica from the aqueous silicate solution. For him, however, the obvious conclusion was that "by means of art, glass returns into its original ingredients once the bond holding them together is broken: the sand can even be regained in the same number and weight" [43]. In other words, van Helmont thought that

this experiment with glass had disproved a fundamental tenet of Aristotelian philosophy, namely, the complete homogeneity of mixtures.

## 4.2. Descartes: the foundation of a glass science

Certainly René Descartes (1596-1650) was not the first observer to be fascinated by the "transmutation of ashes into glass", as he summarized glassmaking in 1644 in his Principles of Philosophy. In this extremely ambitious treatise, his goal was to describe comprehensively the physical world from a few first mechanical principles [44] in the atmosphere of intense intellectual curiosity sustained by the discovery of whole new worlds with the telescope and the microscope (Ch. 10.10). The famous philosopher was also strongly interested in glass in relation to his own optical research that lead him to give a theoretical demonstration of the law of refraction formulated in the early 1620s in the Netherlands (Ch. 10.10). Reflecting on vitrification, Descartes thus explained in his Principles that glass,

> "when still glowing with heat, is fluid because its particles are easily moved [separately from one another] by that force of fire which previously smoothed and bent them. However, when it begins to be cooled, it can take on any figures whatever. And this is common to all bodies which have been liquefied by fire; for while they are still fluid, their particles effortlessly adapt themselves to any figures whatever, and when such bodies subsequently

harden with cold, they retain the figures which they last assumed" [44].

At a time when nothing was known about the microscopic constitution of matter, Descartes described in this way not only what we now refer to as the atomic configurations of a material but also the manner in which these vary with temperature. Descartes went on to explain why glass should be annealed because of differential volume contraction on cooling and build-up of what we call internal stress:

> glass "is also more fragile when it is cooled quickly than when it is cooled slowly; for its pores are fairly open while it is glowing with heat […]. However, when glass cools naturally, these pores become narrower. […] And if the cooling occurs too rapidly, the glass becomes hard before its pores can thus contract: as a result, those globules subsequently always make an effort to separate its particles from one another" [44].

Although they were heralding the beginnings of glass science, Descartes' ideas got completely forgotten until the present time [45]. These groundbreaking conceptions probably suffered from the general criticism laid upon the Principles of Philosophy. This treatise was judged by many as a "romance" even before the Newtonians rejected his vortices, which played so prominent a role in his wholly mechanical system.

## 4.3. The wondrous lacrymae batavicae

Descartes' Principles were nonetheless widely read in

the 17th century. That Newton imitated Descartes by entitling his opus magnum Principles is clear evidence of the critical interest in Cartesian physics raised in England. Regarding glass, the physicist Robert Hooke (1635-1703) might already have had in mind the springiness of the particles implicitly evoked by Descartes when he turned his attention to curious glass drops quenched into water (Fig. III).
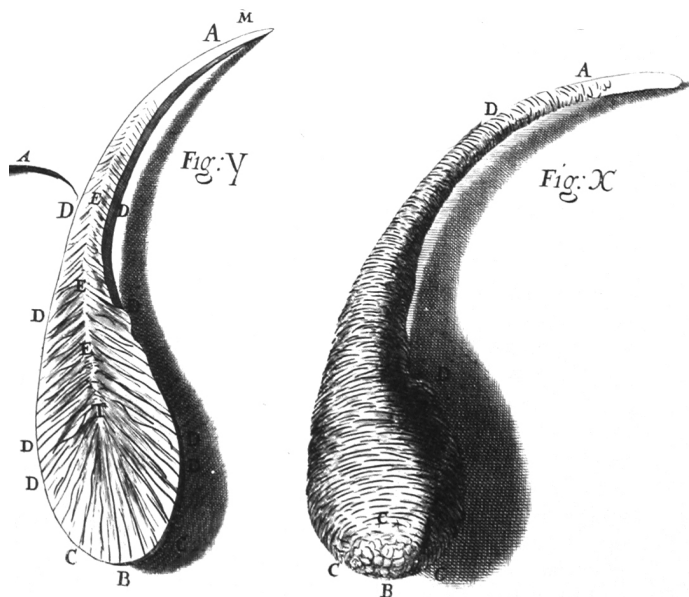


**Fig. 1.** Prince Rupert's drops pictured by Hooke; rupture pattern shown on the left [48].

This early form of tempered glass was probably made before 1625 in Mecklenburg, in Northern Germany, and became called either lacrymae batavicae [Batavian tears, in Latin] or Prince Rupert's drops long after they had been presented by the German-born Prince Rupert of the Rhine (1619-1682) before the Royal Society of London in 1661 [46].
As originally described [47], these glass beads are remarkably resistant to mechanical shock until a final

blow or a breakage of their tail makes them explode and shatter as tiny fragments (Fig. 1) even when coated of strong glue or cement. To interpret their instability, Hooke first reckoned that "the parts of the glass" take up more room when hot and fluid than cold and hard, but also that quenching "the glowing metal in the Water makes it of a hard, springing, and rarified texture" so that "the sudden flying asunder of the parts proceeds from their springiness". In the conclusion of this first study of the mechanical properties of glass, Hooke then stated that " a gradual heating and cooling does anneal or reduce the parts of Glass to a texture that is more loose, and easier to be broken, but not so brittle [48]."

## 5. The chemical revolution

### 5.1. The new chemical researches

It had in fact long been acknowledged that there was not a single earth, but many such as soda, potash [potash], lime or magnesia. Although their constitution remained unknown, they could be distinguished by their differing vitrifiability and solubility in water. The reputedly best soda was produced in Spain from the ashes of a succulent shrub named barilla [Salsola soda], which is rich in sodium oxalate, tartrate and other organic salts that decompose upon combustion after which their ashes combine with atmospheric $CO_2$. Known as Alicante soda, it was far from being pure sodium carbonate with the following average composition: carbonic acid (16.7 wt %), charcoal

(15.0 %), lime (6.4 %), magnesia (2.2 %), alumina (2.3 %), silica (7.3 %), free soda (14.6 %), sodium sulfate (4.2 %), sodium chloride (2.2 %), potash (3.1 %), water and other volatiles (26.0 %) [49]. A simple way to increase its purity was to take advantage of the fact that, in contrast to their alkaline counterparts, alkali earths were soluble in water. This purification did not have only advantages, however, as was noticed by the future Saint-Gobain director Pierre Delaunay Deslandes (1726-1803) who reckoned in 1756 that lime then needed to be added to the batch to ensure the quality and workability of the glass [50]. Because of the high cost of imported soda and the need to satisfy an increasing demand for products ranging from soap to glass, the French Academy of sciences unsuccessfully offered in 1775 a price for the production of pure soda from salt. Various attempts were then made before the chemist Nicolas Leblanc (1742-1806) patented in 1792 a process for producing synthetic soda from salt, sulfuric acid, coal and limestone [51]. As understood only toward the end of the 19th century, hydrochloric acid and sodium sulfate [salt cake] are first produced by the reaction of salt with sulfuric acid:

$$2\ NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\ HCl. \qquad (1)$$

The salt cake reacts with coal to reduce the sulfate to sulfide

$$Na_2SO_4 + 2\ C \rightarrow Na_2S + 2\ CO_2. \qquad (2)$$

The sulfide then react itself with crushed limestone to yield a mix of soda ash and calcium sulfide termed black ash:

$$Na_2S + CaCO_3 \rightarrow Na_2CO_3 + CaS. \qquad (3)$$

In a final leaching step the black ash dissolves in water and soda ash is recovered by evaporation of the solution. Because of its elevated cost, the Leblanc process did not meet with an overwhelming success in glassmaking. It was in particular cheaper to follow the simpler procedure established by Gehlen in 1810, which consisted in effecting the Leblanc reactions in the batch itself with about 100 parts of sand, 50 of Glauber's salt, 17-20 of powdered quick-lime and 4 of charcoal [2,3]. But an undesired greenish hue was obtained in this way, which was strongly detrimental to the quality of the expensive plate glass. Chemical analyses performed by Pelouze showed that this hue was originating in slight iron contamination caused by the reaction with the pots of the excess sulfuric acid present in sodium sulfate, which thus had to be of a high purity [49]. Sodium carbonate — the major chemical produced at that time — nonetheless remained produced with Leblanc's method until the early 1860s when the less expensive Solvay process was invented (Ch. 1.2). The carbonate then slowly supplanted the sulfate as a sodium source as it was ensuring faster sand digestion and, thus shorter melting reactions. Because its major advantages for the fining process had been recognized, however, the sulfate was not completely eliminated. It remains today the main agent used for chemical fining (Ch. 1.3).

*5.2. The discovery of the elements*

Compared with earlier glass treatises, those published from the 19th century clearly differ by their numerous tables of chemical compositions. The change was abrupt. In the 17th century, as noted by W.E.S. Turner (Ch. 9.12), i "there was no realization of the complexity and inconstancy of the glassmaking salt, containing as it did the carbonates of sodium and potassium, calcium and magnesium (these last two in large proportions), of chlorides, sulfates, and phosphates, with silica, alumina, and minor constituents" [52]. Although sodium and potassium salts could at last be differentiated in the mid 18th century, the existence of alkali elements would remain debated until the beginning of the following century when they were at last identified at the same time as the alkaline earths.

Knowing of what the traditionally used salts were made was only a first step toward the modern notions of stoichiometry and chemical composition. Four theoretical concepts derived at the turn of the 18th and 19th centuries were also needed, namely, (i) the law of definite proportions stated in 1794 by Joseph Proust (1754-1826) according to which chemical elements are present in fixed weight ratios in a given compound; (ii) the first atomic theory formulated by John Dalton (1766-1844) in 1803-06; (iii) Gay-Lussac's law of combining gas volumes (1808); and (iv) the hypothesis advanced in 1811 by Amedeo Avogadro (1776-1856) that equal number of molecules occupy equal gas volumes.

At the end of the 18th century the new chemical system propounded by Antoine-Laurent de Lavoisier (1743-1794) had opened completely new horizons. As Lavoisier stated himself in his famous Elements of Chemistry,

"It is likely that we know only some of the metallic substances that exist in nature; all those, for example, that have a greater affinity for oxygen than for carbon, are not prone to be reduced or brought to a metallic state, & they should present themselves to our eyes in the form of oxides, which we mistake for earths" [53].

In a system that associated a base with the new element oxygen in all earths, the problem was to decompose the earths to isolate their bases. In this respect, silica was raising a special difficulty because its remarkable purity in the form of crystal rock could suggest that it was actually a base itself and not an oxide. But attempts at isolating a base from alkali and alkaline earths failed until the invention of the electric pile by Alessandro Volta (1745-1827) and its use in electro-chemical analyses of matter.

In his first electrolysis experiments on alkali salts, Humphrey Davy (1778-1829) realized that their saturated aqueous solutions were inadequate because water decomposition into oxygen and hydrogen was occurring instead. Made either in air with molten soda in platinum spoon or in glass tubes with wet soda, the experiments were difficult because of the instant

combustion of the bases of potash and soda in air or of their quick reaction with glass. "Like the alkahests imagined by the alchemists", noted Davy, these bases "acted more or less upon almost every body to which they were exposed" [54]. In spite of the difficulties also met to determine their properties, Davy determined that they were in 86.1:13.9 and 80:20 weight ratios with oxygen in potash and soda, respectively [actual values: 83:17 and 75:25]. Problems to isolate the bases of the alkaline earths were greater still but those of lime, magnesia and barite and their properties were nonetheless described shortly afterward [55]. Because the bases of silica and a few other earths did not yield, Davy noted [55]:

"Had I been so fortunate to have obtained more certain evidences on this subject, and to have procured the metallic substances I was in search of, I should have proposed for them the names of silicium [from the latin silex, chert], alumium, zirconium, and glucium [beryllium]."

Going one step farther than Gay-Lussac and Thénard with the same procedure, it was eventually Berzelius who isolated the base of silica, which he found to be in a 48.2:51.8 [47:53] weight ratio with oxygen, and guessed to be in a 1:3 atomic ratio [56].

## 6. The crystal connection

### 6.1. The early glass ceramics

In the early 18th century much work was done to understand how porcelain was made and, thus, how to imitate at a lower cost the expensive Chinese ware imported. From his own experimental investigation, the naturalist and physicist René-Antoine Ferchault de Réaumur (1683-1757) understood that porcelain owed its properties to a starting mix of clay such that the material was undergoing partial melting at the high temperatures of the furnaces, which made the product intermediate between terracotta and glass [57]. On the other hand, glassmakers knew well that too much time spent at temperatures appropriate for blowing causes partial transformation of the glass to a whitish material that could no longer be blown. Réaumur figured out that by devitrification one could bring the glass partially back to its initial state and, thus, produce a glass porcelain of an admittedly lower quality, but at a much reduced cost. After extensive experimentation, Réaumur found that only some glasses yielded the white material he was looking for [58]. The new product would be called Réaumur's glass porcelain (Fig. 2).
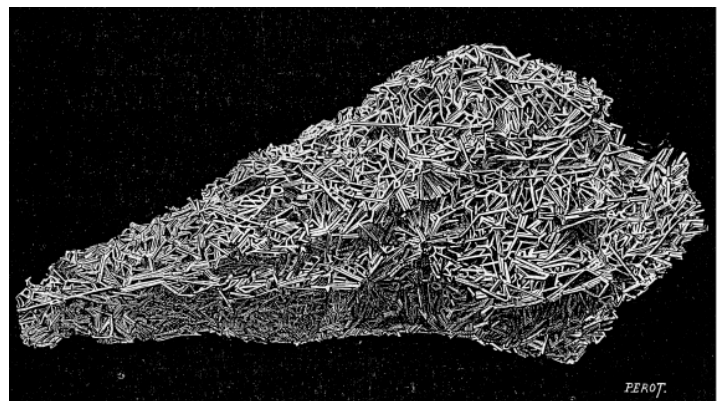


**Fig. 2.** Crystal precipitation in a piece of Réaumur's porcelain. Engraving from [50].

In Scotland, the glass-crystal relationship was then

considered from a completely different standpoint within a debate that was opposing naturalists about whether water or fire was the main geological agent. When the physician James Hutton (1726-1797) explained that the Earth is a heat engine that gives rise to the great cycles of erosion, sedimentation, petrification, and finally mountain-building, his young friend James Hall (1761-1832) thought that experimental support could be given to these ideas. As a volcanic rock, the iron-rich and $SiO_2$-poor basalts (Ch. 7.2.) were assumed to have attained their present positions "in a state of igneous fusion" [59]. When melted in a glass furnace, however, basalt yielded a glass and not the stony rock observed, which seemed to contradict Hutton's theory. Hall thus thought that during its "slow refrigeration in the bowels of the earth", the molten mass "had undergone a change similar that of glass into Réaumur's porcelain; and that by crystallization it had lost the vitreous, and assumed the stony character" [59]. Experiments made by Hall on different kinds of lavas in fact showed that a glass was each time obtained upon rapid cooling of the melt, whereas annealing or slow cooling resulted instead in crystallization identical in all respects to that of the original lava [59,60]. The kinetic nature of vitrification had thus been demonstrated.

These conclusions were soon put to practical use. In France, the chemist Jean-Antoine Chaptal (1756-1832) used basalt as a cheap starting product for the industrial production of bottles in Southern France [61]. After some success, his efforts ended in failure because composition variations of the lava caused melting difficulties and devitrification problems, which did not motivate attempts at solving them because market conditions were favoring clear glass bottles. Molten basalt had thus to wait the very high cooling rates achieved in the production of rock wool to become of real interest in glass making (Ch. 9. 3).

### 6.2. From melting to crystallization

Another important advance made at that time was the melting of quartz. With a blowpipe burning an oxygen-hydrogen mix, the Genevan-born British physician Alexander Marcet (1870-1923), a close friend of Berzelius, first vitrified silica in 1813 in the form of small needles [62]. In larger quantities, Marc-Antoine Gaudin (1801-1880) then succeeded in 1839 to draw fibers that were "resembling steel in elasticity and tenacity" [63]. After three and a half millennia of glassmaking, the very high temperatures required for melting silica without a flux had been made possible by the discoveries of oxygen and hydrogen and of their combustion mechanism. That, according to a common interpretation of a 17th century account [64], vitrification of quartz was first performed by the Berber poet and astrologer 'Abbas Ibn Firnâs (d. 887) is thus clearly an unfounded legend.

Flow during the long heat treatments required for the production of Réaumur's porcelain made it difficult to

keep the complex shape of the original glass piece. Large plates could in contrast be readily produced, which appeared to be much harder and more resistant to thermal shock than the original glass [65]. These advantages of what we now call glass ceramics (Ch. 7.11, 8.5) were thus already recognized at that time. Regardless of high production costs, what probably prevented applications was rapid alteration in air, for instance shown by the surface formation of potassium carbonate [50].

Although Réaumur's goal had been to devitrify partially glass, the nature of the actual transformation effected long remained debated [50]. Was it simply a physical modification of the glass or the precipitation of crystals of a well-defined composition, which thus differed from that of the glass? Important features supporting the latter interpretation were observed by Théophile-Jules Pelouze (1807-1867) in extensive experiments on Réaumur's porcelains. As summarized by Pelouze, "crystalline nuclei" (i) appear at the glass surface; (ii) grow from both sides toward the interior of the plate; (iii) disappear upon heating at temperatures not higher than those at which the starting glass was melted; (iv) reform upon cooling without any weight change; (v) grow with a kinetics that depends much on composition (for example fast for sodium trisilicate but vanishingly low for a potassium and calcium borosilicate); and (vi) have a growth rate considerably increased by the introduction of refractory material, sand, ashes or even batch

or glass powders [66]. The difference between what is now termed homogeneous and heterogeneous nucleation was thus also clearly pointed out.

A at the end of the 19th century, the kinetics of the process was studied in more detail by Gustav Tammann (1861-1938) who established that homogeneous crystallization depends on heat flow and proceeds in two steps, namely, the initial formation of "crystallization centers" followed by growth of the macroscopic crystals [67].
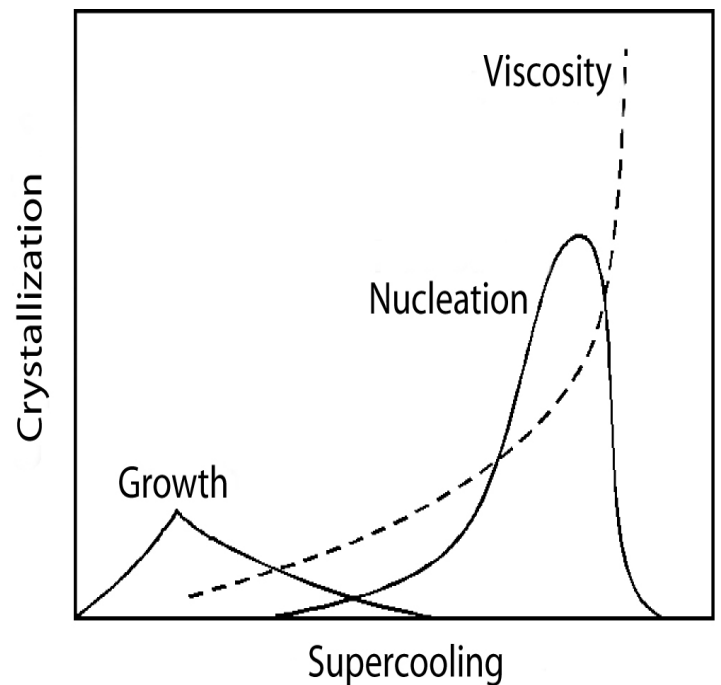


**Fig. 3.** Tammann's depiction of the rates of crystal growth and nucleation with increasing extent of supercooling for a glass-forming liquid whose viscosity increase is also sketched [after 68].

For both nucleation and growth, the rate varies with temperature according to bell-shaped curves (Fig. 3), the growth rate vanishing by definition on the high-

temperature side at the melting point of the crystal or liquidus temperature. In quenching experiments performed on 153 liquids of many kinds, vitrification was obtained 59 times, which led to the conclusion that most liquids could vitrify, at least in small amounts, if cooled rapidly enough [68]. That the ability of a liquid to supercool depends on the nucleation and growth rates of crystals was in addition for Tammann the "key to the relation between glasses and fusions. A glass is a non-crystalline, strongly supercooled melt" [69], without any definite melting point upon heating to high temperatures.

## 7. The multiple roots of glass science

### 7.1. Composition innovations

In the 17th-century, the production of flint glass in England by addition of large amounts of lead oxide to the composition was a forerunner of future changes made in glass composition to yield new, special properties (Ch. 10.10). Because index of refraction scales with density, crystal glass had a distinctly bright and vivid appearance, which instantly met with popular and optical success. Another new family of glass appeared at about the same time in Bohemia. There, potash-lime glass was made from made from saccharoid limestone, potash-rich pine-tree ashes and hyaline quartz as a substitute for rock crystal, which had been extensively mined for the purpose of carving beautiful vessels out of large pieces. The new glass ensured great clarity, even for big pieces, could

be ornamented with enamel because it could sustain high temperatures without softening, and for this reason proved to be most valuable for chemical experiments (Ch. 10.10).

Along with flint, Bohemia glass was extensively investigated by the polymath Mikhail Vasilyevich Lomonosov (1711-1765) who wanted to create a glass factory for the production of colored mosaic pieces, beads, pearls and other fancy or decorative items not made in Russia at that time; before the plant opened in 1753, Lomonosov had already synthesized more than 3000 glasses, which gave him the complete palette of hues he needed to cater to the Imperial court [70]. In practice, this work was restricted to the potash-lime-silica and potash-lead-silica systems to which a host of coloring agents were added [71]. But it suffered from the fact that it was done in the last days of the phlogiston-dominated old chemical system and that Lomonosov was perhaps too busy with his numerous scientific endeavors and the management of his glasswork to be interested in glass itself.

In contrast, the discovery of alkali elements and the possibility to analyze them gave a much sounder basis to the study of what came to be called water glasses (Ch. 7.5) by the chemist and mineralogist Johann Nepomuk Fuchs (1774-1856) who described new applications such as fire protection for theater curtains [72]. But the compositions of the most common kinds of glasses were not determined at once, as

noted in 1830 by Dumas who distinguished soluble, Bohemia, crown, window, plate, bottle, flint and strass glasses in one of the first systematic determinations of chemical compositions [73], and got also interested in those of ancient glasses. Since chemical analyses of minerals had clearly shown the existence of stoichiometry relations, Dumas wanted in fact to check the commonly held idea that glasses are "indefinite mixes of various definite silicates"; to his surprise, however, he thought to have found that the very best crown glass was "a definite compound almost as exact as some mineral species".

Other insights came from investigations of geological materials in which Fuchs participated among many other investigators. Rocks differ widely in the way they react at high temperature. Granite, for instance, is readily melted. From the early $19^{th}$ century, most oxide and sulfide rock-forming minerals were successfully synthesized in the laboratory by mineralogists [e.g., 74]. Efforts were even made at reproducing the texture of rocks. This work involved more than the very few metal oxides that had been used for making glass from the Late Bronze Age. Leaving aside coloring elements, whose concentration is low, these were the oxides of silicon, sodium, calcium, aluminum, potassium and lead. Boron, in the form of borax [actually various hydrates of sodium tetraborate, $Na_2B_4O_7$] and phosphorus from the microcosmic salt [$Na(NH_4)HPO_4$] (Ch. 7.9) were already known at the end of the $18^{th}$ century to be very efficient fluxes,

but these rare materials were so costly that their use was restricted to vitrification assays [1].

A few decades later, the vitrifiability issue was reexamined for a variety of elements recently discovered or not. Interest was again paid to phosphorus, from which a glass termed Graham's salt [$(NaPO_3)_6$] had been produced in 1833 (Ch. 7.9). From 1862, the minister William Vernon Harcourt (1789-1871), best known as a founder in 1831 of the British Association for the Advancement of Science, incorporated 14 new elements in 166 different glasses, which he supplied to the physicist George Gabriel Stokes (1819-1903) for optical investigations [75]. Harcourt even discovered the glass-forming ability of $B_2O_3$ and $P_2O_5$, but his efforts had little practical applications before Michael Faraday (1791-1867) realized that addition of boron oxide was a simple means to obtain more homogenous glasses for better optical performance [76].

In Germany, the great optician Ernst Abbe (1840-1905) wondered whether the narrow range of chemical composition of glass was the reason why both refractive index and dispersion (Ch. 6.1) were always increasing in a way similar to density. Was it also the reason why lenses had known little improvement since the invention of flint glass? At Abbe's instigation, Otto Schott (1851-1935) began in 1881 systematic investigations of the density-optical property relationships of silicate glasses in a work supported by a scientifically oriented German government. A result was the first commercial production of

borosilicate glasses for optical applications. By using all the elements known at that time, Schott could incorporate 28 of them in concentrations higher than 10 wt % [77]. Introduction of barium, a heavy element, for instance caused an increase of the refractive index of glass without increasing the dispersion. Such observations proved especially useful for microscopy and photography applications. From this work, it became possible to tailor a glass composition for a given specific application as conveniently summarized by the so-called Abbe diagram (Ch. 6.1), in which the range of values that can be obtained has tremendously increased over time (Fig. 4).
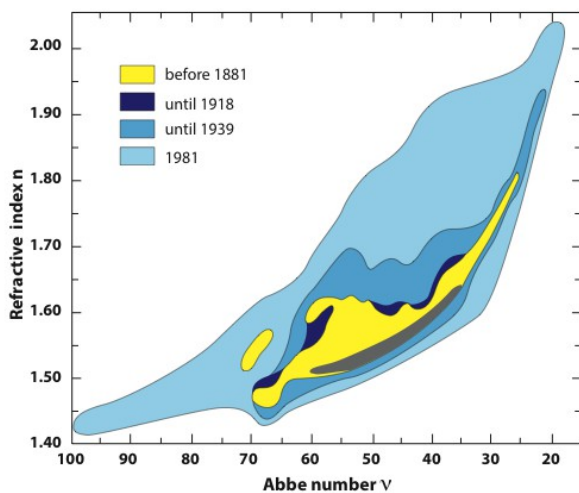


**Fig. 4.** The effects of chemical diversification on the refraction and dispersion of oxide glasses as a function of time; after [77].

Further progress in this respect resulted from specific needs. In the U.S., a search was for example made for glasses with low thermal expansion coefficients because the lights of train cars were breaking under the thermal shock caused by heavy rains. Addition of boron oxide for improving the homogeneity of optical glass already had been described by Faraday [76]. After having also been used by the Schott company to make glass for more stable thermometers, borosilicates resulted in 1908 in the invention of Nonex glass by Corning Glass Works. This lead borosilicate glass was an instant success, but sales soon dropped because the material no longer needed replacement [79]. The use of glass for cooking ware was then considered, but lead-bearing materials were unsuitable for such an application. Further research eventually resulted in 1915 in the famous sodium borosilicate glass dubbed Pyrex, which has an extremely small coefficients of thermal expansion ensured by the presence of about 12 wt % $B_2O_3$ (Ch. 7.6).

The increasing diversity of chemical composition made possible prediction of a given physical property from the composition of the glass. Near room temperature, linear variations of various properties of silicate glasses were observed as a function of the concentration of oxide components [e.g., 80]. Further experimental work revealed deviations from additivity, which were incorporated in more complex models [81]. However, no such effort could be attempted for melts because experimental data would be badly lacking for a very long time.

## 7.2. The contribution of physical chemistry

It was a cosmological problem that first awakened an interest in the physical properties of melts [82]. According to ideas formulated by Descartes in his Principles of Philosophy and then by Leibniz (1646-1716), the Earth had originally been completely melted. Buffon (1707-1788) found support for this thesis in the fact that granite, which was making most of the Earth's crust, could vitrify readily. Buffon was thus led to think that its age could be determined from the time that had been needed to reach its current surface temperature. After him, Joseph Fourier (1768-1830) derived his celebrated heat equation to give a firm mathematical basis to this exercise but appropriate thermal data were lacking to solve it. It was thus to remedy to this situation that William Thomson (1804-1907), better known as Lord Kelvin, inspired in England the first measurements of the enthalpy of melting [83] and in the U.S. of the variation of the melting temperature of a rock with pressure [84].

Geologists were then beginning to determine also the viscosity of magma either from field observations [85] or from direct measurements on molten minerals and rocks [86] Viscosities also became systematically measured in glassmaking contexts as exemplified by the basic soda-lime silica compositions [87]. From the early 19th century, most oxide and sulfide rock-forming minerals had been successfully synthesized in the laboratory by mineralogists [e.g., 74]. But the notion that minerals and their assemblages had well-defined pressure and temperature stability ranges would be lacking until the new science of chemical thermodynamics was established by Josiah Willard Gibbs (1839-1903) [88]. Following Kelvin's impulse, a group of scientists desired to apply Gibbs' principles to the determination of solid-liquid phase-equilibria in oxide systems relevant to geology. They managed to get the support of the steel tycoon Andrew Carnegie (1835-1919) to create in 1905 the Geophysical Laboratory of the Carnegie Institution of Washington where systematic phase equilibria determinations in two-, three- and multicomponent systems would be pursued during more than half a century by Norman L Bowen (1887-1956), George W. Morey (1888-1965) and many other workers [89].

Of particular importance in this respect was the development of platinum-based thermocouples, calibrated via gas thermometry, which made accurate measurements of high temperatures possible [74]. A significant advance was the thermodynamic temperature scale rapidly established up to 1755°C at the Geophysical Laboratory to which the e.m.f. of Pt-Rh and Cu-Constantan thermoelements were referred [90]. With the quenching method designed to establish phase equilibria for systems in which transformations tend to be extremely sluggish [91], work was first devoted to the phase diagrams of binary systems with $Al_2O_3$-$SiO_2$ [92,93], of the $CaO$-$Al_2O_3$-$SiO_2$ ternary [94] and in addition led to the discovery of liquid immiscibility

in binary alkaline earth silicates [95]. Such activity was relevant not only to geology, but also to glassmaking either directly or indirectly through the fundamental benefits drawn for the improvements of refractory materials and of optical glasses [96-98].

Of particular importance to metallurgy was also becoming the physical chemistry of silicate liquids because of the role played by the silica-poor slags in blast furnaces in metal processing and refining (Ch. 7.4). It had been realized in the 19$^{th}$ century that desulphurization and dephosphorization of the metal could be controlled through exchange reactions with the slag phase. Thanks to the advances already made, it appeared that important insights on these reactions would be gained through their thermodynamic modeling. This is why metallurgists pioneered measurements of the activities of oxides in melts [e.g., 99] and phase-equilibria calculations (Ch. 5.3, [100]). Particularly in Germany, they also performed extensive measurements of physical properties such as density and viscosity [cf. studies listed in [101,102]. Likewise, it was with the support of the metallurgical industry that Bockris and coworkers measured the electrical conductivity [103] and viscosity [e.g., 104] of silicate melts and arrived at the modern picture of partially ionic liquids made up of groups of various sizes.

### 7.3. Rupture: from drops to fibers

Tempered glass long remained a scientific curiosity. The springiness of Prince Rupert's drops was consis
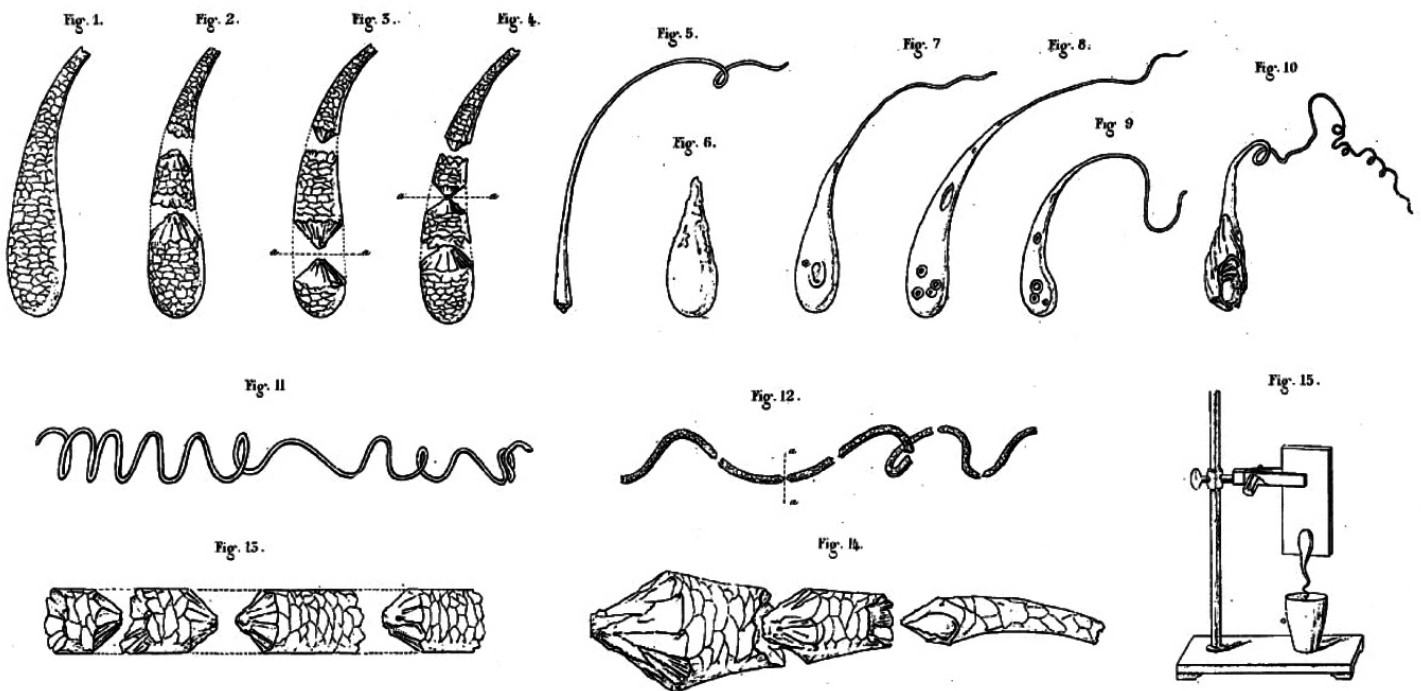


**Fig. 5.** A summary of de Luynes' rupture and HF etching experiments on Prince Rupert drops [104]. Top, left: fracture patterns of drops, the last two sawed horizontally at different places, and drops etched to various degrees without fracture (bubbles becoming apparent). Middle : breakage of quenched fibers. Bottom, rupture of a tempered rod and 1-kg glass piece, and sketch of the HF etching of a drop largely embedded in a plaster plate.

tently assigned to the forced dilation of their interior parts imposed by the quenched surface layers. But controlled HF etching experiments made by Victor de Luynes (1828-1904) showed in 1873 that the extreme strength of a drop is ensured instead by its compressed surface layers whose convergence at the beginning of the tail causes this spot to be the weakest part of the piece [105]. Upon progressive surface etching, the strength smoothly decreases without any fracturing whereas the lack of any preferred microscopic arrangement within the glass is revealed by the orientation of the conical fracture front toward the particular place of the drop where rupture has been triggered (Fig. 5). The unequal "dilation" of the glass layers gives rise to a birefringence also observed under polarized light by de Luynes (cf. Fig. III), who concluded that it is the source of the instability that makes the drop explode even under vibrations or temperature changes.

Although tempered glass had long been known, it is unlikely fortuitous that the first process for producing it industrially was patented the following year by François B.A. Royer de la Bastie (1830-1901). His starting point was especially significant because it represented one of the very first applications of glass derived from theoretical considerations. In agreement with de Luynes' ideas, la Bastie thought that the fragility of glass "results from the weakness of the cohesion of its molecules" so that "it may be expected that by forcing the molecules closer together, and ren-

dering the mass more compact, the strength of and solidity of the material should be increased." And since compression is ineffective in this respect, "even when applied to the material in a fluid or soft condition", the solution was to rely on a tempering system "such as is usually applied to steel", which is why la Bastie immersed the hot glass in suitable oil, grease, wax, resin, tar or pitch [106]. The process designed in this way for glass sheets did not meet with great success. Reasons were early discussed by the famous engineer Frederick Siemens (see Ch. 10.9), who nonetheless acknowledged that it "caused a great sensation at one time" and induced him to give himself "a great attention to the subject" [107]. Siemens was one of the inventors who patented more efficient tempering procedures, but the technological nature of these advances will not be discussed in this chapter as they are clearly beyond its scope (see Ch. 9.2 instead).

For a material not subjected to extreme stresses, tempered glass may exhibit the most dramatic mode of breakage. In Prince Rupert' drops, the rupture front for example moves at velocities measured in the 1450-1900 m/s range [108], such that the ejected glass fragments could break the thick wall of a vessel in which the drop was immersed [109]. But Alan A. Griffith (1893-1963) had not these features in mind when he selected glass to establish his famous theory of rupture, with which the explosive propensity of the drops was at last explained. Griffith was interested instead in the mechanical properties of metals, but he

found glass more convenient for demonstrating the considerable lowering of the strength of materials by surface defects [110]. Such practical reasons led him to chose glass fibers for his experiments, which did show a tremendous increase of the breaking stress
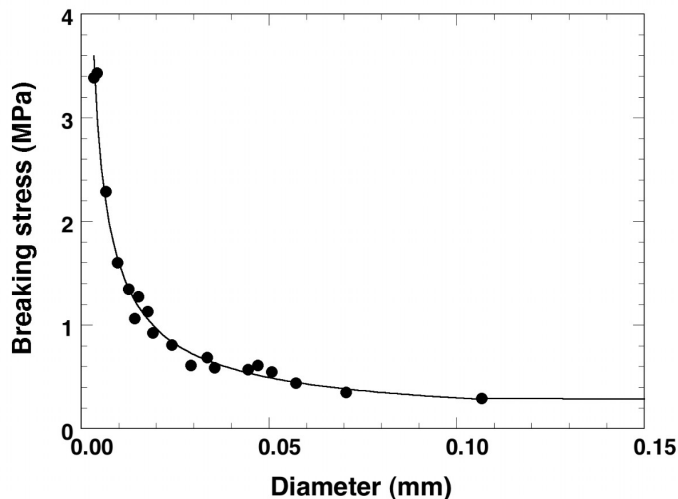


**Fig. 6.** The marked decrease of breaking stress with increasing fiber diameter (1 MPa = 10 bar). Data of [109] for a glass of unspecified composition.

with decreasing fiber diameter (Fig. 6). Because "a fiber consisting of a single line of molecules must possess the theoretical molecular tensile strength", in the form of fibers glass had more strength than steel, confirming the aforementioned early conclusions of Gaudin on the strength of silica fibers [63]. But two decades would be needed to put this advantage to practical use for materials reinforcement (Ch. 1.6).

### 7.4. An elusive glass transition

With the exception of the quenching method, which had to be devised for viscous melts, much of the afor-

ementioned physico-chemical research was not specific to glass-forming liquids. The new concepts that would be formulated, and lead to a better understanding of glass-liquid relationships, nonetheless relied on the wealth of such data gathered for oxide and organic glass-forming liquids. The lack of heat effect upon vitrification pointed out by Tammann was in particular not real. The outstanding accuracy of the
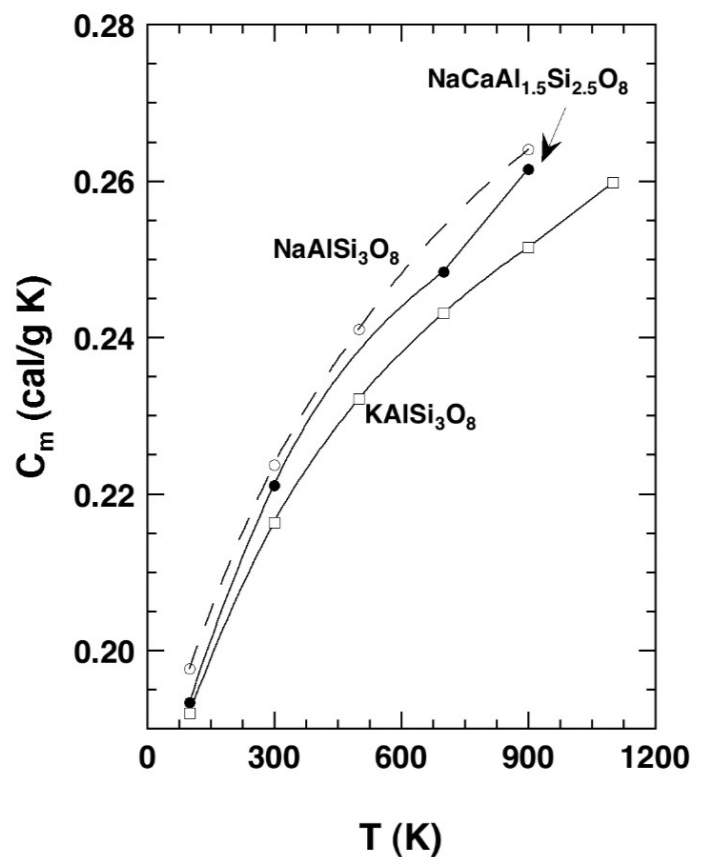


**Fig. 7.** The calorimetric effect of the glass transition: break in the mean heat capacity curve, $C_m = (H_T - H_{273})/(T - 273)$, of $NaCaAl_{1.5}Si_{2.5}O_8$ observed in drop calorimetry experiments. Data from [110].

relative enthalpies (Ch. 3.6) reported for $SiO_2$ and a series of silicates in crystalline and glassy forms by

Walter P. White (1868-1946) made the detection of calorimetric anomalies possible (Fig. 7). In what seems to have been the first mention of the glass transition, White related that

"several of the glasses show a decided increase in specific heat at some fairly elevated temperature. No explanation has been established for any of these facts. It seems probable that the increase in specific heat would have appeared in other glasses if they had been carried higher. It may be a phenomenon of considerable importance, but for its complete investigation a knowledge of the expansion and perhaps of other properties of the glasses is desirable" [111].
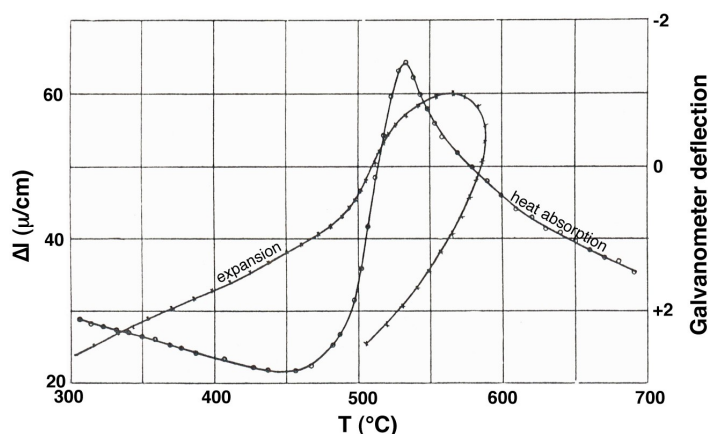


**Fig. 8.** Anomaly of thermal expansion and heat absorption in the same temperature interval upon heating of a light-flint silicate glass; after [114].

As a matter of fact, similarly abrupt variations upon heating of a glass had already been observed for the thermal expansion coefficient [112] or the dielectric constant [113], but these anomalies had then elicited little interest. A few decades later interest in these

phenomena was, by contrast, awakening, especially in relation with the annealing of high-quality optical glasses.

Near the empirical annealing range, anomalous endothermic thermal effects were observed in narrow temperature intervals for other silicate glasses [114]. For a variety of silicate glasses [115], an important observation then was that marked increases in both thermal expansion and heat were taking place in the same temperature intervals (Fig. 8). But the interpretation of these phenomena was not yet clear since
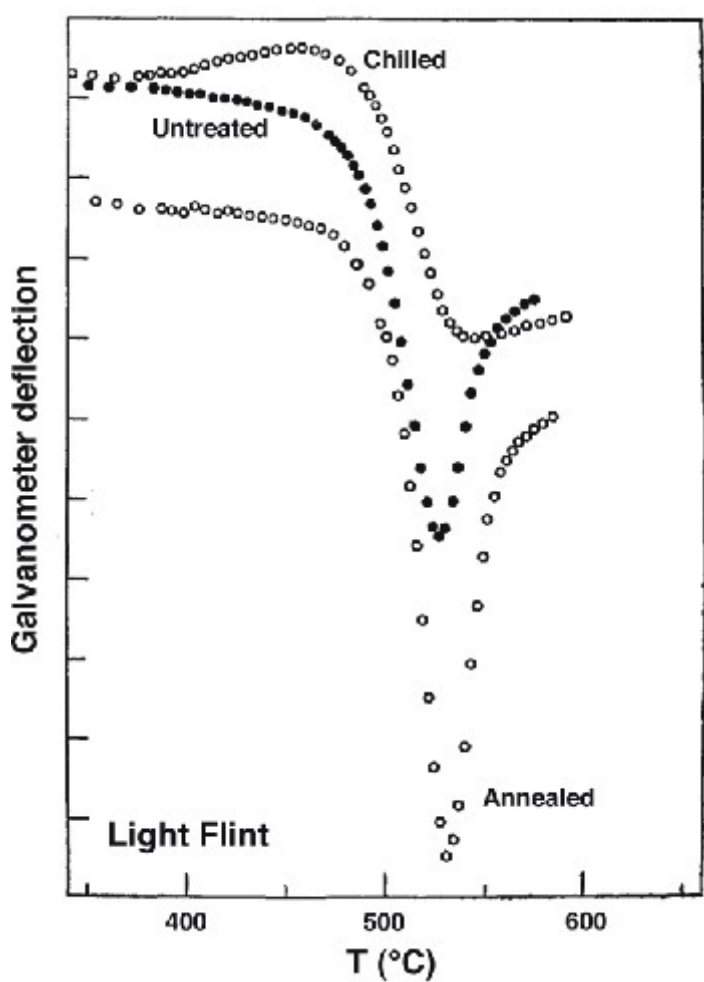


**Fig. 9.** Effect of thermal history on the glass transition of a light flint glass: endothermic peaks recorded in differential thermal analyses; after [115].

it was concluded that:

> "The cause of these phenomena may be the melting of some of the constituents of the glass, or the melting of the compound as a whole. Whether or not we conclude that glass melts or starts to melt in the critical region depends mostly on our definition of solid and liquid" [115].

In the same year 1920, Arthur Q. Tool (1877-1967) and C.G. Eichlin [116] observed that the endothermic effects recorded between 450 and 600°C for different types of glasses shift to higher temperatures with faster heating rates and are larger for annealed than for chilled samples (Fig. 9). An important conclusion drawn from these results was that annealing "may involve more than the mere removal of stresses" from the glass. But the nature of the other processes involved remained unclear. A possibility was "the formation and dissolution of some such crystalline structure or other molecular aggregate", which might also account for the tempering of glass achieved by la Bastie and Siemens without the need of a stress build-up as it was then assumed [116]. Subsequent work by a number of investigators, especially Tool and Eichlin [117], then indicated that a state of equilibrium could be attained through only "molecular rearrangement", in crystallite-free materials, such that "the density of the glass varies somewhat with the treatment."

Another approach resulted from the conclusion drawn in 1920 by Gilbert Newton Lewis (1875-1946) and George Ernest Gibson (1884-1959) that, because of the existence of the entropy of mixing,

> "at the absolute zero there is in general a difference in entropy between a solution and the pure substances of which it is composed. In other words, if we assign zero entropy to the pure substances we cannot take the entropy of the solution as zero" [118].

The existence of such a residual entropy was quickly confirmed by Wietzel who reported that silica glass has at liquid-hydrogen temperatures a higher entropy than crystalline $SiO_2$ forms [119], but this conclusion was not regarded as definitive in view of the uncertainties affecting the extensive calorimetric measurements needed at high temperatures on which it was relying (Ch. 3.6). Thanks to their low melting temperatures, organic glass-forming systems were lending themselves to firmer statements. From measurements on glycerol [$C_3H_5(OH)_3$], Gibson and William F. Giauque (1895-1982) thus concluded that the excess entropy of $5.6 \pm 0.1$ cal/mol K found at 70 K for the supercooled liquid over the crystal "will not be appreciably different at the absolute zero" [120].

In these measurements on glycerol, the abrupt 90 % heat capacity increase measured for the glass at about 190 K was not commented upon. It was in fact similar to "some remarkable changes" previously observed by Gibson's team at around 100°C for ethanol [$C_2H_5OH$] and propanol [$C_3H_7OH$], which had been simply interpreted as "a great increase in the amount of association within the super-cooled liquid" [121].

On the other hand, Alexander A. Lebedev (1893-1969) assumed that glass contained "minute quartz crystals", forming themselves solid solutions, such that "annealing is not so much the removal of stress as the attaining of complete polymorphic transformation" [122]. His main argument was that the birefringence of optical glass disappears upon annealing near 575°C, the temperature of the } transition of quartz. His views formed the basis for the microcrystalline hypothesis, according to which glass was made up of a disordered arrangement of very small crystals whose structure was similar to that of a stable crystalline form [cf. 123].
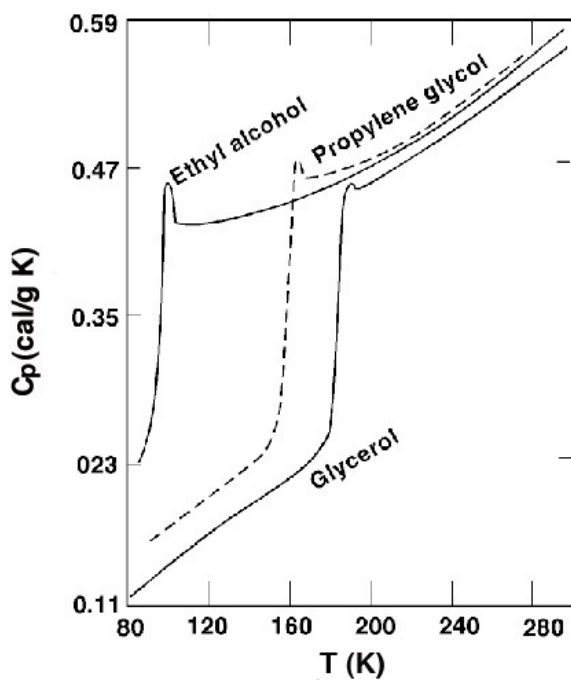


**Fig. 10.** Heat capacity changes of organic substances in the glass transition region; after [123].

These diverging reflections on the structure of glass were at the roots of the confusion affecting the nature of the physical anomalies observed in glass-forming systems, which apparently White alone had grasped at once as indicating the existence of a new kind of transition. Such divergences notwithstanding, glass formation came to be associated not with any discontinuous change in first-order thermodynamic properties (e.g., volume, enthalpy), but with rapid variations of second-order thermodynamic properties. From their calorimetric measurements on organic substances (Fig. 10), George S. Parks (1894-1966) and Huffman eventually recognized the specificity of glass as a distinct state of matter:

"While there is no definite temperature, comparable to the melting point of a crystal, at which all properties undergo a sharp change, there is nevertheless a temperature interval, definite and reproducible, in which a number of properties change with a rapidity approaching that observed in the case of the melting process of a crystal. In brief, there is a softening region instead of a melting point. The glass as it exists below the softening region differs so markedly from the liquid existing above that it might well be considered as a different state of the substance. For this reason we have recently suggested the possibility of regarding glass as a fourth state of matter, distinct from both the liquid and crystalline states and yet showing to some extent characteristics of both these states" [124].

Consistent with Descartes' ideas, a new kind of tran-

sition, the glass transition, was at last defined from variations of second-order thermodynamic properties. Whether in organic or inorganic systems, it was characterized by the same heating/cooling phenomenology as checked by Parks' team with $B_2O_3$ [125], which could be accurately performed at relatively low temperatures (Fig. 11).
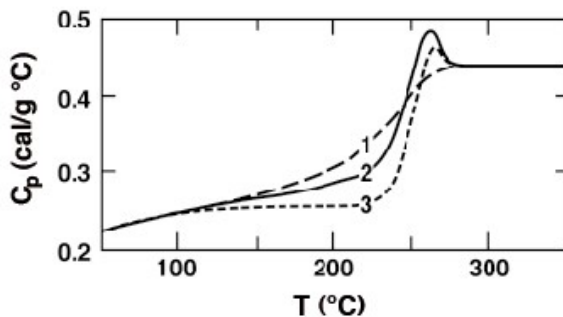


**Fig. 11.** Heat capacity hysteresis observed for the glass transition of $B_2O_3$; measurements made upon cooling (1), heating following slow cooling (2) and heating following rapid cooling (3); data from [124].

Without any reference to polymorphic-like transformations, the very viscous liquid — which was still in internal thermodynamic equilibrium because its state was determined by only two state variables — was separated from the glass by a transition: occurring over a temperature interval of a few tens of degrees, this transition could nonetheless be characterized by a temperature denoted $T_g$. The dependence of glass properties on thermal history first observed in 1845 [14,15] could then be explained simply in terms of the dependence of $T_g$ on the cooling rate (cf. Ch. 3.6).

*7.5. Permanent compaction*

Although temperature is the intensive parameter directly relevant to relevant glassmaking operations, the effects of pressure were also investigated by Tammann. In the same way that one could quench glasses with different thermal histories by changing the cooling rate, one could prepare glasses of $B_2O_3$, $As_2O_3$, $NaPO_3$, phenolphtalein [$C_{20}H_{14}O_4$] and other systems exhibiting different permanent compaction by varying the pressure from which they were quickly decompressed [126].

Because the liquid is more compressible than the glass, the observed permanent compaction arises from the fact that only the elastic part of compression is released when the glass is eventually decompressed at room temperature to ambient pressure. The density of a glass thus increases with the pressure at which the liquid is quenched. It offers an indirect way to estimate the compressibility of the liquid [127]. Interestingly, glasses compressed at low temperature to pressures of a few GPa also undergo permanent compaction. This effect was discovered by the pioneer of high-pressure physics Percy W. Bridgman (1882-1961) and Simon for $SiO_2$ glass compressed beyond 10 GPa at room temperature in minute-long experiments [128]. An 18% compaction was for example observed for a peak pressure of 20 GPa. Especially under nonhydrostatic stresses [129], high pressure could thus induce large irreversible configu-

rational changes at temperatures at which the substance is said to be a glass.

## 7.6. The relaxation problem

Whereas a glass is a hybrid phase characterized by a fixed atomic arrangement, like in a crystal, and by the lack of long-range order, like in a liquid, a melt is a phase whose structure changes rapidly in response to variations of temperature, pressure and other intensive parameters. Because the term configuration designates any microscopic arrangement of matter consistent with a given macroscopic state of the system, in the 1930s the physicists Franz Simon (1893-1956) and John D. Bernal (1901-1971) termed configurational those contributions to physical properties that are associated with structural changes within the liquid [130,131]. These manifest themselves most clearly as the abrupt variations of the heat capacity, thermal expansion coefficient and compressibility at the glass transition.

Configurational properties have also a direct bearing on relaxation, i.e., the variation with time of a given property when the structure of the material adjusts to variations of intensive parameters by tending more or less rapidly toward its new equilibrium configuration. To characterize the rate at which a given property, $Y$, approaches the new equilibrium value, $Y_e$, the relaxation time, $\tau_Y$, has been defined as:

$$\tau_Y = - (Y_t - Y_e)/(\partial Y/\partial t), \qquad (4)$$

where $Y_t$ is the value actually measured at time t. If $\tau_Y$

were constant, i.e., not depending on the instantaneous value of Y, relaxation would be described by a simple exponential law

$$(Y_t - Y_e) = (Y_0 - Y_e) \exp (- t/\tau_Y), \qquad (5)$$

where $Y_0$ is the initial Y value. In other words, after a time $\tau_Y$ the variation of Y would represent a fraction 1/e of the initial difference from the equilibrium value.

An early landmark of relaxation studies was the analysis of the rate at which the strain and birefringence of a glass-forming liquid varies when the internal stresses built on cooling are progressively released upon annealing [132]. This work was of particular importance for optical glass. A noteworthy practical outcome would be standardization of working operations in terms of viscosity for the strain ($10^{13.5}$ Pa s), annealing ($10^{12}$ Pa s), deformation ($10^{10.3}$ Pa s) and softening ($10^{6.6}$ Pa s) points.

Tool and Eichlin [133] noted that these transformations take place at an "effective" temperature, which was later called fictive temperature by Tool [134]:

"It is inferred that the physicochemical condition or state of a glass is reasonably well known only when both the actual temperature and that other temperature at which the glass would be in equilibrium, if heated very rapidly to it, are known. This latter temperature has been termed the equilibrium or fictive temperature of the glass, and a glass is undercooled or superheated according as the fictive temperature is reached by the actual temperature

through heating or cooling, respectively." For viscosity, Lillie [135] showed how equilibrium properties could be measured via reversal experiments made on samples whose fictive temperatures are initially higher and lower than the temperature of
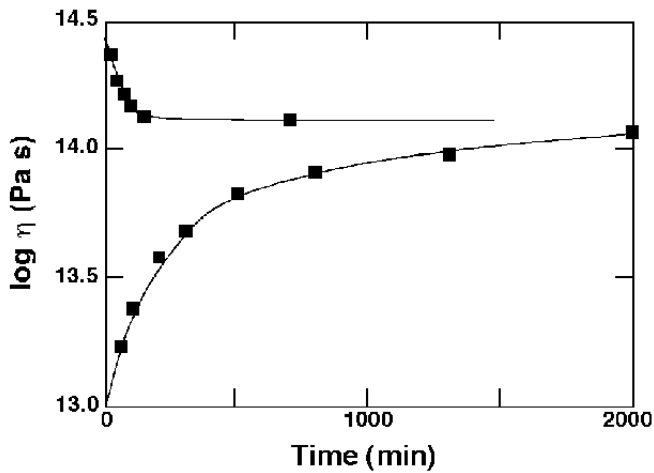


**Fig. 12.** Structural relaxation in viscosity measurements at 486.7°C on a window glass (after [31]). Lower curve referring to a newly drawn sample with a fictive temperature higher than the run temperature; upper curve to a sample first annealed at 477.8°C for 64 hours. Thermodynamic equilibrium reached in about 2000 min as indicated by the convergence of these curves.

interest (Fig. 12). A noteworthy conclusion was that relaxation times depend not only on temperature but also on time and initial extent of departure from the equilibrium state (i.e., fictive temperature). Ever since Tool's pioneering work [134], this is the reason why relaxation models have become complex (Ch. 3.7) whether individual relaxation times are considered intrinsically nonexponential or relaxation is assumed

to be made up of many mechanisms with different relaxation times. In this respect, an important question was to know whether the fictive temperature alone is sufficient to characterize fully the state of a glass at a given temperature and pressure, or if more than one such order parameter are needed for accurate modeling of relaxation processes (cf. Ch. 3.7). The right answer is the latter: from kinetic experiments made on a borosilicate crown annealed either at constant heating rates or at constant temperature, Ritland showed that the density, refractive index, approach to equilibrium and thermal expansion did vary for a same fictive temperature [136].

Phenomenologically, the delayed response characterizing a viscoeleastic material (Ch. 3.7) was not new when it began to be investigated as a result of the work done in the 19th century on various systems in which the mechanical response lasted after the distorting influence had ceased. According to the superposition principle then formulated by Ludwig Boltzmann (1844-1906), the actual response of a material subjected to various excitations can be considered as a linear combination of the individual stress-strain relationships [137]. Regarding viscous deformation, homogeneous glass-forming liquids are such that, as stated by Isaac Newton (1643-1727), "the resistance that arises from the lack of lubricity [the friction] is, other things being equal, proportional to the velocity with which the parts of the fluid are separated from one another" [138]. This proportionality between the

stress and strain rate of a Newtonian fluid was represented by a dashpot in the mechanical model [139] designed by J. Clerk Maxwell (1831-1879), whose other component was a spring accounting for the elastic response given by Hooke's law [140]. This model actually works when relaxation is determined by a single relaxation time for processes whose activation energy is constant. Since these features generally do not hold true for glass-forming liquids, another ancient mathematical device that has proven useful in relaxation studies (Ch. 3.7) is the stretched exponential function, $\exp(-t)$, which had been introduced by Rudolph Kohlrausch (1809-1858) to describe the discharge of a glass-dielectric capacitor [141]. From a dual practical and theoretical standpoint, an important step was recognition in the mid 1920s that the viscosity of glass-forming liquids does not generally follow Arrhenius laws $= {}^0 \exp(\Delta H /RT)$,

(6) where $A = \log {}^0$ is a pre-exponential term and $\Delta H$ the activation enthalpy for viscous flow (Ch. 4.1). To account for the observed non-linear variations of $\log$ against reciprocal temperature (Ch. 4.1), Vogel [142], Fulcher [143] and Tammann and Hesse [144] proposed instead equations of the form

$\log = A + B/(T - T_1)$, (7) where A, B, and $T_1$ are constants. This so-called VFT eqn (7) embodies the fact that viscosity would become infinite at $T_1$, which is sometimes called the Vogel temperature. Two decades later Walter Kauzmann

(1916-2009) pointed out that the large difference between the heat capacities of the supercooled and crystalline phases of a substance would cause their entropy differences to vanish at temperatures not much lower than the experimentally observed glass transitions [145]. These catastrophes yielding negative entropies of melting and the fact that their temperatures are close to the Vogel temperatures have since then been one of the most fundamental features to be accounted for by theories of the glass transition.

### 7.7. *The beginnings of structural studies*

There were two basic prerequisites for the determination of glass structures, namely, the actual existence of atoms and the availability of experimental techniques with which their arrangements could be probed. The microcrystals or molecular rearrangements invoked by Lebedev or Tool were thus speculations relying on fragile evidence as X-ray diffraction studies of the main crystalline silicates had just begun [e.g., 146]. Although the first structural studies were done for glasses from the mid 1920s [e.g., 147,148], they were inconclusive because adequate methods were lacking to deal with the experimental X-ray scattering curves of amorphous substances (Ch. 1.2).

This interest then raised by glass structure led the young William H. Zachariasen (1906-1979) to reflect in the early 1930s on some fundamental rules that disordered arrangements should follow. His starting

point was that a lack of long-range order was not inconsistent with some short-range order imposed by the bonding requirements of each kind of atom.
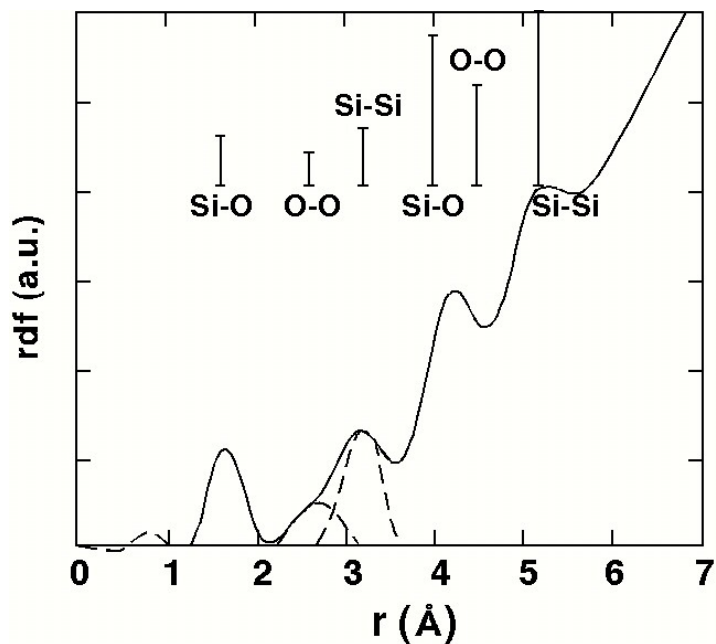


**Fig. 13.** The X-ray radial distribution function of $SiO^2$ glass (after [151]), the first to be determined for silicate glasses. The peak positions yield the distances between first- and second-nearest neighbors, which can be assigned from known ionic radii or interatomic distances in relevant crystals. For well-resolved peaks, the number of neighboring atoms involved can be derived from the peak areas.

Another important feature noticed by Zachariasen was the small energy and volume differences between glasses and crystals. With the assumption that the new principles of structural chemistry established for crystals should also apply to glasses, Zachariasen postultated that both types of phases share the same basic structural elements. Because they lack symmetry and periodicity, however, glasses differ from crystals by the fact that disorder begins right at the scale of first-neighbor distances. Regarding the extent of medium rage order, Zachariasen thus stood in complete opposition to Lebedev to state in his famous 1932 paper that

"An oxide glass may be formed

1. if the sample contains a high percentage of cations which are surrounded by oxygen tetrahedra or by oxygen triangles;

2. if these tetrahedra or triangles share only corners with each other;

3. and if some oxygen atoms are linked to only two such cations and do not form further bonds with any other cations" [149].

On the experimental side, the situation changed when the method of Fourier analysis was designed to determine radial distribution functions of liquids [150]. In the 1930s the method was pioneered by Bertram E. Warren (1902-1991) and his coworkers for oxide and silicate glasses (Fig. 13). In studies of $SiO_2$ and $B_2O_3$ glass they confirmed Zachariasen's first rule by showing that Si and B are coordinated by four and three oxygens, respectively, and each oxygen by two Si or B [151,152]. In addition, they coined the expression random network to describe the 3-d disordered arrangement described by Zachariasen. Further work on soda-silica glass [153] showed that two different kinds of oxygens must be distinguished depending on whether they are bonded to only one or to two silicons (Fig. 14). Together with these notions of non
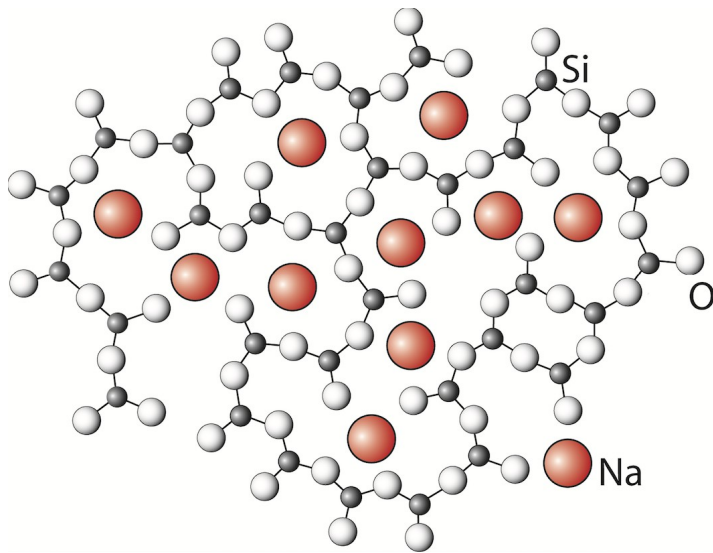
**Fig. 14.** Two-dimensional projection of the structure of a soda-silica glass (after [152]). As derived from X-ray data, this random network also accounted structurally for the existence of gradual (instead of abrupt) softening, viscosity decrease upon $Na_2O$ addition (through fragmentation of the silicate network), and electrical conduction (through hopping of the loosely bound Na atoms).

fier cations was another fundamental concept. Warren and Pincus relied on it to discuss liquid immiscibility in binary metal oxide-silica systems in terms of competition of cations for bonding with nonbridging oxygens, whose outcome is determined by the ratio $Z/r_c$ of the electric charges and ionic radii of the cations [154].

Even before X-ray diffraction was practiced, other methods were used to investigate glass structure. Right after the discovery of the Raman effect in 1928 [155], the spectrum of quartz was recorded by many investigators [e.g., 156] and its resemblance with those of silica, crown and flint glasses pointed out [157]. Although the Raman signal excited by mercury lamps was weak, the early spectra for example recorded for $SiO_2$ and $B_2O_3$ glasses compare remar
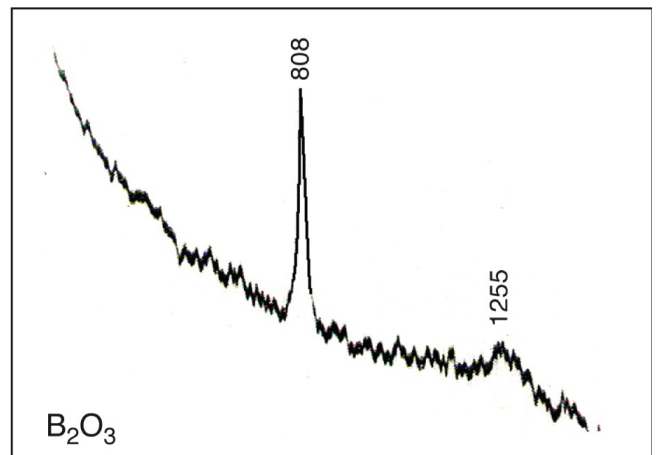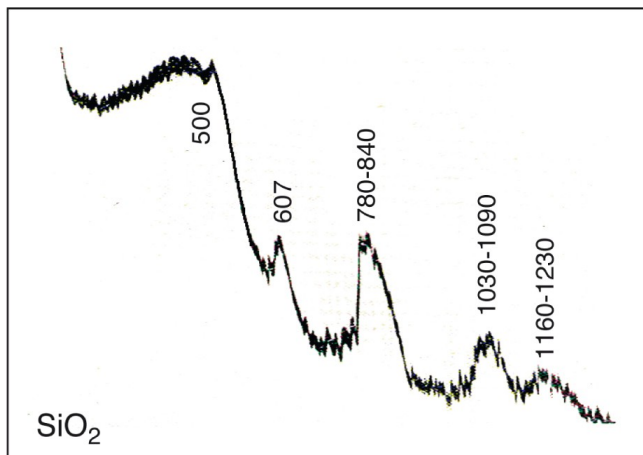


Raman shift (cm$^{-1}$)

**Fig. 15.** Raman spectra of $SiO_2$ and $B_2O_3$ glasses (after [158]). Sharp peak at 808 cm$^{-1}$ in the spectrum of $B_2O_3$ now assigned to boroxol rings (7.6).

bridging and bridging oxygens, respectively, the distinction between network-former and network-modi-

kably well with modern results (Fig. 15). For the variety of silicate glasses studied, characteristic

features could be assigned to specific structural units present in the structure; although the need for more systematic measurements was pointed out to make reliable specific band assignments, substitution of Al for Si for instance indicated a lack of marked structural changes whereas, in agreement with the ideas of Zachariasen and Warren, bands below 550 cm$^{-1}$ were attributed to lattice modes [158,159].

Instead of the parameter $Z/r_c$ used by Warren and Pincus [153], Adolf Dietzel (1902-1993) introduced in 1942 the notion of field strength, $I = Z/a^2$, where a is the distance between ions (metal cation and oxygen, in general), to rationalize the systematic variations of devitrification tendency, compound formation and melting temperatures observed as a function of the nature of cations [160]. That there exists a strong correlation between physical properties and the degree of polymerization of the structure was recognized by Stevels [161,162] who defined a parameter X to designate the average number of nonbridging oxygens per tetrahedrally coordinated cation; this is of course what is now explicitly denoted by NBO/T (Ch. 2.4). In another approach, the structure-composition relationship was interpreted instead in terms of structons, i.e., a limited number of entities made up of a given atom and its nearest neighbors, which changed abruptly with composition [163].

Ironically, the structural heterogeneity claimed by the microcrystalline school bore some analogy with van Helmont's ancient ideas and the strongest evidence for it [see 122] was in fact the result of metastable liquid-liquid phase separation, which was discovered only in the early 1960s [see 164]. Although random network models are probably too extreme in denying significant medium-range order, the issue of crystalline-like ordering has been raised again recently [165]. Nonetheless, Zachariasen's rules still represent a useful starting point for discussions of glass structure (Ch. 2.1), which remain themselves common starting points for structural investigations of liquids [166].

## 8. Perspectives

An interesting contrast is to be noted between chemistry treatises of the 18th century and those of the late 19th century. Glass was an important topic in the former, in particular because of the basic distinction that was then made between the vitrifiable earths and the others [e.g., 5,167]. In the latter treatises, glass was in contrast paid little attention possibly because the identification of alkali, alkaline earth and other elements had made the vitrifiability criterion operationally useless in chemistry and perhaps also because glass was no longer thought to raise new important problems by itself. Representative in this respect were the big physical chemistry treatises of Jacobus Henricus van't Hoff (1852-1910) [168], Wilhelm Ostwald (1853-1932) [169], Walther Nernst (1864-1941) [170] or other authorities. In a short section, Nernst for instance contented himself to endorse Tammann's

ideas about glasses as supercooled liquids by stating that, externally, glass

"has the properties of a solid, owing to great viscosity and considerable rigidity, produced by strong mutual action of the molecules. An amorphous body differs from a crystal, however, in its complete isotropy and absence of a melting point; on heating, it passes continuously from the amorphous to the usual liquid state, as its properties show steady change with rise of temperature, and no breaks anywhere" [170].

Ironically, the glass transition was about to be discovered whereas a long chain of studies had already given rise to the glass electrode [171], which would have so much impact on chemistry (Ch. 5.8). It is in fact a recurring theme in history of science that breakthroughs are made right after important problems seemed to be settled for good.

Building on a long century of advances made in physics and chemistry, a specific glass science crystallized, so to speak, in the critical decade of the 1920s by bringing together physical, chemical, dynamical and structural features. Of particular importance were then organic substances, which were much more amenable to precise measurements than inorganic glasses. For oxide glasses, this new science was early reviewed in books by Tammann [172] and Morey [173]. Comparison of their contents with that of the Encyclopedia illustrates the course followed since then from both experimental and theoretical standpoints.

Like $SiO_2$, some "ancient" glasses are now made in completely new ways for completely new applications such as optical fibers (Ch. 6.4) or aerogels (Ch. 8.3). For other applications wholly original glass compositions have in contrast been designed as illustrated by chalcogenide and fluoride systems (Ch. 6.5, 6.6). As for organic polymers (Ch. 8.7, 8.8), they have given rise to major industries because of the ubiquitous uses they have found.

Also noteworthy are the newer fields of metallic (Ch. 7.10) and bioactive (Ch. 8.4) glasses with their serendipitous beginnings and their variety of applications. The former were first produced when attempts were made at ultra-fast quenching of crystalline solutions [174]. They were then engineered as advised by the old glassmaker adage according to which "fusibility is the greatest when the number of bases is the largest" [50], which was previously applied to the so-called "invert" glasses [175]. Although these materials are $SiO_2$-poor, they bear a number of other oxides so that they vitrify because their configurational entropy is maximized and both their liquidus and crystal nucleation rates are minimized.

Regarding bioactive glasses, the first one was synthesized by Larry Hench (1938-2015) following a chance conversation in 1967 with a U.S. army colonel who was looking after badly injured Vietnam veterans, and challenged him to produce a material that would not be rejected by the human body [176].

Hench's first choice was a $P_2O_5$-bearing $SiO_2$-poor soda-lime silicate composition, which he was expecting to form in vivo a hydroxyapatite layer matching well bone tissue. This glass did work well, not as the expected stable material but, rather, as a source of elements for natural regeneration in a way analogous to that of water glass in industrial processes (Ch. 7.5), raising along the way fascinating problems at the frontier between the inorganic and biological worlds. Of course, it is by definition difficult to guess what additional domains will develop and give rise to new problems in glass science. In this respect, the fields of ultra-stable and hybrid glasses (Ch. 8.9) have already reached more than a critical size, but there is little doubt that others will keep emerging. From a theoretical standpoint, major challenges remain to be overcome before glass science can be considered fully mature. If one uses structure as a probe of the energetics and dynamics of glass-forming systems, then average structural parameters such as NBO/T are for example no real substitutes for the actual distributions of the relevant parameters whose physical significance should be ascertained and variations with temperature and pressure be determined to understand the still elusive nature of configurational changes. On another basic level, the ever increasing compositional diversity of glasses makes the yet unsolved problem of the glass transition still more acute as it transcends any features particular to given classes of materials. "The glass transition is not well understood", already noted in 1972 Angell and Rao [177] who added that "outside the circle of specialists in the area it is not usually even recognized that changes in thermodynamic properties are associated with vitrification". If the latter statement is now probably no longer valid, the important issue is to know how many more decades will be needed to solve the former problem…

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* see Ch. 10.9 for full titles

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